Fundamental Topics in Rheology

Rheology Fundamentals

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Content

1

INTRODUCTION RHEOLOGY: SUBJECT AND LANGUAGE

Rheology as an independent branch of natural sciences emerged more than 60 years ago. Its origin was related to observation of “strange” or abnormal behavior of many well-known materials and difficulty in answering some very “simple” questions. For example:

- paint is evidently a liquid because it can be poured into a bottle, but why does it remain on a vertical wall without sagging down, like any other liquid?
- a colloid solution is a liquid, but why does viscosity of such a liquid, in contrast to other liquids, appear different when we measure it under varying conditions of flow?
- clay looks quite like a solid but everybody knows that it can be shaped; it also takes the form of a vessel like any liquid does; if clay is a solid, why does it behave like a liquid?
- yogurt in a can is rather thick (its viscosity is high) but after intensive mixing its viscosity decreases, to increase again when left to rest, so which value of viscosity should be considered?
- concrete looks quite solid and rigid, but when subjected to an external force it changes its dimensions (and shape) like liquid; which are the reasons for such a behavior?

- parts made out of polymeric materials (plastics) look rather solid and hard, quite similar to parts made out of metal, but they are noticeably different. When a force is applied to a metallic part it will slightly change its shape and will maintain its new shape for a long time. This is not the case with plastics which also change their shape after a force is applied but which continue to change shape. If this material is solid, why does it "stalk"?
- pharmaceutical pastes (for example, toothpaste or a body paste) must be "liquid" to be smoothly applied and not too "liquid" to remain on the skin; are all these pastes liquids or not?
- sealants widely used in construction must be fluid-like to close (to seal) all spaces (joints) and to fill cavities, but then sealant must rapidly "solidify" to prevent its flow out of these spaces; is sealant liquid or not?

These examples can easily be extended. The general feature of all these examples is that they are relevant to many real materials and they all exhibit very complicated superimposition of liquid-like and solid-like properties. It means primarily that commonly-used words "liquid" and "solid" are insufficient and we need to introduce a new terminology as a result of understanding particular features of behavior and properties of all the above-mentioned and many other materials. Moreover, we need new methods to measure and characterize properties of real materials quantitatively and in adequate terms.

The next common feature of all these newly-discussed phenomena is the existence of time effects, i.e., the results of observations depend on a **time scale**. Certainly time by itself has no sense, and the appearance of time effect means that something happens to a material in an experimental time scale. In general, time is a reflection of changes in material structure taking place during the period of observation (or experiment).

Thus, rheology is a branch of natural sciences considering real materials with changing structure. Certainly any natural science pretends to deal with reality and does it by means of **phenomenological models**. Any model is created to reflect not all, but the most important, characteristic features of an object. The ideas of a **liquid** and a **solid** are also models and their formal (mathematical) representation originated from the classical works of Isaac Newton and Robert Hooke.

Newton[1] reflected upon a resistance of liquid to a cylinder rotating in a vessel. His ideas were converted to a more accurate form by Stokes,[2] who formulated a general law of liquid-like behavior, now named the **Newton - Stokes Law**:

$$\sigma = \eta\dot{\gamma} \qquad [1.1]$$

where σ is shear stress, and $\dot{\gamma}$ is rate of deformation. The exact rigorous meaning of these terms will be discussed below, but now, in order to be brief, we can say that this law assumes that a force (or resistance) is proportional to a velocity (of movement). The coefficient of proportionality, η, is called **viscosity** (or coefficient of viscosity).

Hooke[3] formulated a similar proposal concerning properties of solids. The law, named after him, was translated to modern form by Bernoulli, and the **Hooke Law** states that stress, σ_E, is proportional to deformation, ε :

$$\sigma_E = E\varepsilon \qquad [1.2]$$

The coefficient of proportionality is called the **Young modulus**, E. Again the formal meaning of these values will be discussed below, but briefly, the Hooke Law says that the force is proportional to the displacement.

Both models represent properties of many real materials and work well in describing their behavior with considerably high degree of accuracy. However, there are numerous other real materials which are not described by the above-mentioned Newton - Stokes and Hooke laws. Rheology relies on the idea that **non-Newtonian** and **non-Hookean materials** exist in reality. These materials are interesting from both theoretical and applied aspects, and that is why such materials must be the objects of investigation. Indeed, the above-cited examples show that a great number of materials used in engineering practice and in everyday life are “strange” and “abnormal” from the point of view of classical concepts of liquid and solid materials.

This can be treated as the definition of **rheology**: it is a science dealing with materials having properties not described by models of Newton - Stokes and Hooke. It is a negative statement (the rule of contraries). The positive statement says that rheology studies materials having properties described by *any* relationship between force and deformation. In this sense, the Newton - Stokes and Hooke Laws are limiting cases formally lying on the border of rheology.

It is important to emphasize again that every model describes (represents) properties of real materials with a different degree of approximation. The Newton-Stokes and Hooke laws appeared to be insufficiently accurate for many industrial materials, which is why rheology, with its more strict and complex laws and equations, gave much better approximation of reality than the classical Newton - Stokes and Hooke laws known to everybody from his school-years.

Both phenomenological laws (i.e., taken as probable assumptions, but only assumptions) avoid the problem of the inherent structure of matter. Almost everybody is convinced that matter consists of molecules and intermolecular empty space, which means that in reality, any material body is heterogeneous. At the same time, any observer is sure that he sees a body of matter as a homogeneous continuous mass without holes and empty spaces. The obvious way out of these contradictory evidences lies in the idea of the space **scale of observation**.

This scale must be large enough to distinguish individual molecules or their segments. Characteristic size of a molecule (its cross-section or length of several bonds) is 1 nm. Then, only when one deals with sizes of the order of 10 nm, can one neglect molecular structure and treat a body as homogeneous. It means that a characteristic volume is of an order larger than 10^3 nm^3. This is a real size of a physical “point”; which is quite different from a philosophical or geometrical point, the latter is an infinitely small object of zero-size. The physical “point” contains $\approx 10^4$ molecules or segments of macromolecule, and throughout its volume all molecular-size fluctuations are averaged. The number of molecules in such a point is large enough for smoothing and averaging procedures.

Having in mind the real scale of a physical point, we think that we have a right to apply methods of mathematical analysis of infinitesimal quantities (which relate to a geometrical point) to a physical medium. The formal extrapolation of physics-based analysis to infinitely small sizes tacitly avoids the incorrectness of this operation, and the only justification for this is the fact that in almost all practical applications, nobody is interested in what really happens in a *very* small volume.

There are at least two important principle exceptions:

- firstly, a central physical problem exists in explanation of observed macro-facts on the base of the molecular structure of matter. In this approach, one would like to understand what happens to a molecule or how intermolecular interactions occur; then going through micro-volumes containing numerous molecules and averaging molecular phenomena, one would come to the macro-properties of a body.
- secondly, in some applications we meet with “zero” size, if geometrical shapes under consideration have angles and the size at the corner of any an-

gle is (formally) equal to zero. Extrapolation of calculation results to such zero volumes sometimes leads to infinite values, and this is out the realm of physical meaning. That is why analysis of problems of this kind requires special methods.

Pertinent to the above discussion, we shall consider homogeneous continuous media, and both adjectives concern a size less than conditionally ≈10 nm. In larger scales, a body can have *structure* and be heterogeneous. For example, a body can be a mixture of some components with step-like transitions between them. A very typical example of such heterogeneity is a filled polymeric material (e.g., plastics with mineral filler) where a filler forms a statistical or quite well arranged (in reinforced plastics) structure. In some applications we may not be interested in this structure and continue to treat the medium as homogeneous, averaging inner differences up to much higher scales (for example for many astronomic observations, the sun and our Earth are quite homogeneous and moreover can be treated as "points"). In other cases, the role of heterogeneity can be important and even a determining factor (for example, for reinforced plastics), but, in any case, the scale of such heterogeneity has to be much larger than characteristic molecular sizes.

Considering all the above-mentioned limitations and the physical meaning of terms which have been and will be used, let us formulate the main problem of rheology. We have already tried to do it from a different perspective, and with the present background we are able to add some additional details to the discussion.

Rheology studies **behavior** of various real continuous media. What do we mean saying "behavior"? For a body of finite size, it is a relationship between outer action (forces, applied to a body) and inner reaction (changes of a shape of a body). For the continuous media we can extrapolate this approach to a *point* and examine the relationship between forces at this point and deformation, i.e., change of a distance between two arbitrary points in a body.

Thus when we consider what happens in a body **in a point of reference**, we avoid the problem of a geometrical form of a body as a whole and are interested only in its substantial, inherent properties. Now we come to a definition of the subject of rheology: it is determination of mechanical properties of continuous media having a different nature, i.e., ascertaining relationships between forces and movements of a matter "in a point of reference".

In its origin, the term "rheology" has been related to flowing media, since the main root of the word means “to flow” (*rheo* in Greek). Currently, the term is used for any real material because sometimes it is very difficult to estimate whether a material is solid or fluid. As a result, the analytical methods used for both classes of media are very similar.

The place of rheology among other natural sciences and applied problems is shown in Figure 1.1. One can see that rheology is a multidisciplinary science having many points of relationship with fundamental physics and chemistry, as well as having applications to real technological and engineering materials in life.

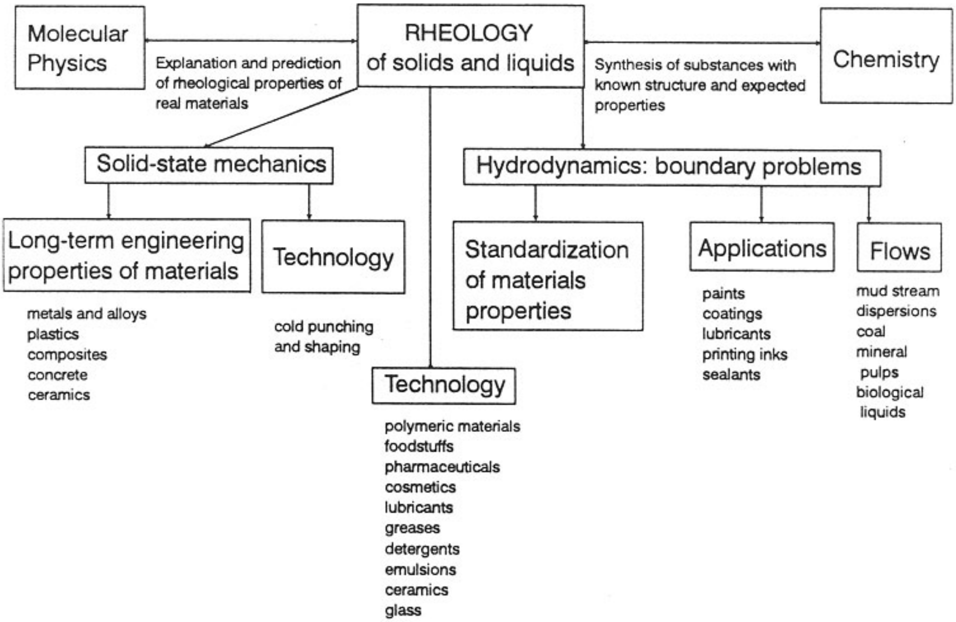

Figure 1.1. Rheology - its place among other sciences considering applied problems.

To recapitulate, it seems useful to point out the main ideas of the Introduction insofar as they will allow us to compose a dictionary of Rheology.

Rheology is a science concerned with mechanical properties of various solid-like, liquid-like, and intermediate technological and natural products (materials). It accomplishes its goals by means of **models** representing principle peculiarities of **behavior** of these materials. The behavior of a material is a relationship between **forces** and **deformations** (or changes of shape) and a model gives a mathematical formulation of the relationship, **rheological properties** being expressed by the structure of a model (i.e., its mathematical image) and values of constants included in a model — characteristic for a material.

Rheological models are related to a **point**, which is a physical object including a sufficient number of molecules in order to neglect the molecular structure of matter and to treat it as **continuum**. The rheological analysis is based on the use of continuum theories, meaning that the following is assumed:

- there is no discontinuity in transition from one geometrical point to another, and the mathematical analysis of infinitesimal quantities can be used; discontinuities appear only at boundaries
- properties of material can change in space (due to the gradient of concentration in multicomponent mixtures, temperature distribution or other reasons) but such change occurs gradually; these changes are reflected in space dependencies of material properties entering equations of continuum theories which must be formulated separately for any part of material surrounded by the boundary surfaces at which discontinuity takes place
- continuity theories include an idea of anisotropy of properties of a material along different directions.

Rheological behavior of a material depends on **time** and **space scales** of observation (experiment). The former is important as a measure of the ratio of the rate of inherent processes in a material to the time of experiment and/or observation; the latter determines the necessity to treat a material as homo- or heterogeneous.

Rheological properties of a material can be understood via balance (or conservation) equations (equations of solid state continuum or fluid dynamics), being a method to transit from properties at a point to an observed behavior of an item or a medium as a whole.

The results of macroscopic description of behavior of real engineering and biological media, based on their rheological properties, are used in numerous applications related to technology of synthesis, processing, and shaping of different materials (plastics and ceramics, emulsions and dispersions in the chemical and food industries, pharmaceuticals, cosmetics, transport, oil industry, etc.), their long-term properties, natural phenomena, such as movement of mud streams and glaciers, and biological problems (dynamics of blood circulation, work of bones). One can conclude that *the first goal* of rheology is a search for stress versus deformation relationships for various technological and engineering materials in order to solve macroscopic problems related to continuum mechanics of these materials.

The second goal of rheology consists of establishing relationships between rheological properties of a material and its molecular composition content. It is an important independent problem related to estimating quality of materials, understanding laws of molecular movements and intermolecular interactions. The term **microrheology**, related to classical works by Einstein,[4] devoted to viscous properties of suspensions, is sometimes used in this line of thought, and it means that the key interest is devoted not only to movements of physical points but also to what happens inside the point during deformation of a medium.

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4. A. Einstein, *Ann. Physik*, **19**, 289 (1906); **34**, 591 (1911).

2

STRESSES

2.1 GENERAL THEORY

Any external action applied to a body leads either to a movement of a body in its entirety or to a deformation of its initial shape, or perhaps to both results simultaneously. The first consequence of an external action - the movement of a body in space or its rotation around its center of gravity, without any changes to its shape - is a subject of study by mechanics, and as such it is not relevant for us in this book. Only what happens inside a body is of principle subject of our discussion.

Briefly speaking, it means that we must consider two possibilities:

- a dynamic situation in which we need to analyze the result of external forces
- a geometric and/or kinematic situation in which it is important how and at which speed distances between different points of a body change, or how local shapes (conditionally drawn inside a body) distort.

Dynamic situation in any point of a medium is expressed by a physical quantity called **stress**.

An initial projection of stress is very simple and obvious. Let us consider a body (bar). The area of its normal section is S (Figure 2.1). The force, F, acts normal to the surface, S. The specific force at any point of the section is equal to F/S and is a **normal stress** or **tensile stress:**

$$\sigma_E = F/S \qquad [2.1]$$

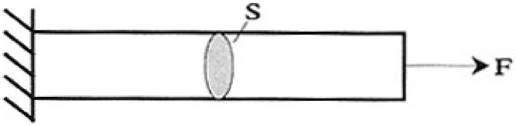

Figure 2.1. A bar loaded by a normal force.

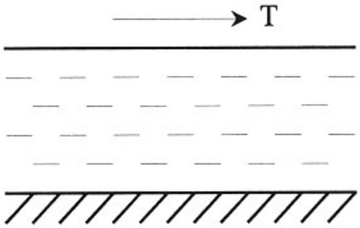

Figure 2.2. Shear of matter.

i.e., *stress is a force related to the unitary surface area*.

The force at a free surface may not be constant but distributed, i.e., be a function of coordinates. For example, a train moving along the rails presses on them at several local zones (where wheels touch a rail), i.e., a force is distributed along a rail and as a result a very complex pattern of stresses acting in the body of a rail appears. In this case, we can mark a small area, ΔS, to find a relative (specific) force acting on the area $\Delta F / \Delta S$. If we decrease the surface area, we eventually come to the limit of the ratio $\Delta F / \Delta S$ at $\Delta S \to 0$ and this limit is a normal stress at the marked point:

$$\sigma_E = \lim_{\Delta S \to 0} (\Delta F / \Delta S) = dF / dS$$

This formula shows clearly that the stress is related to a point and can change from point to point.

We can also imagine a different situation where the force T acts not normal but tangential to the surface as shown in Figure 2.2. If the area of the surface is S, then the tangential or **shear stress** is equal to T/S, or

$$\sigma = T / S \qquad [2.2]$$

These simple and obvious relations must be generalized to an arbitrary orientation of an applied force. One may ask: what are the stresses acting on a surface with any orientation in respect to force? The problem can be solved by two *vectors*: of force, F, and orientation of a surface; the latter is characterized by normal, **n**, to surface (Figure 2.3).

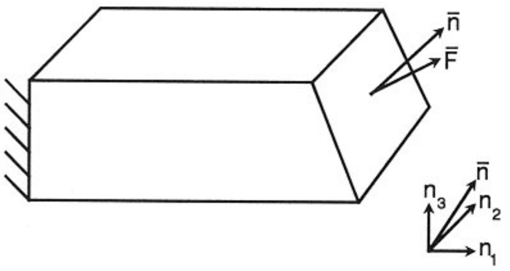

Figure 2.3. Force vector, **F**, and orientation of a surface, **n**.

We know that there are physical concepts which can be presented by one quantity only, such as density of a matter, for example. Such objects are called **scalars**. There are physical characteristics which must be defined not only by their size but also by a *direction* of their action; such as velocity, for example, and not one but three quantities - projections of velocity along three coordinate axes - are necessary to determine velocity. Such physical objects are called **vectors**.

We deal with stresses. For their complete characterization it is necessary to know not only the value of a force acting at a point (this force is a vector by itself) but also its orientation in respect to a surface to which this force is applied (and orientation is also presented by a vector). It means that for complete characterization of a stress we need to know two vectors: of a force and a normal to a surface to which this vector is applied. The physical objects which are determined in such a manner are called **tensors**, and that is why *stress is a tensor*.

Any vector can be represented by its three projections along the orthogonal coordinate axes:

$$\mathbf{n} = n(n_1, n_2, n_3)$$

$$\mathbf{F} = F(F_1, F_2, F_3)$$

Then the nine values can be constructed: three projections of **F** on surfaces determined by any of the three coordinate vectors. As the area of a surface is not essential, all values of F_i $(i = 1, 2, 3)$ must be divided by the area which gives components of a stress tensor, σ_{ij}, where the first index shows the orientation of a force and the second index designates the orientation of a surface.

The result is written in the form of a table (matrix)

$$\sigma_{ij} = \begin{vmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{vmatrix}$$

where the first column represents components of a force (of a vector of a force) applied at the plane normal to the x_1-axis, the second column gives the same for the x_2-axis and the third to x_3-axis. The directions of the normals are indicated by the second indices. The table within the bars is the set (or a list) of all components (projections) of a force vector applied on differently oriented planes at an arbitrary point inside a body. In order to emphasize that this set of parameters presents a single physical object - stress tensor - it is usual to put them between the bars.

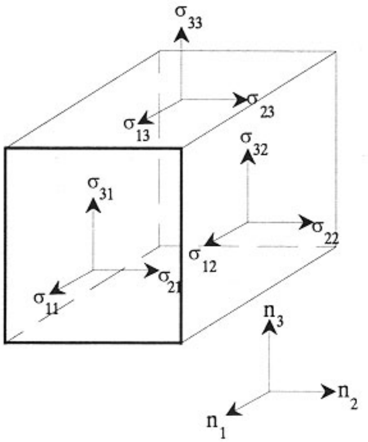

Figure 2.4. Definition of the components of the stress tensor.

The picture which shows all components of a stress tensor acting at a point is drawn in Figure 2.4. One can easily see that components with the same numbers in the index are normal stresses, quite equivalent to the initial definition of the normal stress in Eq 2.1, and all values with different numbers in the index are shear stresses, as in Eq 2.2.

All components of the stress tensor are determined at a point and can be constant or variable in space (inside a medium). It depends on configuration of outer forces applied to a body. For example, the force field is homogeneous for the situation shown in Figure 2.1 and in this case a stress tensor is constant (inside a body). But the stress field (or stress distribution) appears to be very complicated in many other cases, for example in a liquid flowing inside a channel or in a case of roof covered with snow. Some other examples illustrating stress distributions will be discussed at the end of this Chapter.

There are some fundamental facts concerning the stress tensor (and any other tensors as well) and they will be discussed below.

2.2 LAW OF EQUALITY OF CONJUGATED SHEAR STRESSES

Let us consider a plane section of a unit cube in Figure 2.4. The section is shown in Figure 2.5. The rotational equilibrium condition about the central point of the square gives the equality

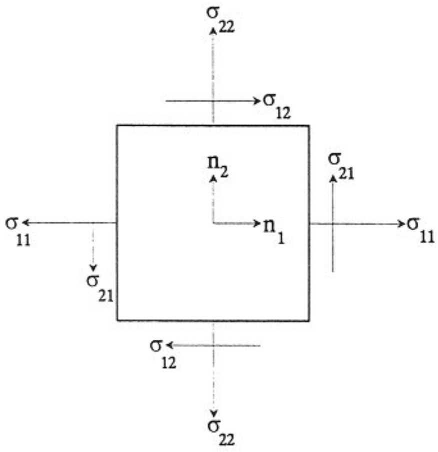

Figure 2.5. Plane stress state.

$$\sigma_{12} = \sigma_{21}$$

The same is true for any other pair of shear stresses:

$$\sigma_{13} = \sigma_{31}; \sigma_{23} = \sigma_{32}$$

These equalities are known as the **Cauchy rule**:[1]

$$\sigma_{ij} = \sigma_{ji}$$

The result means that only three independent shear components of the stress tensor exist, and the stress state at a point is completely defined by *six* independent values; three normal $(\sigma_{11}, \sigma_{22}, \text{and } \sigma_{33})$ and three shear stresses $(\sigma_{12} = \sigma_{21}, \sigma_{13} = \sigma_{31}, \text{and } \sigma_{23} = \sigma_{32})$.

2.3 PRINCIPAL STRESSES

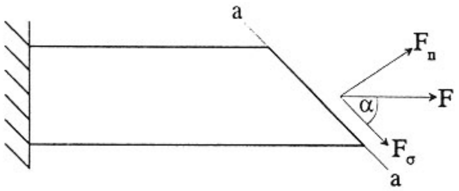

Figure 2.6. Decomposition of the normal force at the arbitrary oriented surface.

The idea of principal stresses (maximal and minimal) appears as a consequence of the dependence of stresses on orientation of a surface. Let us illustrate it by two simple examples generated from Figures 2.1 and 2.2.

The normal stress, σ_E, is calculated as in Eq 2.1. The following question needs to be answered: if the force equals F as before, what are the stresses acting at the surface inclined to the vector **F** at the angle α (Figure 2.6)? It is easily seen that the vector **F** can be decomposed into normal F_n and tangential F_σ components to the surface aa, i.e., there are normal and shear stresses at this surface. The area of this surface is S/sinα, meaning that normal, $\sigma_{E,\alpha}$, and shear, σ_α, stresses (forces divided by the surface area) depend on α and are equal to

$$\sigma_{E,\alpha} = \frac{F_n}{S}\sin\alpha = \frac{F\sin^2\alpha}{S} = \sigma\sin^2\alpha$$

$$\sigma_\alpha = \frac{F_\sigma}{S}\sin\alpha = \frac{F\sin\alpha\cos\alpha}{S} = \frac{\sigma}{2}\sin 2\alpha$$

There are some interesting and peculiar orientations in a body:

at $\alpha = 90^o$ $\sigma_E = \max$ and $\sigma = 0$ (the later is evident from Figure 2.1);
at $\alpha = 45^o$ $\sigma = \sigma_E / 2 = \max$
at $\alpha = 0$ $\sigma_E = 0$ and $\sigma = 0$ (plane free of stresses).

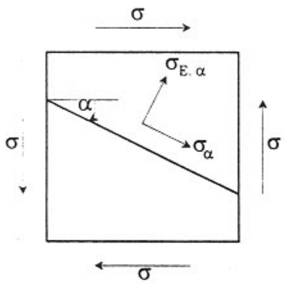

Figure 2.7. Projections of the shear stress at an arbitrary oriented surface.

Figure 2.7 allows one to analyze the situation similar to the picture shown in Figure 2.2. Let the area of both sides of a cube be equal to a unit, so σ is a shear stress. In this case we can write the following equations for $\sigma_{E,\alpha}$ and σ_α:

$$\sigma_{E,\alpha} = 2\sigma\cos\alpha\,\sin\alpha = \sigma\sin 2\alpha$$
$$\sigma_\alpha = \sigma(\cos^2\alpha - \sin^2\alpha) = \sigma\cos 2\alpha$$

Again there are some peculiar orientations:

at $\alpha = 0$ $\sigma_{E,\alpha} = 0$ and $\sigma_\alpha = \sigma$
at $\alpha = 45^o$ $\sigma_{E,\alpha} = \sigma = \max$ and $\sigma_\alpha = 0$
at $\alpha = 90^o$ $\sigma_{E,\alpha} = 0$ and $\sigma_\alpha = \sigma$

(equivalence at $\alpha = 0$ and $\alpha = 90^\circ$ is the consequence of the Cauchy rule).

The discussion shows that, in fact, at any arbitrary orientation (or direction) in a body, both normal and shear stresses can exist irrespective of simple pictures with only normal (Figure 2.1) or only shear (Figure 2.2) stresses. Moreover, there are *always* directions where either normal or shear stresses are maximal. The last result is very important because various media resist application of extension (normal force) or shear (tangential force) in different manner.

For example, it is very difficult to compress a liquid (compression is an action equivalent to application of negative normal stresses) but it is very easy to shear a liquid (to move one layer relative to another like cards in a pile). Another case: when a thin film is stretched (it can be a cover of a balloon stretched by the inner gas pressure), it breaks as a result of an action of normal stresses, whereas shear stresses are practically negligible in this case.

The above-discussed examples are only illustrations of a general idea that all components of a stress tensor depend on orientation of a surface, for which one wants to calculate them. It is a result of projecting a vector along different directions: the size of a projection depends on orientation of the axes in space.

There are general rules and equations for calculating components of the stress tensor at any direction, generalizing equations written above for $\sigma_{E,\alpha}$ and σ_{α}. The main interest and the result of all these calculations and discussions are connected with the existence of such direction in a body where stresses are extremal. Theoretical analysis shows that for any arbitrary stress tensor it is possible to find three orthogonal, i.e., perpendicular to each other, directions, at which normal stresses are extremal and shear stresses are absent. Examples of such situations have been shown above for the cases drawn in Figures 2.6 and 2.7. Indeed, normal stresses $\sigma_{ii} = \max$ at these directions at which shear stresses are absent, $\sigma_{ij} = 0$. These normal stresses are called **principal stresses**. The existence of principal stresses is a general law for any stress tensor.

The concept of principal stresses allows one to find a minimal number of parameters which completely characterize the stress state at any point. It is impossible to compare stress states at different points of a body or in different bodies if only operating with six independent components of the stress tensor acting along different directions. It is much easier to do so dealing with only three normal stresses. For example, one can expect that some materials are ruptured by an action of a normal stress if it reaches a critical level, that is why it is important to know the value of maximal normal stress acting in a material, and this maximal stress is the principal stress.

2.4 INVARIANTS

If we can calculate principal stresses, it means that we can represent the stress state of matter by *three independent* values, and every different stress state is equivalent if principal stresses are the same for all of them. This means, in particular, that various physical phenomena taking place under stress (for example, probability for a "quasi-liquid" to stick to a vertical wall and stay motionless in spite of action of gravitational force; rupture of solid bodies; slow movement and transition to spurt for snow, sand or mud on slopes, etc.) can be considered as a consequence of an action of principal stresses only.

Principal stresses represent stress state in a body (at a given point), regardless of any possible set of normal and shear stresses at any arbitrary orientation of this point. In other words, they are *invariant* in respect to the choice of orientation. Then the question is: how to calculate principal stresses if all components of the stress tensor are known for some arbitrary coordinate system? Theory of tensors gives an answer to this question in the form of a cubic algebraic equation:

$$\sigma^3 - I_1\sigma^2 + I_2\sigma - I_3 = 0 \qquad [2.4]$$

and principal stresses are three roots of this equation designated as $\sigma_1, \sigma_2, \sigma_3$. It is clear that the roots are expressed through coefficients of Eq 2.4, I_1, I_2, and I_3. These coefficients are constructed by means of all components of stress tensor for arbitrary orthogonal orientations in space as:

$$I_1 = \sigma_{11} + \sigma_{22} + \sigma_{33} \qquad [2.5]$$
$$I_2 = \sigma_{11}\sigma_{22} + \sigma_{11}\sigma_{33} + \sigma_{22}\sigma_{33} - (\sigma_{12}^2 + \sigma_{23}^2 + \sigma_{13}^2) \qquad [2.6]$$
$$I_3 = \sigma_{11}\sigma_{22}\sigma_{33} + 2\sigma_{12}\sigma_{23}\sigma_{13} - (\sigma_{11}\sigma_{23}^2 + \sigma_{22}\sigma_{13}^2 + \sigma_{33}\sigma_{12}^2) \qquad [2.7]$$

As the roots of Eq 2.4, the σ_1, σ_2, and σ_3 do not depend on orientation of axes of a unit cube (at a point) in space, on one hand, and they are expressed through values of I_1, I_2, and I_3, on the other. This leads to the conclusion that I_1, I_2, and I_3 are also invariant in respect to the choice of directions of orientation and that is why they are usually called **invariants** of a stress tensor at a point. According to its structure (the power of components), I_1 is a *linear*, I_2 is a *quadratic*, and I_3 is a *cubic invariant*.

Certainly any combination of the invariants, I_1, I_2, and I_3, is also invariant in respect to the orientation of axes in space. Various elegant or cumbersome structures of invariants are possible to be built but it is important to know that three and only three independent values of such kind do exist.

Invariants are characteristics of the physical state of a matter. It means that neither any stress by itself nor its arbitrary combination but only invariants determine a possibility of occurrence of various physical effects such as, for example, phase transitions, storage of elastic energy or dissipation (transition to heat) of work of external forces. There is a fundamental principle saying that *physical effects must be independent of choice of a coordinate system* and that is why invariants, which are values independent of a coordinate system, govern physical phenomena occurring due to application stresses.

In many practical problems, we deal a with two-dimensional or so-named **plane stress state**. The very typical example of it are thin-walled items with stress-free outer surfaces. “Thin” means that the size in direction normal to the surface is much smaller than other two dimensions. Stresses in planes parallel to the free surfaces can be assumed to be absent in comparison with stresses at two other oriented planes. This can be proven by a pure geometrical argument: because stresses are zero on both faces, they might not vary appreciably over the small distance (thickness of the item).

In the plane stress state, all the components containing the index “3" vanish and the full stress tensor looks like this:

$$\sigma_{ij} = \begin{vmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{21} & \sigma_{22} & 0 \\ 0 & 0 & 0 \end{vmatrix} \qquad [2.8]$$

In this case, one principal stress, σ_3, is zero and two others, σ_1 and σ_2, are the roots of a *quadratic* (but not cubic) algebraic equation:

$$\sigma_{1,2} = \frac{\sigma_{11} + \sigma_{22}}{2} \pm \left\{ \left(\frac{\sigma_{11} - \sigma_{22}}{2} \right)^2 + \sigma_{12}^2 \right\}^{1/2}$$

Typical examples of thin (or two-dimensional) elements are various balloons, membranes and covers, barrels and tanks, and so on. And for all these articles and many others, we can use the analysis of the two-dimensional (or plane) stress state.

There are two particularly simple cases of the plane stress state, which are simple (or unidimensional) tension and simple shear. In fact, these cases were mentioned at the very beginning of this chapter, and their tensorial nature is illustrated by the above-discussed Figures 2.6 and 2.7 and rules of a transformation of stress components with rotation of coordinate axes.

2.5 HYDROSTATIC PRESSURE AND DEVIATOR

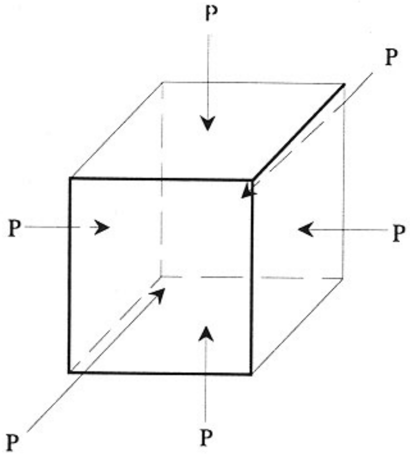

Figure 2.8. All-directional compression (hydrostatic pressure).

It seems quite obvious that only normal stresses can change the volume of a body, while shear stresses distort its form (shape). For this reason it appears to be reasonable to divide a stress tensor into two components, singling out the components connected to action of the normal stresses.

Let us consider the situation of all-direction compression of a body under pressure, p (Figure 2.8). This case is called *hydrostatic pressure*. The main feature of hydrostatic pressure is the absence of shear stresses; hence, all components of the matrix except normal are equal to zero and the stress tensor for this case looks like this:

$$\sigma_{ij} = \begin{vmatrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{vmatrix} \qquad [2.9]$$

i.e., all principal stresses are the same and equal to -p:

$$\sigma_1 = \sigma_2 = \sigma_3 = -p$$

The expression 2.9 can be written in a short form if to use some evident rules for operation with tensors which allow a constant to be taken away from bars. Then

$$\sigma_{ij} = \begin{vmatrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{vmatrix} = p \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

The remainder in bars is called the unit tensor or Kronecker Symbol, δ_{ij}. For the hydrostatic pressure

$$\sigma_{ij} = -p\delta_{ij}, \text{ i.e.} \sigma_{ii} = -p; \ \sigma_{ij} = 0 \ \text{ if } i \neq j$$

For this stress tensor shear, the stresses are absent at any direction in space, and it explains the term "hydrostatic" used for the situation shown in Figure 2.8. The hydrostatic pressure (or simply - pressure) is evidently expressed as

$$p = -\frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3} = -\frac{I_1}{3} \qquad [2.10]$$

The last definition is taken to be true for any stress state, even when σ_{11}, σ_{22}, and σ_{33} are not equal to each other, and Eq 2.10 is considered as a general definition of **pressure**, and the stress tensor, Eq 2.9, is called the **spherical stress tensor**.

There is one intriguing question: whether the value $I_1/3$ calculated according to Eq 2.10, and called pressure, has the same physical meaning as pressure used in any thermodynamic relationship? Certainly, it is true for hydrostatic pressure, but this idea of arbitrary stress state needs a separate proof.

For plane shear stress state, when $\sigma_{12} = \sigma_{21}$, the principal stresses are equal to

$$\sigma_1 = \sigma_E; \ \sigma_2 = \sigma_E; \ \sigma_3 = 0 \qquad [2.11]$$

The same conclusion is correct for all other shear components of the stress tensor. It means that for this situation called **simple shear**, $I_1 = 0$, i.e., hydrostatic pressure does not exist. It proves that indeed *shear stresses do not influence the volume of a body but are able to change its shape only*.

Now we can write down a general expression for any stress tensor with a separated hydrostatic component. In this approach, all shear stresses remain untouched and each diagonal member of the tensor becomes equal to $\sigma_{ii} - p$. This part of the stress tensor (complete tensor minus hydrostatic component) is called **deviator** or deviatoric part of the stress tensor. It is thought that this part of the tensor is responsible for changes of shapes of a body (certainly at a point).

The idea about splitting a stress tensor into spherical and deviatoric parts is well illustrated by the example of uniaxial extension. Surely it is extension and we have a right to expect that it leads to a volume change of a body. But is it all, and is it equivalent to hydrostatic pressure?

Stress tensor for uniaxial extension is written as

$$\sigma_{ij} = \begin{vmatrix} \sigma & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \qquad [2.12]$$

It reflects the situation in Figure 2.1, where all other forces except normal force, F, are absent. There is no reason for the appearance of other stresses except for σ_{11}, and that is why all components in the matrix 2.12 are zeros, except for $\sigma_{11} = \sigma_E$.

Let us separate this tensor into hydrostatic and deviatoric parts. In the case under discussion, the matrix 2.12 shows that

$$\sigma_{11} = \sigma_E ; \ \sigma_{22} = 0 \text{ and } \sigma_{33} = 0$$

From Eq 2.10, it follows that $p = -\sigma_E/3$. Now let us present the stress tensor 2.12 as a sum of hydrostatic pressure and remainder, where this “remainder” is deviator or simply a difference between full stress tensor and hydrostatic pressure. Then the stress tensor for uniaxial extension can be written as:

$$\sigma_{ij} = -p\delta_{ij} + \begin{vmatrix} \frac{2}{3}\sigma_E & 0 & 0 \\ 0 & -\frac{1}{3}\sigma_E & 0 \\ 0 & 0 & -\frac{1}{3}\sigma_E \end{vmatrix} = -p\delta_{ij} + \frac{\sigma_E}{3}\begin{vmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

Any component of the full stress tensor, σ_{ij}, is equal to the sum of components of both addenda with the same indices; for example:

$$\sigma_{11} = -p + \frac{2}{3}\sigma_E = \frac{1}{3}\sigma_E + \frac{2}{3}\sigma_E = \sigma_E \text{ and } \sigma_{22} = -p - \frac{1}{3}\sigma_E = \frac{1}{3}\sigma_E - \frac{1}{3}\sigma_E = 0$$

One can see that the *uniaxial extension is not equivalent to hydrostatic pressure* (the sign is not essential in this discussion) as the former leads to appearance of a deviatoric component of the stress tensor. In particular, it means that we can find such directions in a body where the shear stress exists (opposite to hydrostatic pressure where the shear stresses are absent in principle) as mentioned in discussion of Figure 2.6.

This interpretation of the uniaxial extension explains that in fact one-dimensional tension creates not only negative pressure ("negative" means that stresses are oriented *from* unit areas inside a body) but also different normal stresses acting along all directions. This is a physical reason why in the uniaxial tension all dimensions of a body change: a size increases along the direction of extension but decreases in perpendicular (lateral) directions.

2.6 EQUILIBRIUM (BALANCE) EQUATIONS

The distribution of stresses throughout a body is described by equilibrium (or balance) equations introduced by Navier,[2] Poisson,[3] and Cauchy.[4] In essence they are one form of Newton's Second Law written for a continuum because they state that the sum of all forces at a point is equal to the product of mass (of this point) times acceleration.

A "point" in the theoretical analysis is an elementary (infinitesimal) space with sides oriented along the orthogonal coordinate axes (in Figure 2.9 this space is a cube in the Cartesian coordinates). The idea of the analysis consists of a projection of all outer forces on faces of the cube along three coordinate axes.

Let us consider a change of forces at infinitesimal distance along an axis. If there is no special situation with jumps or breaks in force, we can think that (for example) a force on the left-hand face of the cube (Figure 2.9) equals to σ_{22}, and on the parallel right-hand face it equals to $\sigma'_{22} = \sigma_{22} + (\partial\sigma_{22} / \partial x_2)dx_2$ and the sum of projections of forces is $(\partial\sigma_{22} / \partial x_2)dx_2(dx_1dx_3)$, where (dx_1dx_3) is the surface area of the face.

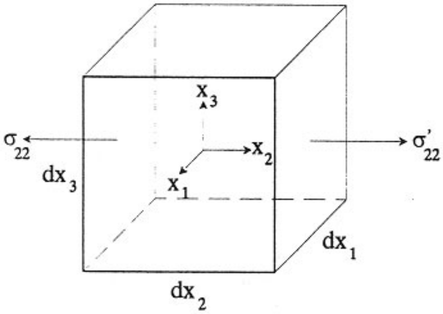

Figure 2.9. Stress difference at parallel surfaces along the infinitesimal distance.

Writing the sum of projections of all stress components parallel to x_2-axis and dividing them by $(dx_1dx_2dx_3)$, we come to *equilibrium* (or *balance equations* or *equations of moment conservation*). For all three coordinate axes, this approach gives the system of equations:

$$\frac{\partial\sigma_{11}}{\partial x_1} + \frac{\partial\sigma_{12}}{\partial x_2} + \frac{\partial\sigma_{13}}{\partial x_3} + X_1 = \rho a_1$$

$$\frac{\partial\sigma_{12}}{\partial x_1} + \frac{\partial\sigma_{22}}{\partial x_2} + \frac{\partial\sigma_{23}}{\partial x_3} + X_2 = \rho a_2 \qquad [2.13]$$

$$\frac{\partial\sigma_{13}}{\partial x_1} + \frac{\partial\sigma_{23}}{\partial x_2} + \frac{\partial\sigma_{33}}{\partial x_3} + X_3 = \rho a_3$$

where $\mathbf{X}(X_1, X_2, X_3)$ is a vector of a body force per unit volume $(dx_1dx_2dx_3)$, $\mathbf{a}(a_1, a_2, a_3)$ is a vector of acceleration and ρ is the density.

For most rheological applications, it is reasonable to treat problems restricted to static equilibrium, and hence $\mathbf{a} = 0$. Besides, in many cases (but not always) vector $\mathbf{X}$ equals zero. The existence of a body force is important, for example, in situations where the movement occurs because of the action of gravity: in sagging paints or sealants from vertical or inclined surfaces, flowing of glaciers and so on.

If we can omit two last members in the balance equations, it allows us to simplify the system, Eq 2.13, and in this case we can write it as follows:

$$\frac{\partial \sigma_{11}}{\partial x_1} + \frac{\partial \sigma_{12}}{\partial x_2} + \frac{\partial \sigma_{13}}{\partial x_3} = 0$$

$$\frac{\partial \sigma_{12}}{\partial x_1} + \frac{\partial \sigma_{22}}{\partial x_2} + \frac{\partial \sigma_{23}}{\partial x_3} = 0 \qquad [2.13a]$$

$$\frac{\partial \sigma_{13}}{\partial x_1} + \frac{\partial \sigma_{23}}{\partial x_2} + \frac{\partial \sigma_{33}}{\partial x_3} = 0$$

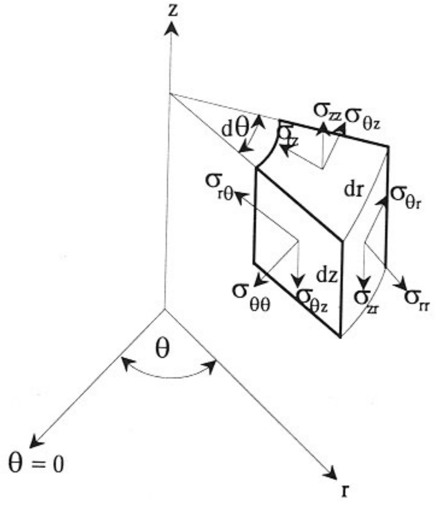

Figure 2.10. Components of the stress tensor in cylindrical polar coordinates.

Equilibrium can be considered in respect to different coordinate systems but not restricted to a Cartesian system. The choice of coordinates is only a question of convenience in solving a concrete boundary problem. The choice of the coordinate system depends, generally speaking, on the shape and type of symmetry of a geometrical space of interest for the application. For example, if we deal with problems related to round shells or tubes with one axis of symmetry, the most convenient coordinate system in this case is cylindrical polar coordinates with r, z, and θ-axes.

Components of the stress tensor in these coordinates are shown in Figure 2.10. The static balance equations (at **a** = 0) for the point (or infinitesimal volume element) shown in Figure 2.10 represent equilibrium in respect to r, z, and θ directions and can be written as:

$$\frac{\partial\sigma_{rr}}{\partial r} + \frac{\partial\sigma_{rz}}{\partial z} + \frac{\partial\sigma_{r\theta}}{r\partial\theta} + \frac{\sigma_{rr} - \sigma_{\theta\theta}}{r} + X_r = 0$$

$$\frac{\partial\sigma_{r\theta}}{\partial r} + \frac{\partial\sigma_{\theta\theta}}{r\partial\theta} + \frac{\partial\sigma_{\theta z}}{\partial z} + \frac{2\sigma_{r\theta}}{r} + X_\theta = 0 \qquad [2.14]$$

$$\frac{\partial\sigma_{zz}}{\partial r} + \frac{\partial\sigma_{\theta z}}{r\partial\theta} + \frac{\partial\sigma_{rz}}{r} + \frac{\partial\sigma_{zz}}{\partial z} + X_z = 0$$

where $\mathbf{X}(X_r, X_\Theta, X_z)$ is a vector of a body force and its projections along the cylindrical coordinates.

Some applied problems are symmetrical about the z-axis, so that all terms containing $\partial / \partial\theta$-terms become zero and the shear stress $\sigma_{r\Theta}$ as well. Besides, in some cases, the cylindrical bodies can be very long and variations of stresses along the axis of symmetry are absent (or can be taken as negligibly small). This allows us to continue simplification of the balance equations, which in this case reduce to

$$\frac{d\sigma_{rr}}{dr} + \frac{\sigma_{rr} - \sigma_{\Theta\Theta}}{r} + X_r = 0 \qquad [2.15]$$

and all shear components of the stress tensor are absent.

2.7 EXAMPLES

It seems interesting and useful to present and discuss typical examples of stress distributions in a body for some model situations.

2.7.1 A BAR LOADED BY THE CONSTANT FORCE (FIGURE 2.1)

This is a very popular scheme of loading, for example, when one suspends a weight on a string or pulls a car from mud with a rope, or stretches a filament in the technology of fiber spinning - all cases deal with a material under the action of uniaxial extension. A similar scheme of loading, but with the opposite sign, appears when a material or a part is compressed in one direction; for example, as in pile loading or in building foundation.

The stress distribution near the butt-end of a bar depends on the manner of counteracting the force. Far enough from the butt-end (typically at a distance larger than the characteristic transversal size of a bar), the distribution of forces at the end becomes unessential for stress distribution throughout the bar and normal stresses are calculated by the very simple and obvious relation 2.1. By the above-discussed method, all components of the stress tensor for different directions can be found.

2.7.2 A BAR STRETCHED BY ITS OWN WEIGHT (FIGURE 2.11)

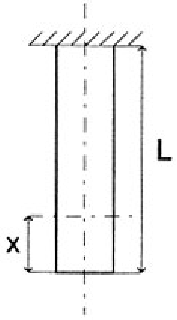

Figure 2.11. A long bar loaded by its own weight.

It can be found in some engineering constructions where parts are suspended at their upper end, or a plastic liquid-like stream, after leaving a nozzle, breaks by its own weight at some distance from the nozzle.

Let a long bar (or a fiber) be suspended by its end. The extensional (normal) stress along the bar appears as a result of stretching by its own weight. According to the equilibrium condition

$$\sigma(x) = \rho x \qquad [2.16]$$

The maximal normal stress is equal to σL, where L is the length of the bar. It means that if the bar is very long, the stress will exceed any acceptable limit and break the bar.

2.7.3 SAGGING OF A FLEXIBLE BAR OR A FIBER (FIGURE 2.12)

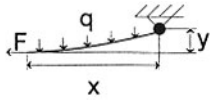

Figure 2.12. A sagging bar (fibre).

Sagging of flexible engineering elements (bars, fibers and so on) is a rather typical situation in many practical applications. The force provoking bar sagging can be caused not only by the own weight of the bar but also by various outer factors (lying snow, push of the wind, and so on). In all these cases, we deal with distributed load, q, expressed as a force divided by the length. The reasonable supposition says that the height of flexure is much lower than the length of the bar, or a span between supports, L, (in Figure 2.12

only a half of the bar is shown).

According to the equilibrium condition (the sum of torques around the point of suspension is equal to zero), we have:

$$Fy - qx\frac{x}{2} = 0$$

or

$$y = \frac{qx^2}{2F}$$

The last formula shows that the shape of the loaded bar is parabolic. It is easy to find the maximal sagging, H:

$$H = \frac{qL^2}{8F} \qquad [2.17]$$

Eq 2.17 allows us to find the necessary tension if we set acceptable flexure, and *vice versa*. The normal stress in the bar is evidently equal to F divided by the cross-section.

2.7.4 INTERNAL PRESSURE IN A THIN-WALLED CYLINDER (FIGURE 2.13)

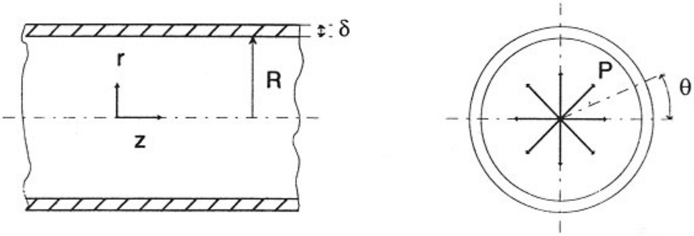

Figure 2.13. A thin-walled tube (cylinder) under internal pressure.

This situation is of general meaning for all vessels working under internal pressure, such as chemical rectors, boilers, and different types of balloons, tubes in tires, plastic films stretched during technological procedure of their shaping, and so on.

Let us try to calculate stresses in the wall of a cylinder loaded by internal pressure, p. We analyze the case when $\delta << R$ (the case named "thin-walled"). The consideration of equilibrium across a radius gives the value of average stress $\sigma_{\Theta\Theta}$ (or simply σ_{Θ}):

$$\sigma_{\Theta}(2L\delta) = 2pRL$$

or

$$\sigma_{\Theta} = \frac{pR}{\delta} \qquad [2.18]$$

(since $\delta << R$, we have a right not to distinguish outer and inner radii of the cylinder).

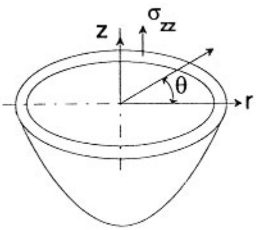

Figure 2.14. Stresses in a spherical lid of a vessel.

Are other components of the stress tensor essential? We can estimate the σ_{rr}-component (or simply σ_{r}). It is evident that $\sigma_{r} = 0$ at the outer surface and $\sigma_{r} = p$ at the inner surface of the cylinder. It means that σ_{r} is of the order of pR. Because we assume that $R/\delta >> 1$, it means that σ_{r} is negligible in comparison with σ_{Θ}. The σ_{zz} and all shear components are absent in the case of thin-walled items, as usual.

The situation changes if we assume that such a vessel must be closed by a lid (Figure 2.14). It is rather evident that there is a force acting on the surface of a ring joining the lid and the cylinder. This force resists the action of internal pressure and it leads to the following equation for the stress component σ_{zz} (or simply σ_{z}):

$$p\pi R^2 = 2\pi R\delta\sigma_{z}$$

Then

$$\sigma_{z} = \frac{pR}{2\delta} \qquad [2.19]$$

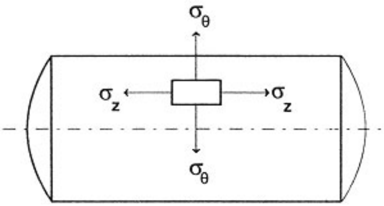

Figure 2.15. Plane stress state in a wall of a cylinder.

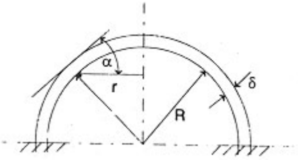

Figure 2.16. Hemispherical cup loaded by its own weight.

Now, we come to the conclusion that there is a two-dimensional (or plane) stress state in the wall of the cylinder as shown in Figure 2.15 for a "unit" (or infinitesimal) square. Both stresses σ_Θ and σ_z are principal as shear stresses are absent. The third principal stress $\sigma_r << \sigma_\Theta$ and σ_z and can be taken equal zero.

2.7.5 HEMISPHERICAL MEMBRANE UNDER ITS OWN WEIGHT (FIGURE 2.16)

We face this type of loading in many engineering constructions, especially when a spherical roof covers a large area of a stadium or a storehouse. This problem (similar to that discussed above) relates to stress fields in shells or plates (membranes). The shape of a membrane in this case is defined as

$$r = R\sin\alpha$$

Let the density of the membrane be ρ. The thickness of a hemisphere is uniform and equal to δ (δ is taken as much smaller than R). Theory gives the following expression for the normal stress acting along the surface of the hemisphere:

$$\sigma = \rho g R \frac{[1-(r/R)^2]^{1/2} - 1}{(r/R)^2} \qquad [2.20]$$

where g is the gravitation constant.

At the support ring (r = R) stresses must balance the total weight of the hemisphere and that is why

$$\sigma = -gR$$

is the maximal value of the principal stress, σ.

2.7.6 TORSION OF A THIN-WALLED CYLINDER (FIGURE 2.17)

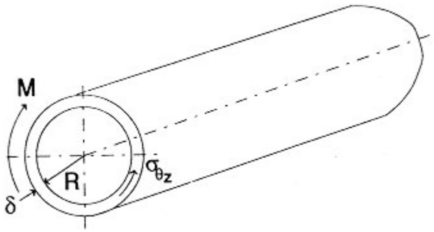

Figure 2.17. Torsion (shear) of a long thin-wall cylinder.

This is a model situation for many applications. For example, it is a scheme of a typical rotational viscometer widely used for measuring rheological properties of different substances. Then this scheme reflects such a classical engineering situation as joining tubes with fitting.

Let the wall of a cylinder, δ, be much smaller than its radius, R, (as in Example (iv)). The cylinder is loaded by the torque, M. In this case, it is reasonable to assume that there is an average (constant) shear stress $\sigma = \sigma_{\Theta z} = \sigma_{z\Theta}$ over the wall section.

From the condition of static equilibrium, one can derive:

$$M = S(R + \delta / 2)\sigma$$

where $S \approx 2\pi(R + \delta / 2)\delta$ is the area of a ring (section of the cylinder). As a result, the shear stress is given as:

$$\sigma = \frac{2M}{\pi(2R + \delta)^2 \delta} \qquad [2.21]$$

In the case under discussion, a torque can be produced by relative turning, rotating or twisting of cylinders (inner or outer with no difference for the result). Eq 2.21 is applicable in this case if the condition $\delta << R$ is fulfilled.

2.7.7 TORSION OF A CONE OVER A PLATE (FIGURE 2.18)

It is practical to analyze this situation because it applies to a so-called “cone-and-plate” viscometer, used in the plastic and rubber industries, as well as to scientific investigations.

We analyze a case when the angle α between surfaces is small. This situation is interesting (and rather simple) because at very low values of the angle α the

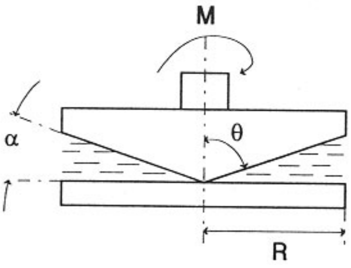

Figure 2.18. Rotation of a cone over a plate.

shear stress, σ, is practically constant throughout the volume of a material between the cone and the plate. Balance of forces gives the following expression for σ:

$$\sigma = C \big/ \sin^2\theta \qquad [2.22]$$

where C is a constant and the angle θ is taken from a vertical axis. Values of θ throughout the gap, between the cone and plate, are very close to π/2, then $\sin^2\theta \approx 1$ and σ = const.

Integrating along the radius R gives the final relationship for torque and shear stress:

$$\sigma = \frac{3M}{2\pi R^3} \qquad [2.23]$$

2.7.8 STRESSES IN A MEDIA MOVING ALONG A CYLINDER (FIGURE 2.19)

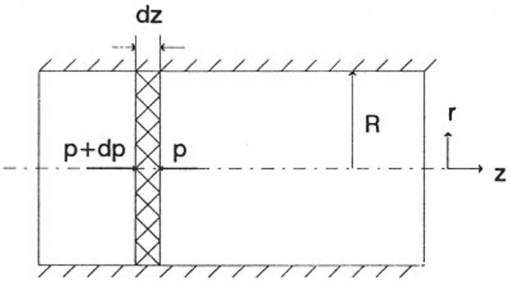

Figure 2.19. Movement of a medium along a cylinder.

This is the simplest and perhaps the most important hydrodynamic pattern having general meaning for transportation of water, oil products, raw materials in the food and pharmaceutical industries, and in numerous other cases.

If to write the balance equation for the element of the length, dz, loaded by pressure gradient, dp/dz, we come to the following relationship:

$$\sigma(2\pi r)dz = \pi r^2 dp$$

or

$$\sigma = \frac{r}{2}\frac{dp}{dz} \qquad [2.24]$$

where $\sigma = \sigma_{zr} = \sigma_{rz}$ is the shear stress, and r is a current radius, i.e., distance from the axis of the cylinder.

The last equation shows that the shear stress at the wall, σ_w, (maximal shear stress) is calculated as

$$\sigma_w = \frac{R}{2}\frac{dp}{dz} \qquad [2.25]$$

and the stress distribution along the radius of the cylinder (or the tube or capillary) is linear:

$$\sigma = \sigma_w \frac{r}{R} \qquad [2.26]$$

The diagram in Figure 2.19 says nothing about other components of the stress tensor; though normal (diagonal) stresses definitely exist (at least pressure, p, creates all-direction compression), only pressure gradient (not pressure itself) influences the shear stresses.

2.7.9 STRESSES AROUND A CIRCULAR HOLE IN A SHEET (FIGURE 2.20)

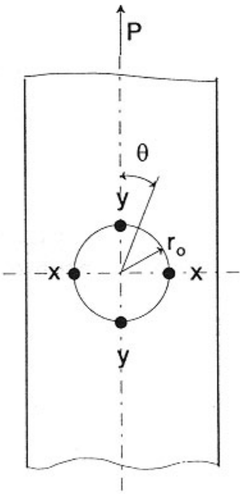

Figure 2.20. A circular hole weakening a flat sheet.

Since practically all parts of engineering and everyday applications have holes of different sizes and shapes, it is very important to know how these holes influence performance characteristics of a part. In technical language, this influence is associated with stress fields appearing in the neighborhood of a hole. A round (circular) hole is the simplest example of possible shapes of holes, though holes can have different shapes.

If a sheet having a circular hole is stretched by a uniform load, p, stress is created around the hole. From the equation of equilibrium, it is possible to find (we omit the details) that the distribution of stresses exists around the hole. All components of the stress tensor depend on relative radius (r_0/r) (r_0 is the radius of the hole and r is a distance from the center of the hole, $r>r_0$) and the angle, θ, between the axis of the load action and an arbitrary direction.

Calculations show that stresses decrease very rapidly away from the edge of the hole (in fact they are decreased as a function of $(r_0/r)^2$).

Most important is the situation at the hole boundary, where the stresses are maximal and equal to:

$$\sigma_{\Theta\Theta} = p(1-\cos\theta) \qquad [2.27]$$

(at $r_0/r = 1$ other components of the stress tensor are absent).

The limiting values of $\sigma_{\Theta} = \sigma_{\Theta\Theta}$ are:

$$\sigma = 3p \text{ at } \theta = \pi / 2 \text{ and } \theta = 3\pi / 2$$
$$\sigma = -p \text{ at } \theta = \text{ and } \theta = \pi$$

This phenomenon is called **stress concentration** (due to cracks) and larger stresses (in comparison with the average value) lead to weakening in bodies containing holes.

In the case shown in Figure 2.20, the side points, X, of the hole are the most vulnerable (in respect of possible fracture) because the stress is three times higher than the average stress, p.

If extension changes to compression (applied stress is equal to -p), the maximal tension occurs at the points Y, and in this situation these points become the areas of likely failure.

2.8 CONCLUDING REMARKS

Stress is the dynamic characteristic *at a point* and is defined as the relative force or the force related to the unit area. Stress values depend on direction of the applied force and the orientation of a surface for which we wish to find forces acting at this surface inside a body. That is why stress is a physical object of **tensor** nature. Stresses can be **normal** (perpendicular) and **shear** (tangential) to the surface where they act.

It is always possible to calculate components of the stress tensor for any direction and to find **principal** directions and principal normal stresses; the latter are extremal and shear stresses are absent at those directions.

There are three special combinations of any arbitrary stress tensor which do not depend on choice of axes orientation in space. These combinations are called **invariants**.

The stress tensor can be divided into two parts, one of which (so-named **spherical**) is responsible for volume and the other (called **deviator**) for shape (or form) changes of a body (at a point).

Calculating stresses through a body is realized by solving differential equations with appropriate boundary conditions. These equations represent the **law of equilibrium** (or **balance**) of all forces applied at a point.

Concrete examples of calculations for some simple geometrical forms show that different situations are possible: uniform and distributed, one-dimensional, plane, or volume stress fields.

The examples discussed above are typical due to simple (model) geometrical forms of bodies under analysis. They allowed us to find stress fields regardless of the particular properties of the material. But in many other cases, it is necessary to analyze not only stress but deformation fields jointly. It leads to the necessity to take into account relationships between stresses and deformations, i.e., rheological properties of matter.

2.9 REFERENCES

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3

DEFORMATION AND DEFORMATION RATE

3.1 DISPLACEMENTS AND DEFORMATIONS

The result of action of outer forces can be either movement of a body in space or change of its shape. Here, we are interested in describing the changes occurring inside a body. The change of a shape of a body is essentially the change of distances between different points on its surface. Thus, change of shape can only occur if there are changes of distances between different sites inside a material, and this phenomenon is called **deformation**.

The change of distances between points inside a body is transmitted to the neighborhood of a point which can be moni-

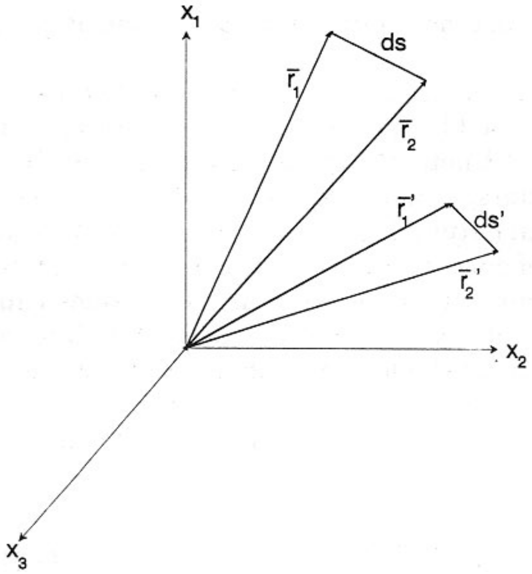

Figure 3.1. Displacement of two points in a body and appearance of deformation.

tored by following the change of very small (infinitesimally small) distances between two points.

Let the distance between two points A and B in a material be ds (Figure 3.1). As a result of some outer action, they both move and their new positions become A′ and B′, and the distance between them now is ds′. The absolute value of (ds’ – ds) is not important, because the initial length ds might be quite arbitrary, only **relative** change of the distance between two sites, determined as

$$\varepsilon = \frac{ds' - ds}{ds} \qquad [3.1]$$

The definition 3.1 is not tied to any coordinate system, meaning that ε is a *scalar*. It can be expressed through components of **tensor of deformation** (or **strain**), ε_{ij}. The position of a site in a body is characterized by its radius-vector, **r**, and, because we have two sites, it is necessary to introduce two vectors: $\mathbf{r}_1$ for the point A and $\mathbf{r}_2$ for the point B. The quantitative determination of deformation can be accomplished by following the relative **displacement** of two vectors, expressed as $(d\mathbf{r}_1 - d\mathbf{r}_2)/d\mathbf{r}_1$. If we assume that a body after deformation remains intact (between sites A and B), the distance between points A’ and B’ is still infinitesimal.

The difference $(d\mathbf{r}_1 - d\mathbf{r}_2)$ is a displacement, **u**. As a difference of two vectors, it is also a vector which can be expressed by its three projections: $\mathbf{u}(u_1, u_2, u_3)$. Relative displacement is characterized not only by its length but also by its orientation in space. Since two vectors, **u** and $\mathbf{x}(x_1, x_2, x_3)$, describe relative displacement, the latter is of tensorial nature. Indeed, deformation and relative displacement are tensors and components of these tensors can be calculated as derivatives $d\mathbf{u}/d\mathbf{x}$. It is also pertinent that there are nine such values (three projections of vector **u** and three of vector **x**), as could be expected for a tensor. The values of all derivatives are dimensionless and they are expressed in absolute numbers or percents.

Accurate calculations of the components of the deformation tensor give the following expression:

$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) + \frac{1}{2}\left(\frac{\partial u_1}{\partial x_i}\frac{\partial u_1}{\partial x_j} + \frac{\partial u_2}{\partial x_i}\frac{\partial u_2}{\partial x_j} + \frac{\partial u_3}{\partial x_i}\frac{\partial u_3}{\partial x_j}\right) \qquad [3.2]$$

The complete expression for ε_{ij} consists of linear (first parentheses) and quadratic (second parentheses) terms. In many cases, derivatives in this formula are very small (<< 1) and their pair products, which enter into the second right-hand member in Eq 3.2, are negligibly smaller than derivatives. Hence they can be omitted, and thus only the two first members (first parentheses) of the equation are essential. It is only true if deformations are small, and that is why the tensor consisting only of first derivatives is called an **infinitesimal deformation (or strain) tensor**. This tensor, d_{ij}, is as follows:

$$d_{ij} = \begin{vmatrix} \frac{\partial u_1}{\partial x_1} & \frac{1}{2}\left(\frac{\partial u_1}{\partial x_2} + \frac{\partial u_2}{\partial x_1}\right) & \frac{1}{2}\left(\frac{\partial u_1}{\partial x_3} + \frac{\partial u_3}{\partial x_1}\right) \\ \frac{1}{2}\left(\frac{\partial u_2}{\partial x_1} + \frac{\partial u_1}{\partial x_2}\right) & \frac{\partial u_2}{\partial x_2} & \frac{1}{2}\left(\frac{\partial u_2}{\partial x_3} + \frac{\partial u_3}{\partial x_2}\right) \\ \frac{1}{2}\left(\frac{\partial u_3}{\partial x_1} + \frac{\partial u_1}{\partial x_3}\right) & \frac{1}{2}\left(\frac{\partial u_3}{\partial x_1} + \frac{\partial u_1}{\partial x_3}\right) & \frac{\partial u_3}{\partial x_3} \end{vmatrix} \qquad [3.3]$$

where the first line represents the projections of deformation along the x_1-axis, and so on.

In this Section we shall discuss only small deformations. The large deformations (if the first derivatives in Eq 3.2 are not small) will be considered in a separate Section below.

Relative displacement is definitely the cause of deformations inside a body. Are both displacement and deformation identical in this case? In order to answer this question, let us calculate the relative displacement which is, by definition, a gradient of **u**:

$$g = \text{grad}\ \mathbf{u}$$

The result can be presented in the form of a matrix:

$$g_{ij} = \begin{vmatrix} \dfrac{\partial u_1}{\partial x_1} & \dfrac{\partial u_1}{\partial x_2} & \dfrac{\partial u_1}{\partial x_3} \\ \dfrac{\partial u_2}{\partial x_1} & \dfrac{\partial u_2}{\partial x_2} & \dfrac{\partial u_2}{\partial x_3} \\ \dfrac{\partial u_3}{\partial x_1} & \dfrac{\partial u_3}{\partial x_2} & \dfrac{\partial u_3}{\partial x_3} \end{vmatrix} \qquad [3.4]$$

where the first line includes derivatives of the u_1-component of displacement along three coordinate axis, the second line is the same for the u_2-component, and the third, for the u_3-component of the vector **u**.

It is quite evident that the tensors d_{ij} and g_{ij} are not equivalent. The difference between them becomes clear if we decompose components of the tensor g_{ij} into two parts in the following manner:

$$g_{ij} = \frac{\partial u_i}{\partial x_j} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) + \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} - \frac{\partial u_j}{\partial x_i}\right) \qquad [3.5]$$

The first, so-called **symmetrical**, part of the tensor g_{ij} coincides with the deformation tensor d_{ij}, but

$$g_{ij} \neq d_{ij}$$

Then, we need to understand the physical meaning of this difference or the meaning of the second, so-called **antisymmetrical,** part of the displacement tensor. Figure 3.2 helps to explain the concept. Let us follow the deformation of a body element drawn as a rectangle. Two displacements, u_2 and $-u_1$, having gradients du_2/dx_1 and $-du_1/dx_2$, may occur as shown in the central part of Figure 3.2. Now, let us superimpose these two displacements, as shown on the right diagram. It is evident that the summation of du_2/dx_1 and $-du_1/dx_2$ does not lead to deformation but to rotation of the body element. It means that the second term in Eq 3.5 represents **rotation**,but not deformation. It can be written in the following form:

$$g_{ij} = d_{ij} + \theta_{ij} \qquad [3.6]$$

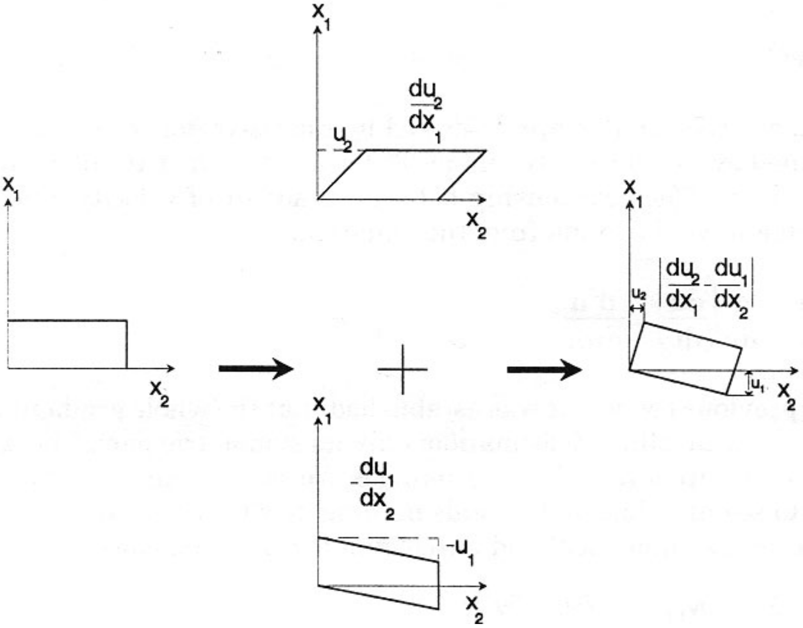

Figure 3.2. Superposition of two shear deformations leading to rotation.

where θ_{ij} consists of differences of the structure

$$\theta_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} - \frac{\partial u_j}{\partial x_i}\right) \qquad [3.7]$$

and describes the rotations (turns) of infinitesimal volumes inside a body. Thus *displacement at any point of a body is a sum of deformation and rotation.*

3.2 DEFORMATION RATE

If *velocity* (as a vector), at any point of a body, is the same, it means that a body moves as a whole and no deformation takes place. The deformation appears only as a consequence of velocity gradient at “a point”, which means that two neighboring sites (the distance between them being infinitesimally small) move with different velocities. If velocity is **v** (a vector value), its gradient is calculated as

$$a_{ij} = d\mathbf{v}/d\mathbf{r} \qquad [3.8]$$

where space coordinates are described by radius-vector, **r.** Thus a_{ij} is a tensor determined by two vectors (**v** and **r**). The velocity is the **rate of displacement**, i.e., $\mathbf{v} = d\mathbf{u}/dt$. The relationship between gradient of velocity and gradient of displacement can be found from the equation:

$$a_{ij} = \frac{d\mathbf{v}}{d\mathbf{r}} = \frac{d}{d\mathbf{r}}\left(\frac{d\mathbf{u}}{dt}\right) = \frac{d^2\mathbf{u}}{d\mathbf{r}dt} = \frac{d}{dt}\left(\frac{d\mathbf{u}}{d\mathbf{r}}\right) = \frac{dg_{ij}}{dt}$$

In the previous section, it was established that the whole gradient of displacement is not controlling deformation, only its symmetric part. The same is true for the deformation rate. The reasoning is the same as above. Differentiation in respect to scalar - time, d/dt, - adds nothing new to the result. By decomposing tensor a_{ij} into symmetrical and antisymmetrical components,

$$a_{ij} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) + \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} - \frac{\partial v_j}{\partial x_i}\right) \qquad [3.9]$$

one obtains

$$a_{ij} = D_{ij} + w_{ij} \qquad [3.10]$$

where D_{ij} is the **rate of deformation** tensor, and w_{ij} is the so-called **vorticity tensor**. As in the previous case, the rate of deformation tensor characterizes local changes of shape. The deformation is related to the first term in Eq 3.9, while the vorticity tensor describes the rate of rotation of local elements of a body without their deformation.

The difference between tensors a_{ij} and D_{ij} (similar to g_{ij} and d_{ij}) can be easily illustrated by a simple example. Let us analyze the rotation of a solid (non-deformable) body around some axes. The velocity, v, at a point located at the distance, r, from the axes is equal to $\omega\mathbf{r}$, where ω is the constant angular velocity. Thus $v = \omega\mathbf{r}$, and the gradient of velocity, grad v = dv/dr, is evidently equal to ω. It means that in rotation of a solid body the gradient of velocity does exist but there is no deformation (because the body was assumed to be non-deformable).

3.3 LARGE DEFORMATIONS

The difference between *small* and *large* deformations depends on the value of derivatives in Eq 3.2. If all derivatives are much smaller than 1, the quadratic terms can be neglected, i.e., products of derivatives (in parentheses), and the tensor d_{ij} is used instead of ε_{ij}.

In the discussion of a concept of large deformations, it is always assumed that *a reference state* for deformation can be established. In this sense, flow of a liquid may not be considered as deformation because all states are equivalent. Liquid does not have initial (or reference) state. That is why only materials having **memory** of their initial state are important here.

Having such an approach, it is very easy to illustrate the essential difference between small and large deformations, using the model from Figure 3.3. Let a bar of the length l_o be stretched by Δl. The simple question is: what is the deformation in this case?

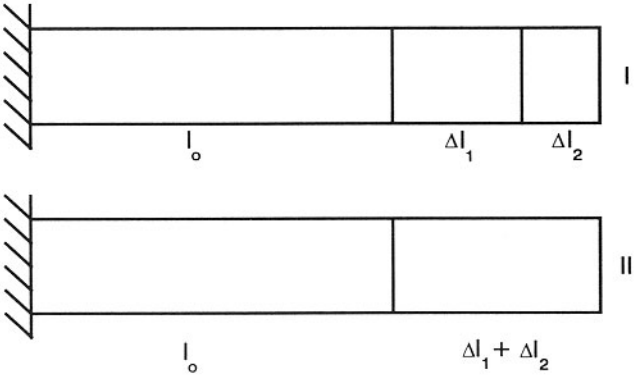

Figure 3.3. Two ways of realization large deformation of uniaxial extension.

In the first case, let $l_o = 1$ and $\Delta l = 0.1$. The so-called **engineering measure** of deformation equals $\varepsilon^* = \Delta l / l = 0.1$ (or 10%), and it is expressed as $\varepsilon_{11} = du_1 / dx_1$. The reasoning becomes much more complicated if Δl is comparable with l, for example, if $\Delta l = 1$. Certainly in this case we also can use an engineering measure of deformation as a characteristic of change of specimen length, and it is equal to 1 (or 100%). But this approach to the definition of deformation contains an inherent contradiction. Let us compare two situations, drawn in Figure 3.3: In the first case (case I), the increase in the length occurs in two steps: initially by Δl_1 and then Δl_2. Then the deformation in the first step is $\varepsilon_1{}^* = \Delta l_1 / l_o$ and $\varepsilon_2{}^* = \Delta l_2 / l_1$ in the second step, because initial length of a sample in the second step is l_1. Then the complete deformation is the sum of both

$$\varepsilon_I{}^* = \varepsilon_1{}^* + \varepsilon_2{}^* = \frac{\Delta l_1}{l_o} + \frac{\Delta l_2}{l_1} = \frac{l_o(\Delta l_1 + \Delta l_2) + \Delta l_1^2}{l_o l_1}$$

In the second case (case II), the increase of the length is achieved in one step. This increase is equal to $(l_1 + l_2)$ and the deformation $\varepsilon_{II}{}^*$ is calculated as

$$\varepsilon_{II}{}^* = \frac{\Delta l_1 + \Delta l_2}{l_o} = \frac{l_o(\Delta l_1 + \Delta l_2) + \Delta l_1^2 + \Delta l_1 \Delta l_2}{l_o l_1}$$

The $\varepsilon_I{}^* \neq \varepsilon_{II}{}^*$ contradicts the physical meaning of the experiment's interpretation because the final result is not the same in both cases; the sample does not "know" which way it was brought to the final state, whereas calculations show a difference. This appears only as a result of large deformations, because if deformations are small, the quadratic terms in formulas for $\varepsilon_I{}^*$ and $\varepsilon_{II}{}^*$ are negligible in comparison to the linear terms, and in this approximation (which is quite reasonable if Δl_1 and $\Delta l_2 << l_o$) both measures of deformation become identical.

From the above, it becomes apparent that there is a need to introduce such measure of deformation which does not depend on the order of operations. Such measure is called a **Hencky measure**,[1] ε^H, defined by:

$$\varepsilon^H = \ln(\Delta l / l) \qquad [3.11]$$

Large deformations analyzed by this measure obey the law of additivity. It is easy to note that in the example discussed above

$$\varepsilon_I^H = \varepsilon_{II}^H$$

i.e., the result does not depend on the history of deformation, as required.

In rheological literature, some other values are used as a **measure** of deformations. In fact, any function of deformation can be treated as a measure of deformation. One of the most widely used is the so-called **Cauchy - Green tensor** of deformation, C_{ij}. It is directly related to the concept of large deformations expressed by Eq 3.2, and the Cauchy-Green tensor is determined as:

$$C_{ij} = \delta_{ij} + 2\varepsilon_{ij} \qquad [3.12]$$

where δ_{ij} is the unit tensor (or Kronecker delta).

The Cauchy - Green tensor characterizes change of the distance between two arbitrary “particles” in a “point”: here again we speak about a point, not as a mathematical idea, but as a physical object which contains many “particles”.

Another tensor of large deformations is frequently used. This is the tensor inverse (or reciprocal) to the Cauchy - Green tensor, C_{ij}, named the **Finger tensor,** C^{-1}_{ij}. According to the definition, the relationship between both is

$$C_{ij}C^{-1}_{ij} = \delta_{ij}$$

Introducing different measures of deformations does not exclude the main question regarding the initial state - point of reference of the deformed state. The value of this question has been already demonstrated by the example of large deformations in uniaxial extensions. For static states this problem can be solved by introducing the Hencky measure of deformations. But the same problem appears and becomes more pertinent for a continuously moving medium where the position of deformed elements of a body is changing in time and we want to describe the process or the rate of deformation.

A similar situation has importance in classical hydrodynamics where transformation is followed (for example, temperature effect or chemical reaction) in moving media. In such a case, the problem is solved by using a so-called material or **substantial derivative**, D/Dt, which can be written for any arbitrary variable, Y, as

$$\frac{DY}{Dt} = \frac{\partial Y}{\partial t} + \sum \frac{v_k \partial Y}{\partial x_k} \qquad [3.13]$$

The main new approach which appears in the theory of large deformations concerns the importance of knowing the rate of deformation not only in a *fixed* coordinate system but in *moving* one, as well. It means that the behavior of a material in moving sites must be described because changes occur not at a point of a space but in a traveling element of a material which deforms along its replacement. This concept is called the **principle of material objectivity** and it states that all physical phenomena, certainly including laws of deformation, must not depend on a coordinate system used for their mathematical formulation.

As a result of large deformations, material elements can travel far away from their initial position, and that is why it is important to apply proper rules of transition from the reference state. Similar to our discussion of large uniaxial extension, it is also important here that the choice of different reference states must not lead to an ambiguous estimation of deformation. An observer who measures properties of a material is always positioned in fixed (unmovable) coordinate system. Hence the general approach consists of formulating ideas concerning possible rheological behavior of a material for a moving (and deforming) element of a medium, recalculating them into a fixed coordinate system, and then comparing the results with an experiment.

This is completely true for the rate of deformation. There are different mathematical ways to realize the idea of transformation of the rate of deformation tensor into a fixed coordinate system and, depending on the choice, various special forms of time derivatives, generalized by Eq 3.13. Moreover, in some theoretical studies, there is a necessity to introduce kinematic tensors of a higher order hich are determined as time derivatives of the Cauchy-Green or Finger ten - sors. They are used if it is assumed that rheological behavior of a material depends, not on the rate of deformation only, but on higher derivatives of deformation, as well. In Chapter 7, devoted to properties of viscoelastic materials, their behavior is modeled by equations containing a sum of n-th order time derivatives of deformation (so-called rheological equations of a differential type). If deformation is large, one needs to use measures of large deformations and calculate their time derivatives.

In the case of the substantial time derivative, D/Dt, the physical meaning of this operation requires us to calculate derivatives for a moving medium which follow time changes in a material point changing its initial position. This problem in the theory of large deformations is solved by introducing time derivatives of a different type. The most popular are the Rivlin - Eriksen, $A_n(t)$, and White - Metzner, $B_n(t)$, tensors of the n-th order.[2] They are determined as

$$A_n(t) = \frac{D^n C_{ij}(t)}{Dt^n}$$

and

$$B_n(t) = -\frac{D^n C^{-1}_{ij}(t)}{Dt^n}$$

where C_{ij} and C^{-1}_{ij} are the Cauchy-Green and Finger tensors, respectively.

Saint-Venant[3] was the first who realized the necessity to consider the concept of large (finite) deformations. Later ideas of the theory of large deformations were discussed and developed by Finger,[4] Zaremba,[5] Cosserat, [6] and Jaumann.[7] Fundamental works were also contributed by Biot.[8] More recently, Rivlin[9] discussed studies on large deformations in numerous publications. A complete treatise on modern theories of large deformations of solids is included in book by Green and Adkins,[10] and for liquids, by Lodge.[11] The use of various measures of large deformations and different types of their time derivatives allows one to arrive at qualitative predictions concerning possible effects in rheological behavior of a material, but it is the task of an experiment to find a model which can adequately describe physical phenomena observed for different real materials.

3.4 PRINCIPAL VALUES AND INVARIANTS OF THE DEFORMATION TENSORS

The principal deformations (strains) are calculated in the same way as principal stress. For the infinitesimal deformation tensor, the principal deformations, d_1, d_2, and d_3, are extensions along three orthogonal directions. It can be illustrated by a very spectacular picture of deformations in the vicinity of some point. For this aim, let us represent an infinitely small volume in a body as a sphere (Figure 3.4) with a center positioned at a point A and radius of the sphere dr (infinitesimal small length). The coordinates of the central point A are x_1, x_2, and x_3. As a result of movements and displacements, the following changes have taken place in a body: the point A has moved to a new position A*, the directions of the radii AB, AC, and AD have changed to the directions A*B*, A*C*, and A*D*, respectively. And the sphere itself has transformed into an ellipsoid with semi-axes of lengths $(1 + d_1)dr$, $(1 + d_2)dr$, and $(1 + d_3)dr$, respectively.

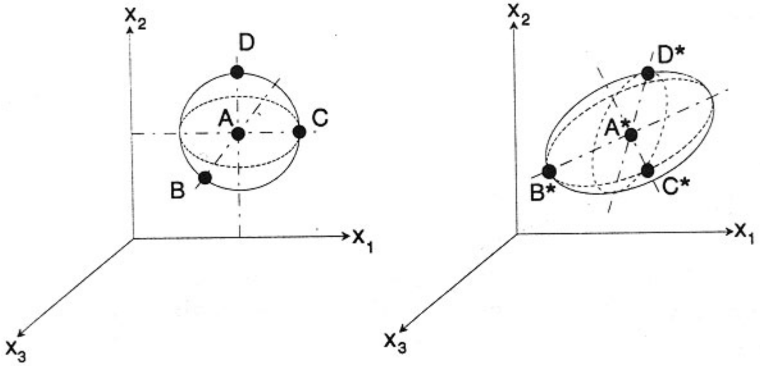

Figure 3.4. Transformation of a sphere into an ellipsoid as a consequence of three principal deformations along their axes.

The deformations characterize the change of the shape of a volume element of a body — transition from a sphere to an ellipsoid. Besides they determine the relative change of the volume, ε_v, which can be written as follows:

$$\varepsilon_v = \frac{V_{ell} - V_{sph}}{V_{sph}} \qquad [3.14]$$

Simple calculation shows that

$$\varepsilon_v = (1 + d_1)(1 + d_2)(1 + d_3) - 1 \qquad [3.15]$$

It is very easy to show that ε_v is expressed through invariants of the deformation tensor because change of volume must not be associated with the choice of the coordinate system, and the invariants do not depend on the coordinate axes. If deformations are small and it is possible to neglect quadratic terms in comparison with linear terms, the Eq 3.15 gives a particularly evident result:

$$\varepsilon_v = d_1 + d_2 + d_3 \qquad [3.16]$$

i.e., *volumetric changes are equal to the first (linear) invariant of the tensor of infinitesimal deformations* and that is the physical meaning of the latter.

The volumetric changes in deformation can also be represented through extension ratios. For this purpose, let us (conditionally) cut out a small rectangular parallel pipe, at a some site in a body, oriented along the principal axes. Let the length of its edges be a, b and c before deformation, and become a*, b*, and c* as a result of deformation. Then the extension ratios are:

$$\lambda_1 = a^* / a; \ \lambda_2 = b^* / b; \ \lambda_3 = c^* / c$$

and the volume change is calculated as

$$\frac{\Delta V + V}{V} = \frac{a^* b^* c^*}{abc} = \lambda_1 \lambda_2 \lambda_3$$

The last formula allows one to state a very simple rule of constancy of volume in deformations of any type:

$$\lambda_1 \lambda_2 \lambda_3 = 1 \qquad [3.17]$$

Like any other tensor, the deformation tensor, d_{ij}, can be decomposed into spherical and deviatoric parts. Considering that the first invariant is the volume change, we can write:

$$d_{ij} = \frac{\varepsilon_v}{3} \delta_{ij} + d_{ij}^{(dev)}$$

where the second member in the right-hand part of the equation is a deviatoric part, $d_{ij}^{(dev)}$, of the d_{ij}-tensor which describes shape transformation occurring without changes in volume.

3.5 UNIAXIAL ELONGATION. POISSON RATIO

Let a bar of sufficient length to be stretched and increase its length by $\Delta l / l_0$ or the extension ratio, λ, be $(\Delta l + l_0) / l_0$. If $(du_1/dx_1) = \lambda - 1$, one can write

$$\varepsilon_{11} = \frac{du_1}{dx_1} + \frac{1}{2}\left(\frac{du_1}{dx_1}\right)^2 = (\lambda - 1) + \frac{1}{2}(\lambda - 1)^2 = \frac{1}{2}(\lambda^2 - 1) \qquad [3.18]$$

Additional to being stretched in the axial direction, the bar undergoes changes in the lateral direction. The relation between relative changes of dimensions in the lateral and axial directions cannot be established on the basis of a purely geometrical picture of deformations because this relation is an inherent, independent property of a material. The quantitative characteristics of this property is the ratio of relative lateral contraction to the relative longitudinal extension and this special property of a material is called the **Poisson ratio**.

For simplicity, let the bar have a round cross-section with the radius, r_o, and the length, l_o. If its elongation is Δl, and, as a result of stretching, radius is decreased by Δr, then, by definition, the Poisson ratio, μ, is:

$$\mu = \frac{\Delta r / r_o}{\Delta l / l_o} \qquad [3.19]$$

It is now easy to calculate the volume change, resulting from uniaxial stretching. The relative change of volume $\Delta V/V$ is

$$\Delta V / V = \frac{(r_o + \Delta r)^2 (l_o + \Delta l) - r_o^2 l_o}{r_o^2 l_o} \qquad [3.20]$$

If $\Delta l << l_o$ and consequently $\Delta r << r_o$ (small deformations), the last formula gives

$$\Delta V / V = (1 - 2\mu) \qquad [3.21]$$

Poisson ratio is a measure of volume changes during small deformations. From Eq 3.21, one can see that deformations occur without volume changes when and if $\mu = 0.5$. For real solid materials, $\mu < 0.5$, meaning that their elongation is accompanied by increase in volume. Only for some rubbers $\mu = 0.5$.

It is interesting to use the general method of decomposing the deformation tensor, d_{ij}, into spherical and deviatoric terms for uniaxial extension. If $\lambda << 1$, and deformation is equal to ε, the deformation tensor for such case can be written as:

$$d_{ij} = \begin{vmatrix} \varepsilon & 0 & 0 \\ 0 & -\mu\varepsilon & 0 \\ 0 & 0 & -\mu\varepsilon \end{vmatrix} = \frac{1-2\mu}{3}\varepsilon\delta_{ij} + \frac{1+\mu}{3}\varepsilon \begin{vmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

The structure of this sum is very similar to the structure of the stress tensor decomposition into two parts (compare with the analogous procedure in Chapter 2). A similar approach will also be taken in the next Chapter for the discussion of elasticity theory.

More precise analysis of Eq 3.20 shows, however, that for large deformations Eq 3.2 is not valid, and *the rule of* $\mu = 0.5$ *as the condition for maintaining the constant volume at stretching has no general meaning*. Indeed, preserving the formal definition 3.19 for the Poisson ratio, according to Eq 3.20, we have for $\Delta V/V=0$:

$$1-2\mu(1+\varepsilon)+\mu^2\varepsilon(1+\varepsilon)=0 \qquad [3.22]$$

If $\varepsilon << 1$, Eq 3.22 is converted to an ordinary condition such that $\mu = 0.5$, but in the more general case it is not true. For example, let the bar be stretched by 9 times (it is quite possible for rubber ribbons or melted fibers). It means that $\Delta l / l_o = 8$ and the volume can remain unchanged if the final radius becomes equal to 1/3 of its initial value. Then $\Delta r / r_o = 2/3$. In this case according to Eq 3.22, and formal definition 3.19, $\mu = 1/12$. This example shows that adaptation of infinitesimal deformation mechanics ($\mu = 0.5$ as a necessary condition for constant volume at extension) to the range of large deformations must not be done in a straightforward manner.

3.6 SIMPLE SHEAR AND PURE SHEAR

Simple shear is a very important type of deformation because movement of all fluids and liquid-like materials is based on the principle of sliding of neighboring layers relative to each other. The schemes of simple shear for an element of a body in the case of small deformations, and in the general case of arbitrary deformation, are shown in Figure 3.5 a and b, respectively. Along the direction of shear marked by an arrow, a displacement, u_1, takes place. Its gradient, du_1/dx_2, is determined by the slope which will be denoted as γ:

$$\gamma = \tan\alpha = du_1 \big/ dx_2$$

Since the length of linear elements, which were oriented before deformation in the x_2-direction, is changed in shear, one more displacement component, u_2, appears. It is related to the change in the length of the segment OA, which after displacement now becomes OA*:

$$\frac{OA^* - OA}{OA} = \left(1 + \gamma^2\right)^{1/2} - 1 \qquad [3.23]$$

The value of $\gamma = du_1/dx_2$ for simple shear determines all components of the tensor at large deformations. According to the deformation of the ε_{ij} tensor, its components are:

$$\varepsilon_{12} = \varepsilon_{21} = \frac{1}{2}\gamma$$

$$\varepsilon_{22} = \frac{1}{2}\gamma^2$$

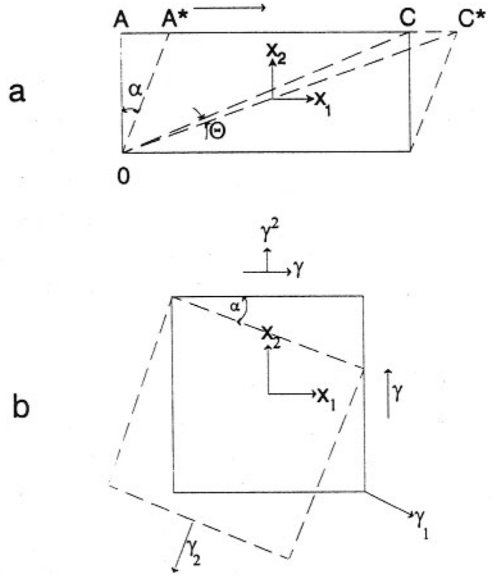

Figure 3.5. Small (a) and large (b) deformations in simple shear.

This tensor is graphically illustrated in Figure 3.5 b in which the components of the tensor, ε_{ij}, are marked by arrows (factor 1/2 is omitted in drawing this Figure). The appearance of a diagonal component in the deformation tensor in a simple shear is a direct consequence of large deformations because ε_{22} is proportional to γ^2 and its value becomes negligible if $\gamma << 1$. This phenomenon is known as the **Poynting effect**, observed in twisting of wires: their length slightly changes in this case. Twisting is an example of shear deformation, and the observed change of the length in the axis direction is restricted to ε_{22}-component of the deformation tensor.

Let us now discuss some models of simple shear which are often used in rheological literature and are illustrative for the tensorial nature of the deformation tensor.

The angle, β, between the direction of shear, x_1, and the orientation of the principal axis is calculated as

$$\beta = \frac{1}{2}\mathrm{atan}(\gamma / 2) \qquad [3.24]$$

The main components of the deformation tensor may be written as follows:

$$\gamma_1 = \frac{1}{2}(\lambda_1^1 - 1);\ \gamma_2 = \frac{1}{2}(\lambda_2^2 - 1);\ \gamma_3 = \frac{1}{2}(\lambda_3^2 - 1) \qquad [3.25]$$

where λ_1, λ_2, and λ_3 are principal elongations (or extension ratios in the directions of principal axes). These values are related to the angle β in Eq 3.24, and to the plane deformation state (as in Figure 3.5); they are as follows:

$$\gamma_1 = \cot\beta,\ \gamma_2 = \tan\beta, \text{ and } \gamma_3 = 1$$

A result obtained from the last set of formulas for λ_i indicates that in simple shear no volume change occurs because $\gamma_1\gamma_2\gamma_3 = 1$ in accordance with Eq 3.17.

Components of the Cauchy - Green tensor in shear are important for theoretical discussion concerning rheological models of elastic liquids. Calculations give the following expression for C_{ij}:

$$C_{ij} = \begin{vmatrix} 1 & \gamma & 0 \\ \gamma & 1+\gamma^2 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

In a simple shear, not only the lengths of linear elements change (e.g., along the principal directions), but rotation of the elements of a body also takes place. This effect is illustrated in Figure 3.5, where the angle of turn (rotation), θ, of the diagonal from OC to OC* position, is shown.

Shear deformation, AA*, in this Figure, is due to displacement, and α is its gradient. Any gradient of displacement consists of deformation and rotation, which in general form is expressed by Eq 3.5. For small displacement, the angle of rotation, $\theta = \alpha \,/\, 2$, must be used, unlike for large deformations, where the general Eq 3.5 is applicable.

It is possible to find such shear conditions where no rotation occurs. This case, called **pure shear**, is based on definition of the ω_{ij} from Eq 3.7. It is seen that $\omega_{ij} = 0$ if all differences of the displacement gradient equal zero. For the simple shear, this condition has following form: $du_1/dx_2 = du_2/dx_1$.

Geometrical image of a pure shear is drawn in Figure 3.6. In pure shear the diagonal AB of the small square (at some point) moves, due to deformation, into new position A*B*, parallel to its initial position, and the diagonal OM does not change its position at all, being only extended to OM*; therefore, no element of the body undergoes rotation.

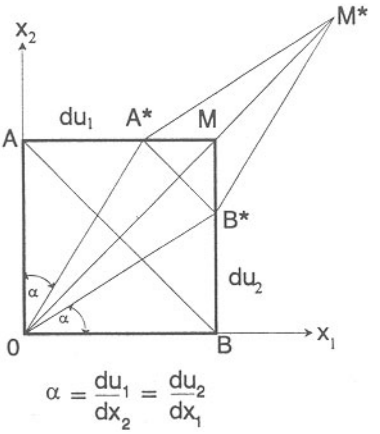

Figure 3.6. Scheme of pure shear.

Figure 3.6 can be obtained in a different way. It is quite evident that the transition from the square OAMB to the rhomb OA*M*B* can be achieved by pressing the square along the direction AB, with simultaneous stretching along the direction OM. It means that pure shear can be considered (and can be realized) through the superposition of two uniaxial extension deformations (with different signs).

From the point of view of continuum mechanics, the difference between simple and pure shear is not significant, since deformations occur in the infinitely small volumes “at a point” and the rotation of infinitesimal elements of a body as a whole has no effect on its deformation. But in real materials this difference can appear to be essential, because an act of deformation involves certain volumes which may include a large number of molecules or their constituent parts. That is why rotation in simple shear does influence the rheological behavior of deformable (in particular flowing) materials and is taken into consideration in formulating laws of deformations in the form of time derivatives used to calculate the rate of deformation, as mentioned above.

3.7 EXAMPLES

Unlike stress analysis, the calculation of deformation fields cannot be carried out for an arbitrary scheme of loading because reaction of a material to an external force depends on inherent properties of a medium and its geometrical size and shape. That is why calculation of deformation is possible only for materials having established properties. The same force creates unlimited deformation in a liquid and only small deformation in a steel object.

The deformation can be found, regardless of rheological properties of a material, only for homogeneous deformation fields. Some principle examples have been already discussed in the preceding Sections of this Chapter, and here we shall summarize the main results.

3.7.1 UNIAXIAL EXTENSION OF A BAR (BEAM, FIBER)

It is one of the most frequently met cases in technology (e.g., orientational extension of fibers) and everyday life. Stress analysis of uniaxial extension was discussed in Chapter 2. Now, we shall summarize the main relationships describing deformation.

Let the extension ratio of a uniform bar loaded along its axis be equal to λ (initial length l_o, the length after deformation l, the extension ratio $\lambda = l/l_o$). The engineering measure of deformation, ε^*, is $(\lambda - 1)$. If $\varepsilon^* << 1$ then

$$\varepsilon_{11} = \varepsilon^*$$

In uniaxial extension, lateral contraction takes place, and its value is determined by the Poisson ratio

$$\varepsilon_{22} = \varepsilon_{33} = -\mu\varepsilon_{11} = -\mu\varepsilon^*$$

In some cases, it is especially important to know the components of complete deformation, for example, if we wish to divide the full deformation into plastic and elastic parts (such problem is pertinent to fiber spinning technology where the main goal is to produce highly oriented fibers). It is necessary to use the measure of deformation which is additive to the prehistory of loading and the Hencky measure of deformations, ε^H, as already discussed, to satisfy the requirement. For uniaxial extension

$$\varepsilon^H = \ln(1 + \varepsilon^*) = \ln\lambda$$

In the case of large deformations, ε_{11}-component of the deformation tensor has the following structure:

$$\varepsilon_{11} = \varepsilon^* + \frac{1}{2}\varepsilon^{*2} = (\lambda - 1) + \frac{1}{2}(\lambda - 1)^2 = \frac{1}{2}(\lambda^2 - 1)$$

In applications of the theory of large deformations to rubbers and rubbery polymeric solutions, the Cauchy - Green and Finger methods of large deformation calculations are widely used. Their values in our case are as follows:

$$C_{11} = \lambda^2;\ C^{-1}_{11} = \lambda^{-2}$$

Other components of C_{ij} and C^{-1}_{ij}-tensors are expressed through deformations, ε_{22} and ε_{33}, depending on the Poisson ratio.

3.7.2 SHEAR

Shear deformations are very typical for all hydrodynamic problems, including the flow of low viscosity liquids (water, oil, gasoline), liquid-like and plastic materials, such as paints, sealants, clay, polymer solutions and melts, colloids, and many others. Besides, many engineering applications rely on shear: twisting of bars and tubes, cutting and threading are operations in which shear plays a dominant role.

Main theoretical results concerning large deformations in shear were discussed in detail in the last section of this Chapter and need not be repeated.

Shear rate, determining peculiarities of flow, may have variable impact even under the same geometrical conditions and stress, depending on rheological properties of a medium. Hence, only for homogeneous flow can the shear rate be estimated beforehand. Such flow occurs in a very thin gap between two parallel surfaces, with one of them fixed and the other moving with constant velocity, v.

This condition is typical for flow in narrow gaps of bearings, and more important, it is widely used for measurement of rheological properties of various liquids in so-called rotational viscometers.

If the width of a gap, h, between surfaces moving in parallel to each other is small, the shear rate, $\dot{\gamma}$, in a flowing liquid is calculated as

$$\dot{\gamma} = v/h$$

This formula also applies when both surfaces are curved but the size of the gap is much smaller than the radius of curvature; for example, if flow occurs in a very narrow gap between two coaxial cylinders, one of which is rotating with constant velocity.

3.7.3 PLANE DEFORMATION (STRAIN) STATE

Plane (two-dimensional) stress and deformation (strain) state appears in thin items, stretching films, membranes, shells, and so on. The stress fields for some typical situations have been analyzed in Chapter 2. The calculation of the deformation field, regardless of rheological properties of matter, can be performed for homogeneous static (equilibrium) state (e.g., a sphere (balloon) filled with gas, having known pressure, up to the certain size).

Let the initial radius of a balloon be R_o, and after increase of inner pressure the radius becomes R. The initial width of a cover is δ_o and $\delta_o << R_o$. The extension ratio equals $\lambda = R/R_o$. The directions along the radius of a sphere and tangential to its surface are principal directions because shear stresses and deformations are absent in thin shells, as discussed in Chapter 2.

The surface of the cover increases as a result of deformations, and for $(R - R_o)/R_o << 1$ we have:

$$\varepsilon_2 = \varepsilon_3 = \frac{r - R_o}{R_o} = \lambda - 1$$

where the directions 2 and 3 are tangential to the surface of the cover.

The third principal deformation, ε_1, (the direction 1 is along the radius) can be calculated using Eq 3.21, considering volumes of a material before and after deformation. It is easily seen that in the case under discussion

$$\Delta V/V = 1 - (R^2\delta/R_o^2\delta_o)$$

It means that

$$R^2\delta \,/\, R_o^2\delta_o = 2\mu$$

and

$$\delta \,/\, \delta_o = 2\mu(R_o \,/\, R)^2 = \frac{2\mu}{\lambda^2}$$

Then

$$\varepsilon_1 = (\delta - \delta_o) \,/\, \delta_o = \frac{2\mu}{\lambda^2} - 1$$

If volume of a material under deformations is constant (for example, if the cover is made out of rubber), $\mu = 0.5$ and we have

$$\varepsilon_1 = \frac{1}{\lambda^2} - 1$$

3.7.4 THREE-DIMENSIONAL DEFORMED STATE

Many engineering applications can benefit from analysis of these relationships. Important to note is that consideration must be given to the real rheological properties of the material in question. Some general principles are worth citing because they apply to analysis of large deformations of rubbers.

If the values of principal extension ratios are λ_1, λ_2, and λ_3, or the engineering deformations along principal axes are

$$\varepsilon_i{}^* = \lambda_i - 1$$

then the values of the Cauchy-Green and Finger tensors are:

$$C_1 = \lambda_1^2;\ C_2 = \lambda_2^2;\ C_3 = \lambda_3^2$$

$$C_1^{-1} = \lambda_1^{-2};\ C_2^{-1} = \lambda_2^{-2};\ C_3^{-1} = \lambda_3^{-2}$$

The first invariants of C and C^{-1} tensors are

$$C_I = (\lambda_1\lambda_2\lambda_3)^2 \text{ and } C_{II}^{-1} = (\lambda_1\lambda_2\lambda_3)^{-2}$$

As discussed above (see Eq 3.17), the equality $\lambda_1\lambda_2\lambda_3 = 1$ means that deformation proceeds without changes of volume. Hence the condition of constant volume in three-dimensional deformations of arbitrary type is: $C_I = C_{II}^{-1} = 1$.

3.8 CONCLUDING REMARKS

Action of outer forces results in **displacement** of the points of continuum. If displacements are inhomogeneous throughout a body, and relative displacements appear, they lead to **deformations**, which are the consequence of changes of infinitesimal distances between different points inside a body. Displacement is a *vector*, but relative displacement and deformation are objects of *tensorial nature*, because to describe them both it is necessary to operate with two vectors. The relative displacement is described by a radius-vector of two points for which displacement is considered, and the deformation by a vector of displacement and a radius-vector of a point, where the displacement occurs.

Deformation is only a part of relative displacement, which also includes **rotation** of elements of a body as a whole.

Deformations can be small (or **infinitesimally small**) or large. The boundary is determined by the value of relative displacement (or gradient of displacement), which is a dimensionless value. If this value is small (<< 1), it is reasonable to neglect the square of this value in comparison with the value itself. One can thus neglect all quadratic terms included in the relationship. In this case, deformations can be treated as infinitesimally small.

If **large deformations** are considered, some new effects appear. First of all, physical phenomena occur at a site which moves and during deformation vacates its initial position. Description of all occurrences (including deformation itself) must be done in relation to a moving point. An observer, carrying out experiments with a material, follows its behavior and treats the results of measurements in a fixed coordinate system. Hence it is necessary to know the rules of transformations and the tensor values used for projecting deformations from a moving to a fixed coordinate system.

Large deformations are characterized by special measures of deformation, such as the **Hencky measure** (a logarithmic measure subjective to additivity rule), **Cauchy - Green**, and **Finger tensors** of large deformations.

Time derivative of displacement of a point is its velocity, time derivative of relative displacement is a gradient of velocity, and time derivative of deformation is **rate of deformation**. Time derivatives of tensors are also tensors, and for calculation of the rate of deformation, special rules exist which take into consideration large deformations and movement of a deforming site in space. Gradient of velocity is a sum of rate of deformation and **vorticity** tensor as elements of a body which can not only deform but simultaneously rotate it.

In the process of uniaxial longitudinal extension, a body undergoes lateral compression. The ratio of relative changes of lateral and longitudinal sizes is called the **Poisson ratio**, which is an inherent property of a material. For the range of small deformations the volume of a body remains unchanged if the Poisson ratio equals 0.5, but in large deformations this simple rule is not obeyed.

There is a special interesting case of deformation when volume changes are not taking place, which is a **simple shear**. At large shear deformations, diagonal components of the deformation tensor appear, and they lead to some effects of a second order, such as elongation of long items at their twisting (**Poynting effect**). Simple shear is accompanied by rotation of elementary volumes in space. It may reflect behavior of a material. In order to exclude rotation, it is necessary to apply **pure shear** in which rotation does not exist. This type of deformation is equivalent to a two-dimensional situation of superposition of extension and compression in mutually perpendicular directions.

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4

RHEOLOGICAL EQUATIONS OF STATE

4.1 MAIN RHEOLOGICAL EFFECTS

The concept of **rheological equation of state** (or **constitutive equation**) occupies the central position in modern rheology. It is a relationship between stresses acting at a point and deformations occurring as a result of their action. Such a relationship determines all mechanical phenomena which can be expected in the observation of mechanical behavior of a material. Rheological equations of state serve the purpose of understanding and describing qualitatively and (the most desirable) quantitatively various “anomalous” effects observed in real life for real materials. Some macroforms of these effects were mentioned in Chapter 1 and they are now described in rheological language in terms of stresses, deformations, and rates of deformation.

The number of various rheological “anomalies” is large; any kind of deformation of material which does not obey the simplest, classical rheological equations (Newton and Hooke Laws) inevitably leads to different, new qualitative, or at least quantitative, phenomena which are not described by the concept of a Newtonian fluid and a Hookean solid body. Each of these phenomena can be considered as a “rheological effect”. However, there are several fundamental experiments which definitely indicate that material is either “classic” or “rheological”. These experimental observations are discussed below.

4.1.1 NON-NEWTONIAN VISCOSITY

If we define viscosity, η, by Eq 1.1 as a ratio of shear stress, σ, and shear rate, $\dot{\gamma}$, and then carry out measurements at different values of σ or $\dot{\gamma}$, the ratio $\sigma / \dot{\gamma}$ should be constant because viscosity is a *property* of liquid. Liquids having constant viscosity for any $\dot{\gamma}$ are called Newtonian liquids and their viscosity is called **Newtonian viscosity**. In many real cases, the ratio $\sigma / \dot{\gamma}$ is not constant, and it is called **apparent** (or non-Newtonian) **viscosity**, even though the same symbol, η, is used. Dependence of the apparent viscosity on shear stress or shear rate is called **flow curve**. It can be displayed in any of three coordinate systems, $\eta - \sigma$, $\eta - \dot{\gamma}$, or $\sigma - \dot{\gamma}$, as shown in Figure 4.1. The apparent viscosity decreases in this example, and such effect is frequently called **shear thinning**. This is the most typical case, but viscosity can also increase with shear rate increasing (the so-called **shear-thickening**). Sometimes, viscosity decreases or increases (for the same material) in a different range of shear rate.

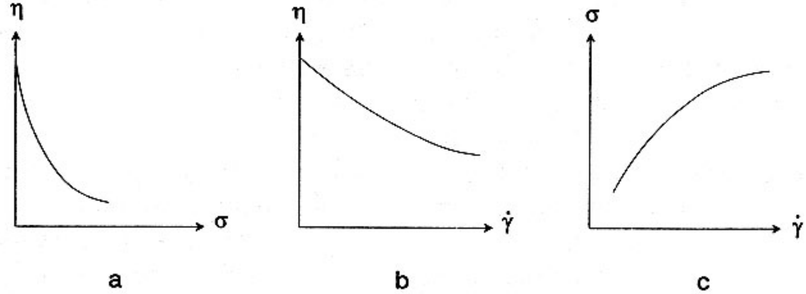

Figure 4.1. Different images of a flow curve: dependencies $\eta(\sigma)$ - a, $\eta(\dot{\gamma})$ - b and $\sigma(\dot{\gamma})$ - c.

In many applications, it is important to know how apparent viscosity changes when shear rates (and stresses) are changing in a very wide range. In order to make this dependence more visual, logarithmic scales are frequently used. The graph constructed in $\log\dot{\gamma}$ - $\log\sigma$ coordinates is also called a flow curve. The flow curve of any Newtonian liquid is a straight line inclined by 45° to both axis; therefore measurement points fulfill the condition of constancy of the $\sigma / \dot{\gamma}$ ratio.

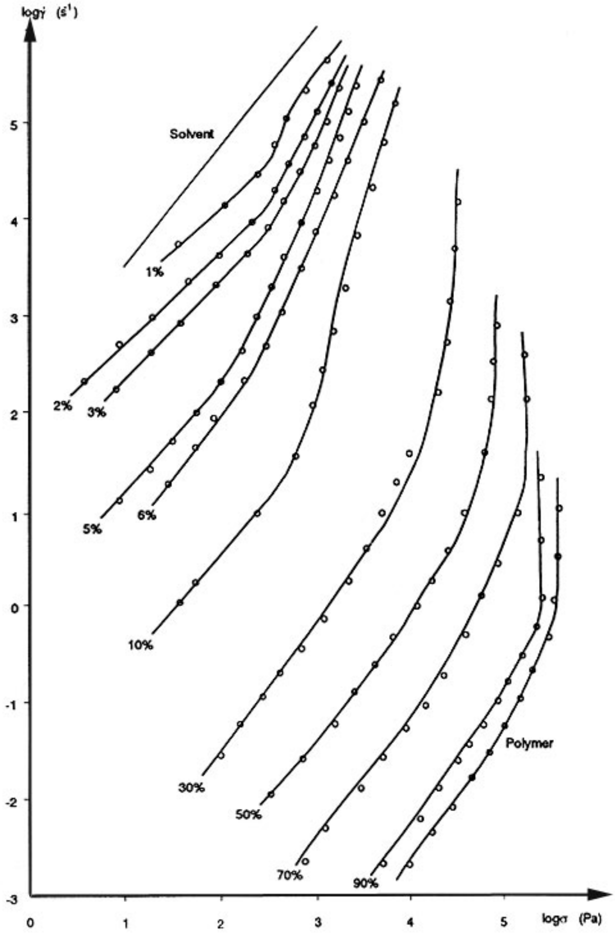

Figure 4.2. Flow curves of polybutadiene solutions in methyl naphthalene. Upper line - flow curve of a pure solvent. Lower curve - flow curve of a pure polymer. All other curves are drawn for solutions. Concentration of the polymer in weight percentage as labeled. T = 25°C.

Non-Newtonian behavior of a liquid was, for the first time, observed by Ostwald[1] for colloid dispersions, and was explained by the changes of a structure of colloid as a result of deformation. Some authors continue to call the ratio $\sigma / \dot{\gamma}$ a **structure viscosity** (struktur Viskosität[1]), even though the origin of this effect is not necessary related to the rupture of a "structure" of a flowing liquid.

Some typical examples of non-Newtonian behavior are given in Figures 4.2 and 4.3 for polymeric systems and in Figure 4.4 for a bentonite solution. In all cases shown in these Figures, the effect of non-Newtonian flow is very pronounced, though it appears in different forms: as a gradual decrease of apparent viscosity in Figures 4.2 and 4.3, and as a sudden jump from very high to very low viscosity in Figure 4.4.

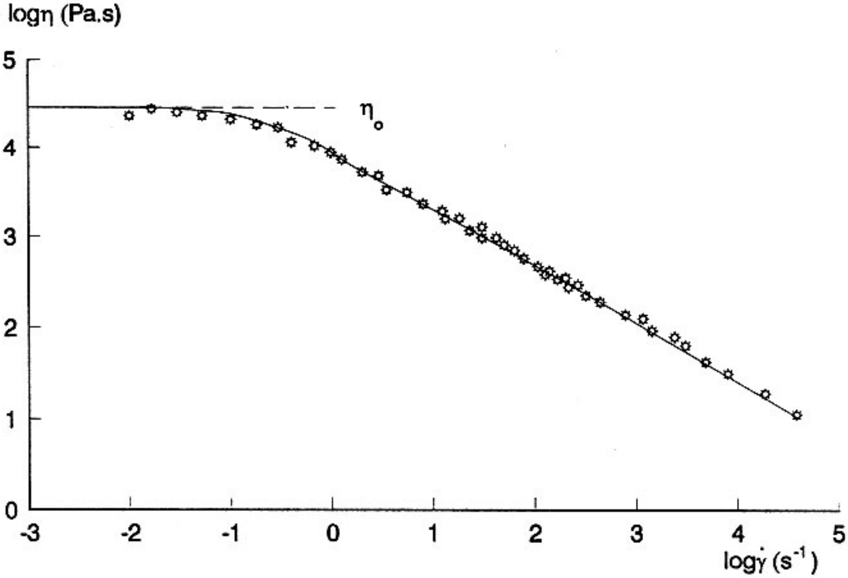

Figure 4.3. Flow curve of a polyethylene melt. Experiments conducted for a typical polydisperse polymer. Melt index of a sample was 2 g/10 min. T = 150°C.

One of the main problems in description of flow curves is the existence of limiting values of apparent viscosity at $\sigma \to 0$ or $\dot{\gamma} \to 0$, and at $\sigma \to \infty$ and $\dot{\gamma} \to \infty$, which are important to consider in interpretation of the physical meaning of non-Newtonian behavior and in quantitative description of a flow curve.

Flow curves in Figure 4.2 are typical of polymer solutions. The solvent used behaves like a Newtonian liquid (flow curve is a straight line inclined by 45° to both axes). In rather dilute solutions, flow curves display three regions. At low shear rates (formally at $\sigma \to 0$ and $\dot{\gamma} \to 0$), Newtonian behavior is observed (straight line inclined by 45° to both axes), and apparent viscosity corresponding to this region of a flow curve is called **zero-shear** or **initial** or **maximum Newtonian viscosity**. Then the decrease of apparent viscosity (declining from the straight line) is observed - typical of non-Newtonian behavior. Finally, the upper part of a flow curve again has Newtonian behavior. The value of apparent viscosity at these high shear rates and stresses (formally at $\sigma \to 0$ and $\dot{\gamma} \to 0$) can be called **upper, limiting,** or **minimum Newtonian viscosity**.

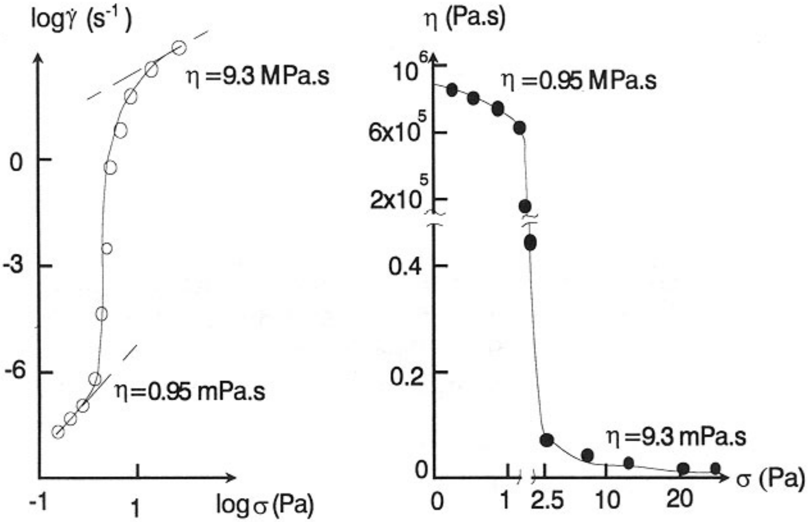

Figure 4.4. Non-Newtonian viscous behavior of 10% suspension of natural bentonite (in $\log\dot{\gamma}$ - $\log\sigma$ and $\eta - \sigma$ coordinates). Limiting values of apparent viscosity at shear stresses $\sigma \to 0$ (η = 0.95 mPas) and at $\sigma \to \infty$ (η= 9.3 MPas) are shown. After L. A. Abduraghimova, P. A. Rehbinder, and N. N. Serb-Serbina, *Kolloid Zh.*, **17** (3), 184 - 195 (1955).

Further increase of polymer concentration leads to increasingly more noticeable deviation from Newtonian behavior, though in all cases the Newtonian viscosity, at low shear rates, is apparent. Highly concentrated solutions (30% and higher) have a broader range of non-Newtonian behavior, followed by the flow curve which becomes close to a vertical line. This behavior is particularly strong for a pure polymer. It may be argued whether this region of the graph corresponds to real flow with rapid decrease of apparent viscosity or it reflects other, special type of behavior of a material, but undoubtedly these experimental observations demonstrate peculiar rheological properties of these media.

There is no doubt that the initial Newtonian viscosity region exists for all, including very concentrated, solutions. Also, the upper Newtonian region of flow curves cannot be reached (or maybe does not exist) for concentrated solutions. The general reason for this is a loss of flow stability at high shear rates (a very close analogy of this behavior is a well-known transition from laminar to turbulent flow for regular liquids).

Another example of rheological properties is represented in Figure 4.3 for polymer melt. A continuous and gradual decrease of apparent viscosity occurs in a very wide range of shear rates. The whole decrease of apparent viscosity exceeds 1000 times in comparison with the initial value. The initial Newtonian region in the flow curve appears in this Figure only as a hint; it may even be suspected that this branch does exist.

Figure 4.4 represents a flow curve with a very sharp drop of viscosity at some value of shear stress, σ_y, or in a narrow range of shear stresses. The initial Newtonian viscosity, η_o, can also be found here as a limit of η at $\sigma \to 0$. The magnitude of η_o exceeds the apparent viscosity, in other regions, by several decimal orders of magnitude. In fact, viscosity drops by 8 decimal orders of magnitude, from 0.95 MPa·s to 9.3 mPa·s. That is why it is reasonable to treat the behavior of a material at $\sigma << \sigma_y$ as solid-like (even though the material is a liquid and flows even though its viscosity is very high). The transition through σ_y might be considered as a transition from solid-like to liquid-like behavior, and only the part of the flow curve at $\sigma > \sigma_y$ as the flow curve.

The materials having sharp transition from solid-like to liquid-like behavior, at sufficiently high shear stresses to cause flow, are called **visco-plastics**, and the transition stress is called **yield stress** (or yield point). The flow curve in Figure 4.4 can be treated as a flow curve of a non-Newtonian liquid with rapid viscosity decrease or as a dependence of apparent viscosity on shear stress, characteristic for visco-plastic bodies. Both definitions are reasonable. In many cases, it is very difficult to find a proper assignment for experimentally observed viscosity versus shear stress dependence of real materials rapidly changing their structure under deformation.

Many attempts were made to describe flow curves of various materials by analytical functions of different type, both on theoretical and empirical levels. For the flow curves with distinctly expressed range of initial Newtonian viscosity, the following equations are frequently applied:

Cross equation:[2]

$$\eta = \frac{\eta_o}{1 + |\lambda\dot{\gamma}|^m} \qquad [4.1]$$

Carreau equation:[3]

$$\eta = \frac{\eta_o}{[1 + (\lambda\dot{\gamma})^2]^{-p}} \qquad [4.2]$$

Yasuda *et al.* equation:[4]

$$\eta = \frac{\eta_o}{[1 + (\lambda\dot{\gamma})^a]^{(n-1)/a}} \qquad [4.3]$$

Vinogradov - Malkin equation:[5] $$\eta = \frac{\eta_o}{1 + A\dot{\gamma}^{\alpha} + B\dot{\gamma}^{2\alpha}} \qquad [4.4]$$

In all equations, η is apparent viscosity, depending on shear rate, η_o is zero-shear viscosity, all other symbols are empirical or semi-empirical constants.

All the equations are similar in their structure. They differ in a number of parameters: two in Eqs 4.1 and 4.2, and three in Eqs 4.3 and 4.4. It is interesting to emphasize two main peculiarities of these equations: all have a limit at $\dot{\gamma} \to 0$ equal to η_o. At sufficiently high values of shear rate, they transit to the so-called **power law** (Ostwald - de Waele equation),[6] which can be written as

$$\sigma = K\dot{\gamma}^n \qquad [4.5]$$

where K and n are empirical parameters.

All equations show that, at $\dot{\gamma} \to \infty$, apparent viscosity diminishes to zero. It means that it was assumed that there is a great decrease in apparent viscosity, when shear rate increases, in comparison with η_o, so that the limiting value of apparent viscosity at $\dot{\gamma} \to \infty$ is negligibly small. There are situations (for example, relatively dilute polymer solutions) when the total decrease in apparent viscosity is not large, and the minimal value of apparent viscosity at $\dot{\gamma} \to \infty$ is frequently observed. In many cases, the possibility to reach the limiting viscosity is restricted because, at very high shear rates, flow instabilities of a different kind appear.

Discussing the problem of apparent viscosity, it is important to note that the definition of viscosity applies to steady flow (no time-related changes). In some cases it is important to consider viscosity in transient regimes of shear deformations. For pure viscous liquids, nothing is changing in this case. In other cases, $\dot{\gamma}$ must be treated, not as a rate of full deformation, but only as a rate of flow, i.e., rate of irreversible deformation. If the deformation is reversible (elastic), it has nothing in common with viscous flow and definition of viscosity. Thus, in transient flow, only a part of deformation is related to the flow; the rate of this deformation must be taken into account in calculating viscosity.

The flow curve measurements have various applications. Two of them are of primary value. First, it is always necessary to know viscous properties of a real material to solve any hydrodynamic problem related to flow of the material - in particular, to design processing equipment and predict conditions of its use in practice (e.g., calculation of rate of flow and pressure drop). Second, the flow curve reflects chemical content and/or physical structure of a material, and as such it can be used as a method of analysis of material quality.

4.1.2 PLASTIC BEHAVIOR

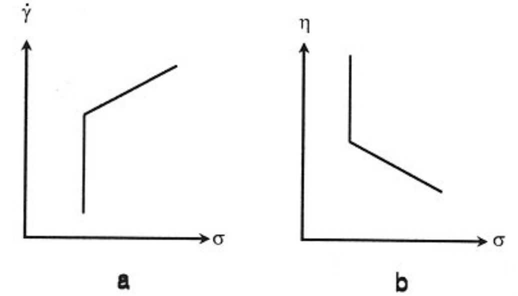

Figure 4.5. Characteristic "flow curve" for a visco-plastic medium in $\dot{\gamma} - \sigma$ (a) and $\eta - \sigma$ (b) coordinates.

Visco-plasticity can be formally treated as a viscous flow: viscosity is infinite at $\sigma < \sigma_y$, and it decreases in a very narrow range of shear stress near σ_y, as discussed above. Plastic material cannot be deformed at $\sigma < \sigma_y$, and it flows at $\sigma > \sigma_y$. The yield stress, σ_y, is characterized by a rapid change of viscosity at $\sigma \to \sigma_y$ (Figure 4.5). For some materials, such as many pastes, greases, bentonites, and paints, this pattern of behavior is very close to reality (see Figure 4.4). For other materials - for example, polymer melts containing solid filler, rubber compounds, sealants - the transition through the yield stress appears milder, as demonstrated in Figure 4.6.

Formal description of visco-plastic behavior is based on a model of abrupt jump of viscosity at σ_y and existence of yield stress. Two analytical equations are usually used to characterize visco-plastic behavior:

Bingham equation[7] $\sigma = \sigma_y + \eta_p \dot{\gamma}$ at $\sigma < \sigma_y$ [4.7]

Casson equation[8] $\sigma^{1/2} = \sigma_y^{1/2} + K\dot{\gamma}^{1/2}$ at $\sigma < \sigma_y$ [4.8]

where σ_y is the yield stress, and η_p and K are empirical constants. The constant η_p is sometimes called the "plastic" or Bingham viscosity.

Eq 4.7 represents a linear model. It predicts the decrease of apparent viscosity in the flow range:

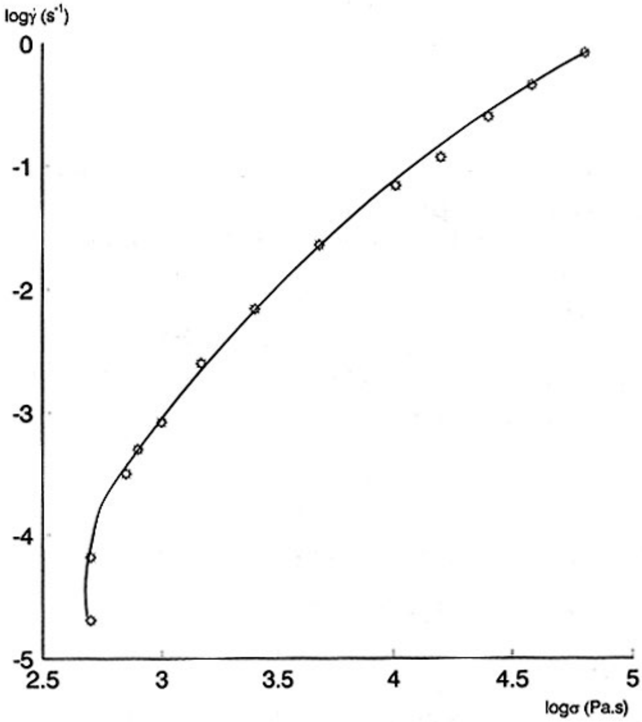

Figure 4.6. Flow curve for a filled polymer melt - polyisobutylene containing 5 wt% carbon black, 60^{o}C - demonstrating gradual approach of the yield point.

$$\eta = \frac{\sigma}{\dot{\gamma}} = \eta_p + \frac{\sigma_y}{\dot{\gamma}} \qquad [4.9]$$

The apparent viscosity decreases when the shear rate increases, as shown in Figure 4.5 b.

If viscosity at $\sigma > \sigma_y$ is constant, the behavior is not described by the Bingham equation and can be represented by the following equation:

$$\eta = \infty \quad \text{at} \quad \sigma < \sigma_y \qquad \eta = \eta_0 \quad \text{at} \quad \sigma > \sigma_y \qquad [4.10]$$

The existence of a range of low stresses in which a visco-plastic material is solid-like leads to rather peculiar properties. If such material is pressed through a round channel, the stress at the axis equals zero. In fact, there is a core in the entire central zone where shear stress is very low. It means that there is a zone, in the central part of a channel, where shear stress is lower than σ_y; therefore this part of visco-plastic material does not flow but moves as a solid plug. Such behavior is frequently called **plug-flow**.

The term **plasticity**[9] (and the concept of plastic behavior) is also used for solids which can be elastic (up to the yield point), and then deform to unlimited extent when this critical stress is reached. The term "flow" has a rather peculiar meaning for such materials as metals; nevertheless, they really flow (i.e., are deformed irreversibly) at $\sigma > \sigma_y$. The plastic behavior of solids at $\sigma > \sigma_y$ is essential in such technological operations as punching of golden articles (coins and so on) or rolling of ingot steel.

In summary, it is necessary to emphasize that Eqs 4.1 through 4.10 are **not** rheological equations of state, they only contain empirical description of experimental data obtained in unidimensional shear deformations.

4.1.3 WEISSENBERG EFFECT

Weissenberg has described a set of "strange" pictures of behavior of some liquids (Figure 4.7).[10] If a rod is rotated inside a "rheological" liquid, such a liquid, instead of being displaced from the rotor by centrifugal force towards the walls of a vessel, begins to wind around the rotor and climb it (Figure 4.7 - case 1). In the case of two coaxial cylinders (inner hollow), the rotation of the outer cylinder forces liquid into the inner cylinder (Figure 4.7 - case 2). Another characteristic example concerns liquid between two parallel discs. When the outer disc is rotated around a common axis, the inner disc is lifted up by normal force generated due to rotation (Figure 4.7 - case 3), and if a hole would be made in the center of one of the discs, this "strange" liquid instead of being removed from the space between the discs to the periphery of the discs, is pressed through the hole. Such behavior means that the force not only acts normal to the surfaces of the discs but in the radial direction to the central axis as well.

The above-mentioned and some other related observations are known under the general name of the **Weissenberg effect**. Phenomena associated with this effect are very common in technological applications, because reactors with rotating mixing elements, mixers of different geometry and type, are regular

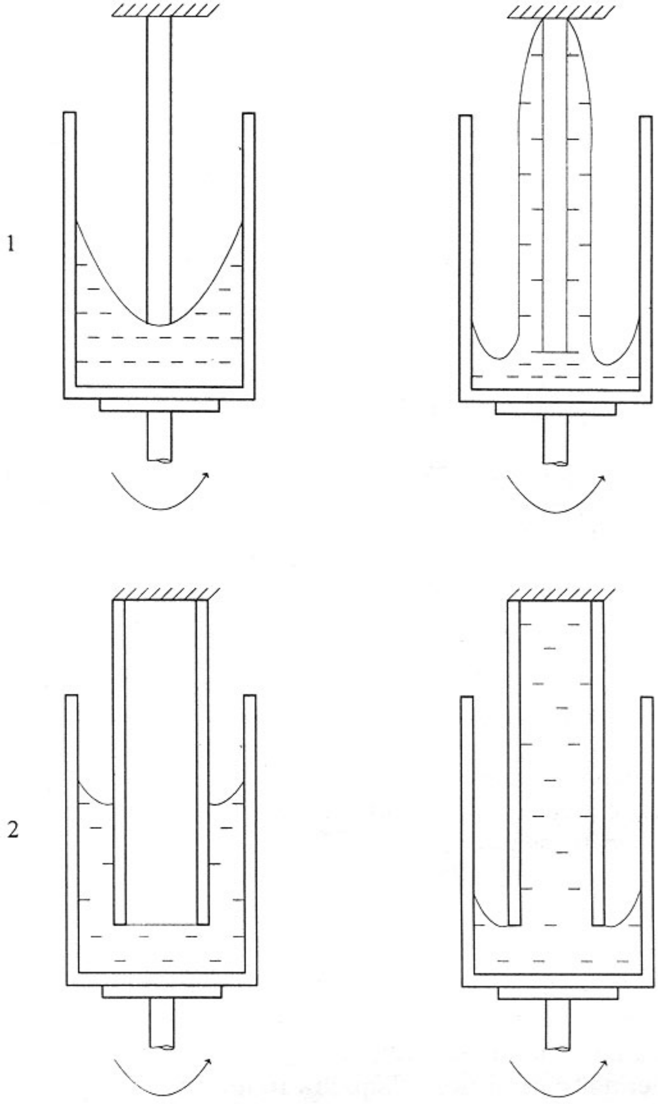

Figure 4.7. Typical phenomena usually associated with the Weissenberg effect: a rod rotating in a liquid (1); rotating outer cylinder with liquid filling the center of a hollow cylinder (2); a liquid between two parallel rotating disks (3). (Continued on the next page.)

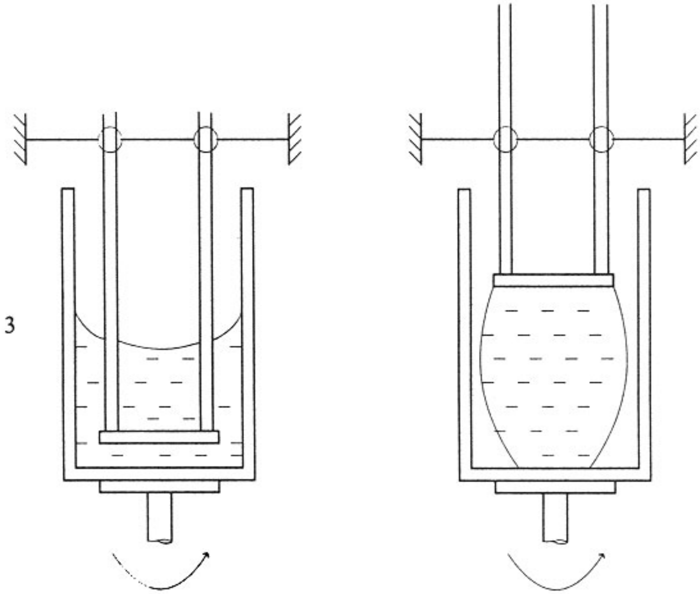

Figure 4.7. Continuation; see caption on the previous page.

equipment in various branches of the chemical, food and pharmaceutical industries. Moreover, the last example of the Weissenberg effect shown in Figure 4.7 (case 3) was used to design a special type of machine for polymer processing, the so-called *screwless extruder*. In this design, a material is mixed between two discs and pressed through a nozzle by an action of forces originated from the Weissenberg effect. Normal forces appearing due to rotation of parallel discs also give additional support in slide bearings if a “rheological” liquid is used as a lubricant. Some investigators think that the Weissenberg effect provides the ability of articulations in biological organisms and that deficiency in this phenomenon leads to an illness (“squeak in joints”).

It is interesting to understand the rheological origin of this effects, i.e., what happens at the reference point. The common feature of all phenomena is appearance of forces acting in the direction of shear and in the perpendicular direction. It is equivalent to appearance of **normal stresses in shear**, even though, at the first sight, it would be reasonable to suspect that only shear stress acts in a simple shear. This is true for many liquids, but not always. Normal stress (diagonal component of the stress tensor) also acts, and the diagram of stresses is shown in Figure 4.8.

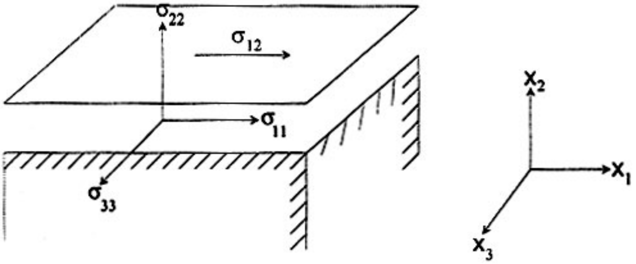

Figure 4.8. Notation of normal stresses at plane simple shear.

It is possible to anticipate that normal components of stress tensor are related to appearance of a diagonal component in the tensor of large deformations. Their existence can be explained by large elastic deformations developed in flow (it may be argued whether this explanation is general, but undoubtedly the large elastic deformations lead to normal stresses). The appearance of normal stresses in a simple shear is a main rheological reason for the Weissenberg effect.

In order to characterize the phenomenon, not absolute values of normal stresses but their differences are important. If, for example, hydrostatic pressure is superimposed, it will change all normal components of the stress tensor but would not influence flow. (If this pressure is not very high, it is possible to neglect the compressibility of a liquid - true in many real situations.) The differences of normal stresses are defined as follows:

first difference of normal stresses: $\sigma_1 = \sigma_{11} - \sigma_{22}$

second difference of normal stresses: $\sigma_2 = \sigma_{22} - \sigma_{33}$

(σ_1 and σ_2 are not invariants of the stress tensor, though they are written in the same manner).

In rheological literature, very often, not σ_1 and σ_2 are used but their coefficients (analogous to the use of viscosity coefficient instead of shear stress). The first and the second normal stress coefficients are defined as

$$\Psi_1 = \frac{\sigma_{11} - \sigma_{22}}{\dot{\gamma}^2}; \ \Psi_2 = \frac{\sigma_{22} - \sigma_{33}}{\dot{\gamma}^2} \qquad [4.11]$$

Normal stress in shear flow is an effect of the second order, and that is why, at least in first approximation, σ_1 and σ_2 are proportional to squared shear stress, σ^2, and coefficients of normal stresses are proportional to η^2. In all known cases, $\sigma_1 >> \sigma_2$. Normal stress as an effect of the second order is much smaller than shear stress at low shear rates, or to be more precise: $(\sigma_{11} - \sigma_{22}) / \sigma_{12} << 1$. With shear rate increasing, the normal stresses grow very quickly (proportional to squared shear rate), and at high shear rate, normal stresses become larger than shear stress, therefore they are critical for analysis of flow of some liquids (for example, concentrated polymer solutions and melts).

4.1.4 TRANSIENT DEFORMATIONS IN SHEAR (OF LIQUIDS)

For regular liquids, the step-wise setting of constant shear rate leads to an immediate beginning of flow. Shear stress, which maintains the steady flow, remains constant all the time (eliminating inertial effects). After the cessation of flow, stress instantaneously drops to zero. There are some liquids (and they are the object of rheological studies) for which development and disappearance of stresses is far from the simplest scheme.

Figure 4.9 demonstrates the effect of step-wise setting of constant shear rate.[11] The left side of the diagram represents “regular” and the right side “rheological” liquids. The main observations for the latter are as follows:

- at low shear rate, there is a very prolonged time interval of slowly developing shear stresses, and this interval becomes shorter if shear rate is increased
- at high shear rates, shear stresses pass through a maximum (sometimes several maxima can be observed) before reaching the state of steady flow
- after sudden cessation of flow, shear stress decays (*relaxes*); the initial relaxation rate increases with increasing initial shear rate.

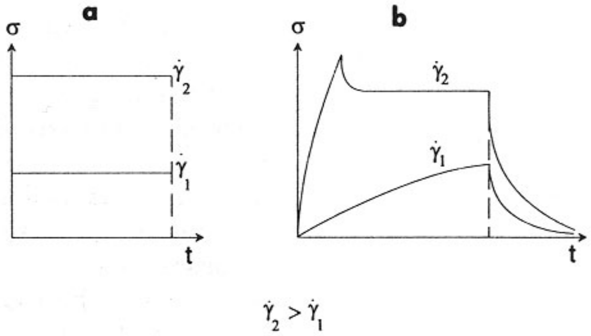

Figure 4.9. Development of shear stresses at preset constant shear rate for regular (a) and "rheological" (b) liquids.

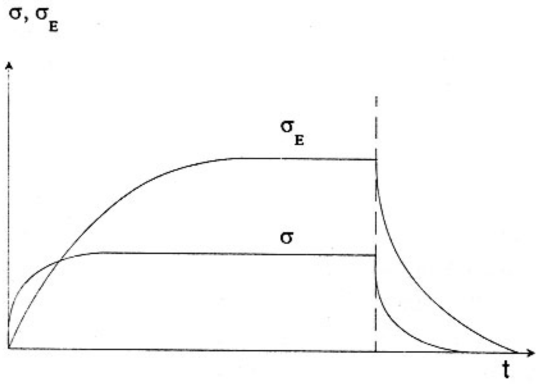

Figure 4.10. Comparison of development (at constant shear rate) and decay (after cessation of flow) of shear and normal stresses.

Besides this complex behavior, the Weissenberg effect (normal stresses at simple shear) also exists. The evolution of normal stresses (regardless of σ_1 and σ_2), before the steady state and during relaxation, is similar to the development and decay of shear stresses. The main peculiarity consists of much slower change of normal than shear stress, either in pre-stationary (pre-steady) state of deformations or during relaxation.[12] This effect is illustrated in Figure 4.10 for relatively low shear rate when a maximum of stresses is not attained.

Transient behavior is also observed at other types of deformations (not only at constant shear rate). If shear stress is set constant, then rate of deformation will be changing in time in a manner shown in Figure 4.11. The steady flow regime is reached after a transient range of deformation, when shear rate is changing due to a change of a relative effect of plastic and elastic components, along with deformation rate.

Transient rheological behavior is a very characteristic *time effect*, leading to a complex relationship between stress and rate of deformation. The most evident manifestations of this effect can be observed at preset constant stress or shear rate. The reasons for the effects can vary, but the main models of the behavior are:

- thixotropic (rheopectic) phenomena
- visco-elastic behavior of a material.

Both typical phenomena are discussed in separate Sections below. Important practical applications are numerous, especially in cases when time for transient behavior is rather long and comparable with duration of flow. For example, it is applicable to flow in short dies, sudden changes of the diameter of a channel, or local hindrances in outer or inner flows. In all these, and many other cases, it would be incorrect to characterize properties of a liquid by its flow curve alone, i.e., the relationship between stresses and rates of deformation, measured only at "equilibrium" conditions (after completion of transient processes). It is therefore important to understand the reasons for these effects in different media and describe them in relation to the whole complexity of the properties of matter.

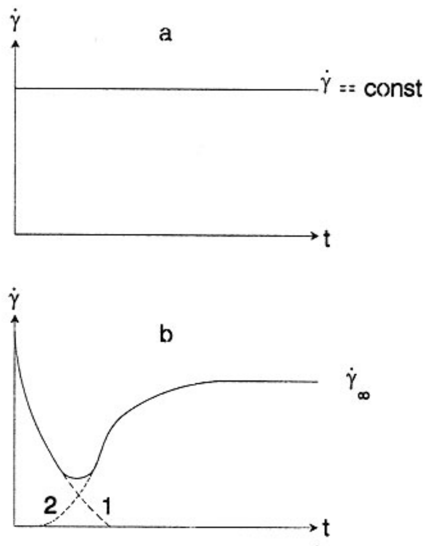

Figure 4.11. Development of shear rate at constant stress for regular (a) and "rheological" (b) liquids. Dotted lines show change of elastic (1) and plastic (2) components of deformation.

4.1.5 UNIAXIAL EXTENSION

Uniaxial extension of liquids is a very important method of deformation encountered in fiber formation, orientational drawing, and formation of thin films. From a theoretical point of view, uniaxial extension differs geometrically from deformation in shear flow. In shear, the tangential stress determines behavior of a material, whereas in uniaxial extension only normal stresses are applied. It is thus very important to understand how different materials manifest their inherent properties under varying conditions of loading to construct three-dimensional rheological equations of state.

If a liquid is stretched, it flows (similar to shearing), and the **elongational viscosity**, λ, can be determined as a ratio of normal stress, σ_E, to the gradient of velocity, $\dot{\varepsilon}$ (equal, in this case, to the rate of axial deformation):

$$\lambda = \frac{\sigma_E}{\dot{\varepsilon}} \qquad [4.12]$$

For Newtonian liquids, their elongational viscosity equals 3η. The equality

$$\lambda = 3\eta \qquad [4.13]$$

is called the **Trouton law** and the value λ is called the **Trouton viscosity**.[13]

In the range of low deformation rates, Eq 4.13 is valid as a limiting case for any liquid. For some liquids, increase in the rate of deformation leads to a change of their elongational viscosity. As a rule, the elongational viscosity increases at higher rates of deformation, but opposite cases also have been observed.

The most appropriate method of elongational viscosity measurement would be to draw a sample until a regime of steady state flow is reached, and then normal stress and rate of deformation are measured to calculate elongational viscosity according to its rigorous definition expressed by Eq 4.12. Unfortunately, in most cases, such an obvious procedure is not applicable because the stretched material usually ruptures before a steady state is reached. The rupture of samples at high draw ratios (factor limiting experiments in extension) is a principle difference between shearing, which can continue for an unlimited time, and extension. In discussion of experimental data obtained for flow in uniaxial extension, it must be remembered that data (as a rule) relate to the transient behavior of a material.

A general picture of normal stress distribution during extension of “rheological” liquid at different rates of deformation is given in Figure 4.12. At low rates of extension (curve 1), stress reaches constant level, corresponding to steady elongational flow with constant Trouton viscosity. But at high rates of extension, there is no limiting state related to a viscous flow and stress grows with acceleration (curve 2) up to the rupture of the sample.[14] The latter case is a typical

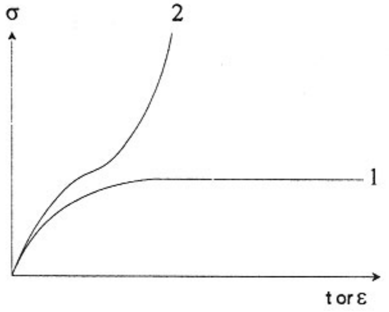

Figure 4.12. Development of stresses in uniaxial extension of "rheological" liquid at low (curve 1) and high (curve 2) rates of deformation.

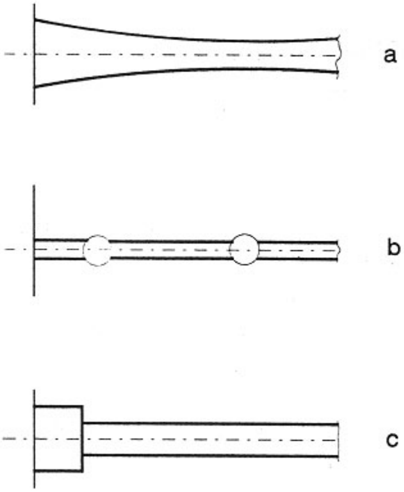

Figure 4.13. Drawings demonstrating characteristic modes of deformation in stretching of a regular material (a), "rheological" liquid (b) and solid (c).

example of transient behavior and it is inappropriate to treat curve 2 in Figure 4.12 as a reflection of viscosity growth in extension.

It is worth noting that rupture of "rheological" media also occurs in some different ways than ultimate breaking of regular materials. Schematically, they are pictured in Figure 4.13: the upper drawing shows that rupture of ordinary material occurs after a continuous process of sample flow, leading to its rupture in the weakest section. The next drawing (b) relates to "rheological" liquid (e.g., rubber glue): during stretching, spherical droplets are formed along the stream and rupture follows. The lower drawing (c) shows rupture of stretched solids. Regular material deforms as shown in Figure 4.13a, but "rheological" solid forms a sharp local contraction - **necking** - and following deformation, occurs through a transition from a parent material to a neck.

4.1.6 INSTABILITIES AND SECONDARY FLOWS[15]

Stability of flow is of general interest in numerous applications: sailing ships, pipe-lines for liquid materials (water, oil products, etc.), flow of material in dies, paint milling, water spraying, production of plastic parts with high quality surfaces, and so on.

In "regular" liquids, instabilities appear as a result of capillary or inertial forces. The first reason leads to surface effects, such as breaking up a stream into many droplets. The second reason is a base of the so-called Reynolds turbulence, which appears as a chaotic movement of liquid particles in any flow. Reynolds turbulence occurs when inertial forces exceed viscous damping of occasional disturbances. Turbulent flow occurs when and if the critical value of the **Reynolds Number**, Re, is exceeded. Re is determined as

$$\mathrm{Re} = \frac{Vd\rho}{\eta} \qquad [4.14]$$

where V is characteristic velocity, d characteristic linear size, η viscosity, and ρ density.

The critical value of the Reynolds Number, corresponding to possible transition from laminar to turbulent flow in cylindrical channel, is about 2300 (the Reynolds Number, like any other criteria of similarity, is a dimensionless value).

Reynolds (inertial) turbulence can also take place in the flow of non-Newtonian liquids, but the most interesting fact is that in the flow of “rheological” liquids, unexpected effects appear. In some cases, flow becomes unstable at values of the Reynolds Number different from that characteristic for regular liquids at the equivalent conditions of flow. It indicates that different mechanisms of instability can exist. Since the critical value of the Reynolds Number reflects viscous properties of liquid, these new mechanisms of instability must reflect other rheological properties of material. Then, the main problem consists of understanding these mechanisms and correlating them with rheological properties of media.

Instabilities of different types accompany many technological processes. For example, they are the cause of haziness of extruded films, rough surface of cable insulation, waviness of fibers in spinning, and so on. Instabilities in flow have been observed for various “rheological” liquids and can manifest themselves in different forms. There is a common opinion that the general reason for instability of many “rheological” liquids is their elasticity and viscoelastic effects - a primary characteristic of polymeric liquids (melts and solutions).

The concept of viscoelasticity (Chapter 7) requires us to consider at least one parameter reflecting elastic properties of material in addition to its viscosity. It can be the modulus of elasticity, E, but it is preferable to use a measure of the rate of inherent rearrangement processes in a material (not specifying its nature). This time constant, called **relaxation time**, θ, is defined, at least for dimensional reasons, as

$$\theta = \frac{\eta}{E} \qquad [4.15]$$

This value must be used as a second (additional to viscosity) characteristic property of a liquid.

It is therefore reasonable to introduce a new dimensionless criterion to measure a ratio between viscous and elastic forces in flow, such as the **Weissenberg Number**, We, defined as

$$We = \frac{V\theta}{d} \qquad [4.16]$$

The Weissenberg Number is close but not quite equivalent to the **Deborah Number**, De:

$$De = \frac{\theta}{T} \qquad [4.17]$$

where T is a characteristic time of flow. The value (V/d) can be treated as a characteristic time constant but it is more reasonable to use the Weissenberg number in steady flow and the Deborah Number in time-depending flows, where T is a time factor for transient flows.

Phenomena of instability in flow of "rheological" liquids can be manifested differently, depending on the geometrical mode of flow and the inherent properties of a liquid. However, the following manifestations are the most characteristic:

- extrudate distortions (sometimes called "melt fracture")
- secondary flows (flows in straight channels of a simple geometrical form, such as flow between coaxial cylinders) superimposed on primary flow
- interfacial and surface instabilities (boundary distortions in flow of multicomponent systems, breaking free streams, and so on)
- rheological phenomenon in inertial turbulence (Toms effect).

4.1.6.1 Extrudate Distortions (Melt Fracture)[16]

Extrudate distortions are observed when polymer in the form of a concentrated solution or melt is forced through a die (orifice or capillary) and when free recovery of deformations, stored during constrained flow in channels, occurs. This type of instability is of special importance for polymer processing because it limits the desired tendency to increase production rate. Besides the discussion of reasons and quantitative description of boundaries of stability (directly related to rheological properties of matter), it is an interesting general problem of continuous mechanics, and as such, it was treated in numerous theoretical studies.

Photographs in Figure 4.14 show two situations. The left picture demonstrates a stream leaving an orifice (visible at the upper part of the photograph) at low

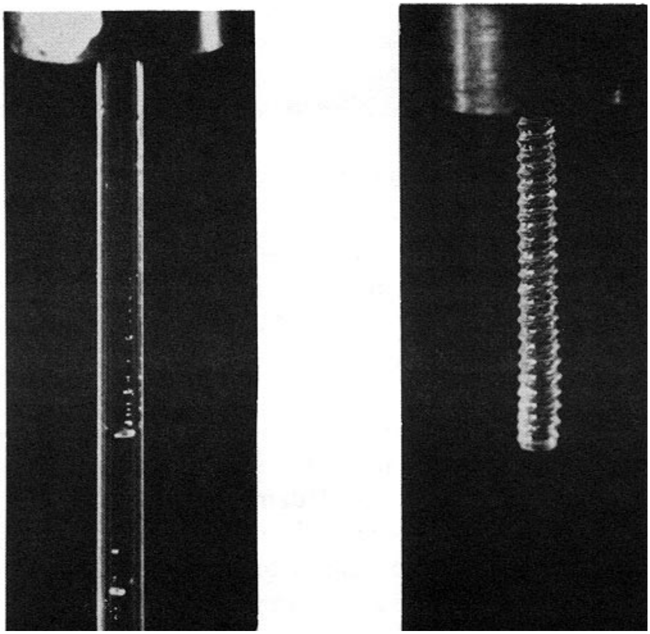

Figure 4.14. Instability in flow appearing in the form of regular (screw-like) defects: left - smooth stream in stable flow; right - instable flow.

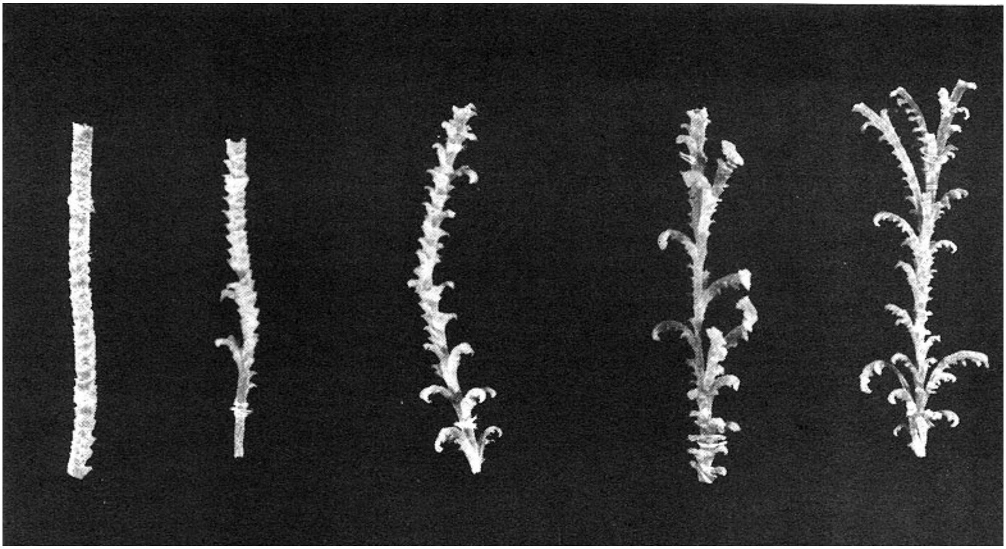

Figure 4.15. Instability of flow leading to disruption of a stream: transition from left to right corresponds to increase of velocity (shear rate).

speed. The flow is stable and the surface of the stream is quite smooth. The right photograph demonstrates what happens to the same material when the speed of flow exceeds some limit. The regular defects resembling a screw appear on the surface as a manifestation of instability. In this case, the instability arises as periodic oscillation.

Photographs in Figure 4.15 show more severe consequences of flow instability. The photographs show frozen samples of streams leaving a die. The shear rate was increasing from left to right. During the flow inside the orifice, large inherent forces (or energy) were stored in the material, and when the polymer melt was released from a die (capillary or orifice) at high velocity, the stream disintegrated, fragmenting into separate elements.

Numerous observations, similar to those presented in Figures 4.14 and 4.15, show that, as a rule, extrudate distortions start from slight skin defects. Then they are enlarged to regular surface defects (sometimes called “shark-skin”), forming gross regular variations of a cross-sectional area and shape (sometimes looking like a helical screw on extrudate) which can be an evident result of a "stick-slip" mechanism, when alternating rough and smooth zones appear on the surface of an extrudate. Finally, the instability of this type reaches a form of chaotic distortions and ruptures of stream, as documented in Figure 4.15, illustrating the meaning of "melt fracture". Many direct observations of flow lines (made by markers suspended in a flowing liquid through transparent walls of a channel) showed that movement of a liquid inside a channel at high velocities, when an extrudate becomes irregular, is unstable and movement of markers is chaotic. It is direct evidence of flow instability.

The appearance of gross distortions of periodic or aperiodic types in the flow of polymers (melts and concentrated solutions) can be accompanied by an abrupt jump of the flow rate - "**spurt**" - during flow through a capillary (die) under constant pressure.[17] This effect is explained by loss of fluidity and sliding along a solid wall, due to relaxation transition of a linear polymer into a rubbery state. This is the reason why "liquid" begins to behave, not like a fluid, but similar to a solid, rubber-like material which does not flow but slides as a plug along a channel.

The main result of numerous experiments shows that instability in flow in the form of "extrudate distortion" occurs at very low values of the Reynolds Number, sometimes as low as 10^{-5}, because viscosity of a melt is very high, and (most important) the effect under discussion does not correlate with any definite value of the Reynolds Number. It is therefore necessary to find an explanation of this effect other than the Reynolds turbulence.

There are at least two causes for extrudate distortions. At relatively low flow rates, surface distortions occur as a consequence of non-linear effects in deformation of "rheological" liquids - such phenomena as their elasticity and/or normal stress in shear flow. Gross extrudate distortions such as melt fracture are related to a non-linear phenomenon such as phase (or relaxation) transition. The melt-fracture instability appears at some critical value of the Weissenberg Number, namely about 5. The exact value of the Weissenberg Number depends on details of the method used for its estimation. In original publications, one can find critical values of the Weissenberg Number in shear flows in the range from 1 to 10.[18] Perhaps the scatter of these values can be explained by difficulties in determination of an exact moment when flow instability occurs and/or by difficulties in distinguishing between different mechanisms leading to similar features of unstable flow. Indeed, strong non-linear effects and phase (relaxation) transition in flow can superimpose and therefore lead to somewhat deceiving conclusions concerning quantitative criterion of instability.

Extrudate distortion is velocity dependent, and begins beyond some limiting velocity of flow. Extrudate distortion has an industrial importance because it limits the increase in flow rate, and thus, output in many technological applications such as fiber spinning, extrusion, etc. The understanding of the principles and controlling rheological parameters allows one to evaluate the processability of materials and select them, based on laboratory data.

4.1.6.2 Secondary Flow

The initial stage of instability occurs due to the so-called **secondary flow**. Secondary flow is formation of closed vortices in planes perpendicular to the direction of the main (primary) flow, governed by the movement of solid boundaries in a liquid sample. For example, secondary flow in a straight cylindrical channel produces circular flow lines in planes perpendicular to the axis of a channel. Secondary flow does not appear in “rheological liquids” in channels having a circular cross-section but can be found in channels with cross-sections of other geometrical forms.

Secondary flow increases resistance to flow, meaning that the energy consumption in transportation of “rheological” liquids is increased in comparison to a regular liquid of the same viscosity. On increasing the flow rate, the secondary flow causes much stronger instability, and that is why they are so closely related to such gross effects as flow distortions.

The most well-known case of secondary flow in Couette flow is called **Taylor instability**.[19] It is shown in Figure 4.16 along with some other cases of secondary flows. If a liquid is placed in a gap between two coaxial cylinders, and one of them is rotated, the main flow takes place in a circular direction, and a secondary flow forms closed flow lines, called Taylor cells (Figure 4.16a). A quite equivalent situation occurs in the flow between two parallel plates driven by the motion parallel to the plates. This case is known as plane Couette flow. It is equivalent to the motion of coaxial cylinders with radii much larger than the gap between the cylinders, and the curvature effect is neglected.

Secondary flows (closed vortices), observed in the flow of a “rheological’ liquid in a gap between a cone and a plate when a cone is rotated around its axis, are shown in Figure 4.16b.

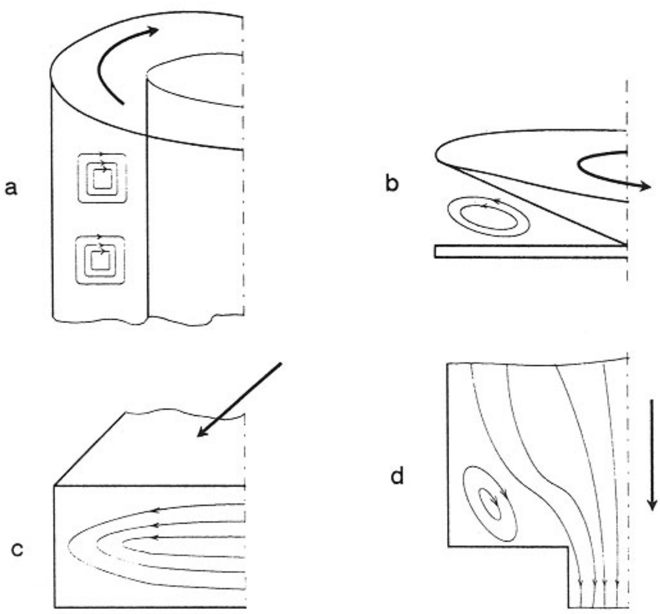

Figure 4.16. Secondary flows in different channels: between two rotating coaxial cylinders (a), along a non-round element (b), in channel crosssection (c), near a sudden change of cross-section surface area (d).

If a liquid is forced to flow through a straight channel with an elliptical or rectangular cross-section in the direction of the main flow along the axis of a channel, the secondary flow forms closed flow lines in the cross-section of a channel (Figure 4.16c). The most spectacular secondary flow, in the form of closed vortices, occurs in a "rheological" liquid flow through a sudden narrowing (Figure 4.16d).

Instability of the Taylor vortices is explained for regular Newtonian liquids as a result of inertial effects (analogous to the Reynolds turbulence). Taylor instability occurs in any Newtonian liquid if a critical value of the Reynolds Number is exceeded. Theoretical analysis of the flow of a Newtonian liquid shows that the stability threshold for flow between two coaxial cylinders is determined by the value of the **Taylor Number,** T, calculated as

$$T = -2b(\mathrm{Re})^2\varepsilon \qquad [4.18]$$

where

$$b = \frac{\Omega_o - \Omega_i}{\Omega_i}$$

Ω_i and Ω_o are the rates of rotation of the inner and outer cylinders, respectively; if $\Omega_o = 0$, $b = -1$, $\varepsilon = \delta / R_i$ is the ratio of the gap to the radius of the inner cylinder and

$$\mathrm{Re} = \frac{\Omega_i R_i \delta\rho}{\eta} \qquad [4.19]$$

is the Reynolds Number determined for a circular flow between coaxial cylinders.

The height of the Taylor cells formed in a Newtonian liquid in a section along the axis of cylinders is roughly equal to the width of a gap, i.e., the form of cells is close to square.

One of the main theoretical findings for a Newtonian liquid is the existence of the minimal value of the critical Taylor Number equal to 3390 (at b = -1).

Elasticity of "rheological" liquids strongly influences the stability of flow. Experiments show that elasticity (for example, characterized by the normal stresses) can stabilize the Couette flow. Besides, some investigators observe new types of instability in the Couette flow; for example, wavy cells with boundaries periodically changing with time.[20] Appearance of cells of different type, as documented, depends on rheological properties of a liquid.

Instabilities observed in highly elastic (rubbery) liquids are quite different than those described for Newtonian or weakly elastic liquids. Firstly, instability occurs irrespective of the Taylor Number (for example, it can happen even at T close to zero, quite analogous to instability of the melt fracture type which also appears irrespective of the Reynolds Number and even at Re close to zero). Secondly, cells can be of very irregular form, reminding us of rough extrudate disturbances in capillary flow. Thirdly, it is possible to observe instability of the oscillatory type, again reminding us of periodic distortions of an extrudate.

Instability related to a secondary flow also can be observed in other circular (rotational) devices, as is shown in Figure 4.16b. The cone-and-plate system is very often used in experimental rheology for viscosity and normal stress measurement, and in this case the angle between a cone and a plate does not exceed 4 - 5°.

Inertial instability in a form of closed vortices appears in circular flow of a Newtonian liquid between a cone and a plate at sufficiently high values of the Reynolds Number. In circular flow of a "rheological" liquid, instability begins from distortion of a meniscus due to elastic effects. These distortions can be rather extensive.

More severe effects cause a rupture of a liquid sheared between a cone and a plate. It does not happen immediately after the beginning of rotation, but after a period of deformation. This effect also can be considered as analogous to flow disturbances and melt fracture of an extrudate leaving a die.

A very important type of secondary flow occurs when there is a sudden narrowing in axisymmetrical geometry of a channel (Figure 4.16d). This situation is typical in a transition from one diameter of a pipe to a smaller diameter; for example, in liquid transportation or in a die in industrial extruders or capillary viscometers.

Many visual experiments demonstrated that vortices appear at the corners, as shown in Fig. 4.17. Experiments proved that the shape and behavior of such vortices are characteristic for properties of a "rheological" liquid. However, in a typical case, at low flow rate, the stable vortices exist at the corners. Increasing the rate of flow (equivalent to the increase in the Weissenberg Number), regular pulsation of vortices occurs. Further increase in flow rate causes pulsations to become irregular. It is interesting to emphasize that these transitions in behavior of vortices correspond to the character of flow inside a die and distortions of an extrudate. Thus the observations regard the transition from typical secondary flow to a chaotic instability of turbulent type.

Another interesting feature of flow through sudden decrease in cross-section surface area is axial extension of a liquid near the axis of a stream. With increasing flow rate, the draw ratio increases, creating a combination of instability of secondary and extensional flow. In particular, when a rate of extension exceeds some threshold value, fracture of flow lines is observable along the axis, i.e., flow ruptures in a continuum media. This phenomenon is a limiting case of instability in extensional flow. It superimposes on vortex formation, and a result of

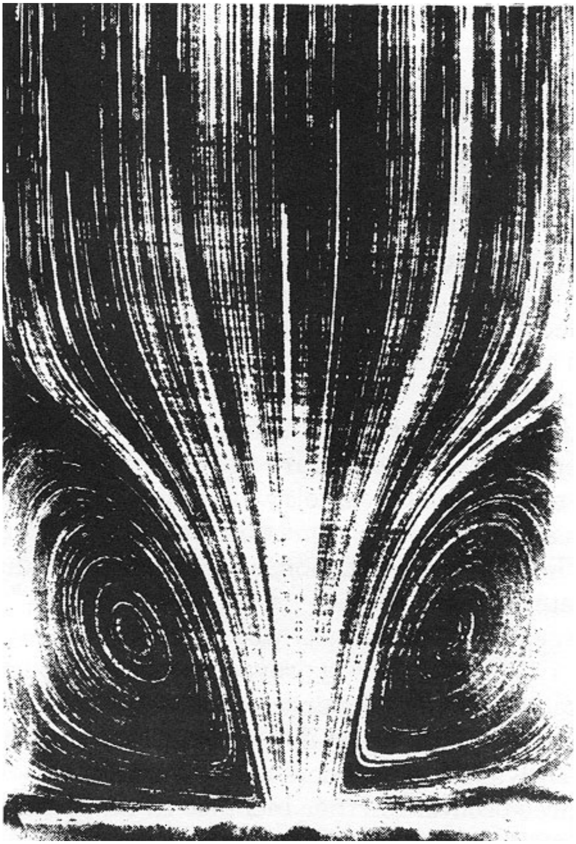

Figure 4.17. Photograph illustrating the appearance of closed vortices near a sharp corner around a sudden reduction of cross-section surface area.

these effects leads to extrudate distortion and melt fracture, with all the technological significance of these effects for processing of viscoelastic materials, as mentioned before.

In summary, in shear curvilinear flows, for example, in gaps between two coaxial cylinders, a cone and a plate, in three-dimensional flows in sudden change of cross-section, instabilities of different types occur. The first type is related to normal stress influencing critical conditions responsible for secondary flows, causing formation of regular vortices (this is a weak non-linear effect). In this case, the secondary flow appears as a chaotic movement of particles in a liquid or irregular distortion of smooth surfaces of a stream. The second type causes severe distortion of a media in oscillatory-type movement (this can be treated as a strong non-linear effect). The irregular instability which occurs as a result of ruptures in a continuum media can be considered as a result of phase (or relaxational) transitions, and can be treated as a “phase” non-linear effect. The effect close to it is a phase separation which occurs due to shearing,[21] observed in mixtures and solutions.

4.1.6.3 Waving in Extensional Flows

There are very interesting and unusual effects observed during stretching of “rheological” liquids. These effects are important in many technological processes, such as the commercial process of fiber spinning and orientation, where the natural tendency to increase the process rate is contrary to the requirements to prevent process instability caused by “fast” flow.

In practice, the following phenomena are met which can cause instabilities of different type.

Draw resonance is a wavy periodic change in stream (fiber) diameter occurring at constant feed (take-up) rate.[22] It is impossible to avoid occasional small fluctuations in fiber diameter, but instability is the phenomenon which increases these fluctuations. It is reasonable to assume that draw resonance is due to elastic behavior of a liquid, and this phenomenon can be described in terms of non-Newtonian behavior in uniaxial extension, thus the Deborah Number is the determining parameter for this phenomenon. Draw resonance affects quality of fibers (expected to have uniform cross-section).

Jet breaking occurs in a Newtonian liquid due to surface tension (capillary waves break up a stream, as explained in the classical works by Rayleigh).[23] The reason for jet breaking is a growth of small occasional wavy variations in a diameter of a jet until a cylindrical jet breaks up into droplets.[24] The main difference between a regular and “rheological” liquid is in the form of a jet before break-up. As mentioned in discussion of extensional flow of “rheological” liquids, a stream is initially converted to a series of elongated droplets connected by threads. These threads can be stretched at a rather large ratio (especially if the resistance to stretching increases on drawing), leading to stream stabilization. That is why “rheological” liquids, for example, very diluted water solutions of some polymeric substances, can be successfully used in fire extinguishing when it is desirable to prevent jet breaking and to increase the distance of stream delivery.

Necking was already mentioned in discussion of uniaxial tension of solid viscoelastic materials. It is an abrupt deviation from uniform (homogeneous) deformation.[25] It is an instability of the phase type, consisting of self-sustaining change in the diameter of a stretched filament. This effect is typical for large deformations of solid materials. It is related to relaxation or phase (recrystallization) phenomena. It also occurs during extension of liquids (polymer melts). Necking is very important in such technological operations as orientation of amorphous materials and orientational crystallization in fiber spinning.

Rupture of a stream, observed in uniaxial extensional flows, is the final stage of instabilities. It can happen as a result of development of surface waviness in draw resonance or jet break-up (surface instability) or as a result of cohesive fracture even though it is encountered in liquids. It is important to mention that this cohesive fracture occurs at the same magnitude of stress as in melt fracture of an extrudate leaving a die. It emphasizes the correlation between the strength (rupture) of a material and major distortion observed in concentrated solutions of polymers and melts.

4.1.6.4 Interfacial and Surface Instability

In coating processes, shear flows of films with a free surface are observed. A technologist expects that a liquid film on a solid base should be smooth and homogeneous - not always the case because of surface instabilities in a flow of a coating liquid.[26] It is important in surface coating, especially in automotive application where anticorrosive coatings are used.

The model of such a situation is a flow of a liquid film along an inclined plate. A stream with a free surface can become unstable, as demonstrated by imperfections of a free surface. An analogous phenomenon is observed in multicomponent flow through channels. Waves are formed at the boundaries of two liquids.

Interfacial and surface instabilities occur for Newtonian liquids due to inertial effects. The stability of flow is controlled by the Reynolds Number and the surface tension. The influence of the Weissenberg Number, controlling surface instability, is an additional factor typical of “rheological” liquids. Theory predicts that elasticity of liquid, even at very low values of the Reynolds Number, can lead to waviness of a surface, which is a purely rheological effect.

4.1.6.5 Rheological Phenomenon in Inertial Turbulence (Toms Effect)

Inertial turbulence exists in "rheological" liquids similar to many other effects of instability discussed above. Also in this case, special properties of some "rheological" liquids lead to a very abnormal (compared with regular liquids) phenomenon known as the **Toms effect**.[27] It is a very interesting, unusual, and important phenomenon worthy of separate discussion.

In order to understand the meaning of the Toms effect, it is necessary to repeat some fundamental concepts of classical hydrodynamics of viscous (Newtonian) liquids.

It is well-known (see also Chapter 5) that pressure drops during the flow of viscous liquid through a cylindrical tube (capillary, channel), i.e., the difference of hydrostatic pressures at the ends of a tube, ΔP, is related to the volumetric flow rate, Q. If and until the flow rate is not very high, the relationship between these two main macro-characteristics of a stream is expressed by the **Hagen - Poiseuille equation,**[28] which can be written as follows

$$\Delta P = \frac{128\eta LQ}{\pi D^4} \qquad [4.20]$$

where D is a diameter of a tube, L length, η viscosity. Alternative form of Eq 4.20, when substituting the volumetric flow rate by an average velocity, V, is as follows:

$$Q = \frac{1}{4}\pi D^2 V$$

Then we have

$$\Delta P = \frac{32\eta LV}{D^2} \qquad [4.21]$$

Finally, let us introduce dimensionless characteristics of flow, i.e., the Reynolds Number, defined in Eq 4.14, with V in this formula being an average velocity. The second dimensionless number is a coefficient of friction, λ, which is determined as

$$\lambda = \frac{\Delta P}{\frac{1}{2}\rho V^2}\frac{D}{L} \qquad [4.22]$$

Now, the Hagen - Poiseuille equation can be written with dimensional variables

$$\lambda = \frac{64}{\mathrm{Re}} \qquad [4.23]$$

Sometimes both numbers λ and Re are determined, not through diameter, D, but by radius, R, of a tube, then

$$\mathrm{Re}_R = \frac{VR\rho}{\eta}; \quad \lambda_R = \frac{\Delta P}{\frac{1}{2}\rho V^2}\frac{R}{L}$$

So the Hagen - Poiseuille equation looks like this:

$$\lambda_R = \frac{16}{\mathrm{Re}_R}$$

Changing D for R does not influence the result, and both dimensionless forms are equivalent to the initial Eq 4.20. Application of dimensionless Numbers λ and Re is of general meaning for hydrodynamics flow through tubes, because such an approach allows one to generalize data for different liquids and tubes of various geometrical sizes (diameter and length) by representing them in dimensionless coordinates λ and Re in one relationship. It is generally accepted to analyze the pressure versus output (flow rate) relationship in terms of λ and Re for any flow velocity, not only when Eq 4.20 is fulfilled.

It is well known that the Hagen - Poiseuille equation corresponds to the experimental data only up to some critical value of the Reynolds Number, Re*, which is close to 2300 (i.e., log Re* = 3.36). Increasing flow rate (or the Reynolds Number), the transient regime is attained, which lies in the range of Re* to Re**, and at Re >Re**, turbulent flow occurs.

The dependence of the friction coefficient on the Reynolds Number, for a fully developed turbulent regime of flow, in the range of the Re values up to 10^5, is well described by the empirical **Blazius equation**[29]

$$\lambda = \frac{0.3164}{\mathrm{Re}^{0.25}} \qquad [4.24]$$

The generalized λ(Re) dependence, established on the basis of numerous research experiments covering all regimes of flow, is drawn in Figure 4.18. In this graph, constructed in log - log coordinates, the line P corresponds to the Hagen - Poiseuille equation, and the line B is drawn according to the Blazius equation. Evidently, the transition from laminar to turbulent flow results in a great increase of resistance to flow, with corresponding increase of energy due to the movement of a liquid. The critical values of the Reynolds Numbers Re* and Re** are also marked in Figure 4.18.

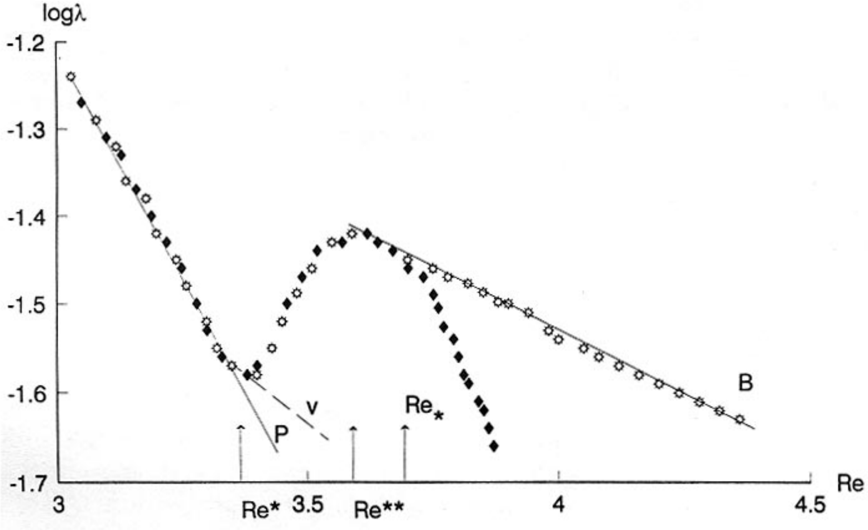

Figure 4.18. General view of the dependence of friction coefficient on the Reynolds Number. ♦ - regular (Newtonian) liquid, ○ - “rheological” liquid, P - Hagen - Poiseuille equation, B - Blazius equation, V - Virk asymptote.

The Toms effect in “rheological” liquids describes the decrease in resistance to flow (**drag reduction**) in adding very small amounts of some components to a regular liquid (the latter can be, for example, water or oil). These special additives are, as a rule, polymers of very high molecular weight (with very long flexible chain) and their concentration in solution can be as small as 1 - 100 ppm (parts of an additive per 1 million parts of a liquid). These micro-quantities of additives are the reason for the appearance of new rheological properties of matter.

The effect appears from some threshold value of Re, marked in Figure 4.18 as Re*. Black points in Figure 4.18 correspond to a pure liquid (solvent) and the light points to “rheological” liquid (very dilute polymer solution). In the laminar and transitional ranges, both sets of points fall into the same dependence. The same is true at the beginning of a turbulent regime of flow, but at Re > Re* the situation changes radically and a coefficient of friction for a “rheological” liquid becomes lower than for regular liquid.

Many publications have been devoted to the Toms effect. The main results about general peculiarities of the Toms effect are:

- the value of Re* decreases on increase of solution concentration; in the limiting case, Re* can become as low as Re**, and the transient regime of flow between Re* and Re** disappears
- the degree of drag reduction depends on the material properties (type of liquid and an additive, concentration of a solution, and so on), i.e., the effect depends on rheological properties of a liquid
- there is a limiting (asymptotic) degree of drag reduction in polymer solutions, common for all materials; it can be represented by dimensionless variables as described by the equation called the **Virk asymptote**:[30]

$$\lambda = 2.36\mathrm{Re}^{-0.58} \qquad [4.25]$$

The Virk asymptote is draw in Figure 4.18 under the symbol V.

Comparison of graphs B and V in Figure 4.18 shows that the maximal effect of drag reduction can reach 75%. Certainly, it is a very strong effect, and as such, it finds practical applications in liquid transportation. Also, special additives are used as a smoothing agents of fast movement of ships when turbulence requires additional energy use. The additives, by decreasing resistance, promote attaining higher speeds at the same engine power.

4.1.7 THIXOTROPY AND RHEOPEXY

Very often, real materials change their properties with time due to the structure transformations resulting from an action of external forces or rebuilding their initial structure at rest. The reason for change can be a preliminary deformation: in this case, rheological properties (in the simplest case - viscosity) change along with deformation and continue to change at rest after cessation of deformation. Such phenomena do not exist in Newtonian liquids having constant viscosity.

The change of properties can be fully reversible, though it may require a long time or even special actions (for example increase of temperature to accelerate processes during the material's rest). Some changes initiated by deformation can be stored in a material and then recovery may be incomplete. Both cases are real and observed; for example, in yogurt on mixing, in preparation of rubber compounds, shearing of thickened greases, pouring building materials, and so on.

If viscosity decreases during mixing and returns to the initial level on rest after shearing, such a phenomenon is called **thixotropy**.[31] The reverse phenomenon is called **rheopexy**. The definitions of thixotropy and rheopexy are valid not only for regimes of steady flow but also for transient deformations. The use of these terms is not always very definite, and thixotropic and rheopectic effects are frequently mixed with other viscoelastic effects.

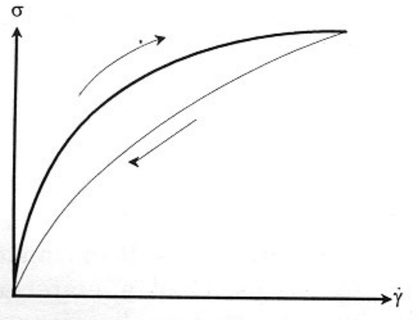

Figure 4.19. Hysteresis loop in continuous change of shear rate formed due to thixotropic properties of a liquid. An arrow shows the direction of changes of experimental conditions in viscosity measurement.

A typical example of thixotropic behavior of liquid is given in Figure 4.18, showing the relationship of viscosity versus shear rate. The upper part of a curve was measured on increasing shear rate; on reverse measurement (shear rate decreasing from maximum to minimum), viscosity is lower than on ascending shear rate change. The lower part of the curve represents viscosity of a medium with structure changed by previous deformation. Measurements are used to characterize thixotropic properties of material and their quantitative measure is an area of a hysteresis loop between two curves in Figure 4.19.

Structural effects in highly filled liquids can lead to a very peculiar rheological phenomenon called **dilatancy**, which is volume increase caused by shear. Deformation of moist sand or concrete are typical examples of dilatancy. Mixture becomes dry under pressure but recovers and becomes moist after the pressure is removed.[32] Solid particles in such materials are in a state of close packing. Under shear, particles must be separated and liquid acts as a lubricant. Particle coating by liquid increases volume.[33]

The change of rheological properties on deformation and rest reflects the structural rearrangement caused by application of external forces. In this sense, thixotropy is a consequence of structure rupture and rheopexy of structure build-up. It can be expected that external forces more likely promote rupture rather than a build-up of structure, and that is why thixotropic effects are more common than rheopexy, the latter being a very special case in materials with some kind of unusual intermolecular interactions; for example, strong ionic interaction or hydrogen bonding.

It is important to emphasize that in both cases, a new class of phenomena is discussed within the frame of rheology, that is, kinetics of physical or chemical processes in a material related to the effect of stress. Kinetic effects in rheological systems can be called **rheokinetics** or **chemorheology**.

There are two main cases of chemorheological effects. One of them is a change of stresses (relaxation) in deformed materials as a result of chemical reaction initiated by stress. This phenomenon is particularly important for rubbers, as was investigated in fundamental works by Tobolsky.[34] The second case regards chemical reactions of polymerization, curing of oligomers, and chemical transformations in polymeric chains.[35] All these chemical reactions result in considerable changes of rheological properties (not only viscosity) of a material. Certainly this type of phenomena is especially important in applications of polymer technology (synthesis and processing).

Changes in the matter structure are followed by changes in its properties. They lead to new values of parameters characterizing these properties; for example, viscosity of a liquid or modulus of elasticity of a solid. The set of these parameters differs for any actual state of a material structure. Results also depend on the conditions of measurements of these properties. From this description, it is apparent that the behavior of material is non-linear, and the effects are caused by transformations of a physical structure of matter. That is why rheological effects related to structural transformations of a material can be called **physical non-linearity** of rheological behavior. In discussion of non-Newtonian flow, it already has been mentioned that the idea of physical non-linearity, as a reason for this effect, was introduced by Ostwald[1] under the name of structure viscosity. A similar reason can lead to other rheological effects.

4.1.8 NON-LINEAR ELASTICITY

According to the Hooke Law the dependence of elastic deformations on stress is linear and the modulus of elasticity (the ratio of stress and deformation) is a material constant. This idea looks quite natural because any complicated function, such as $\sigma = f(\varepsilon)$, can be expanded into a power series. The first (linear) member will always be dominating, because at $\varepsilon << 1$ and at $n > 1$, the $\varepsilon^n << \varepsilon$. Thus, higher members of the series are negligible in comparison with the linear members.

Sometimes large elastic deformations are treated as a second-order effect. If one expands the function $\sigma = f(\varepsilon)$ into a power series, then the term “large elastic deformations” means that the second (quadratic) member of a series becomes comparable to the linear member. When $\varepsilon << 1$, the quadratic member is negligible, but as ε approaches 1 and exceeds it, then the “second-order” effect becomes dominant.

Even for some ordinary materials, at rather low deformations, the Hooke Law appears not exactly true, the dependence $\sigma(\varepsilon)$ is non-linear and, as demonstrated by Bernoulli, approximately at the same time when Hooke formulated his Law, properties of some materials are better described by power law:

$$\sigma_E = K\varepsilon^m$$

where K and m are empirical constants (m is not equal to 1).

It is worth mentioning that Bernoulli conducted his experiments with biological materials which are rather complicated in their structure, while Hooke dealt with rather simple homogeneous materials.

The properties become more complex for materials which can withstand large deformations ($\varepsilon > 1$). This is a case especially important for rubbers, some polymer solutions, and colloid systems (for example, dispersions of aluminum naphthenates). Draw ratio, λ, for these materials can reach values of an order of 10 and even more. In such cases, the non-linearity of stress versus deformation dependence is evident as a typical rheological effect.

There are some popular equations for describing dependence of draw ratio on the stress of rubbers. The most often used formula, the so-called Kuhn-Guth-Mark equation,[36,37] can be written (for uniaxial extension) as

$$\sigma_E = G_\infty(\lambda^2 - \lambda^{-1}) \qquad [4.26]$$

where G_∞ is an equilibrium modulus, and λ draw ratio.

Sometimes "conventional" stress, σ_o, (drawing force divided by initial cross-section of a sample) is used instead of the true stress, σ, (force divided by a current cross-section of a sample, taking into account changes of the cross-section along drawing). If the volume of a sample does not change during deformation (very close to reality for rubbers), the relationship between conventional and true stresses is very simple

$$\sigma_o = \sigma_E \lambda$$

and Eq 4.26 takes the following form

$$\sigma_o = G_\infty(\lambda - \lambda^{-2}) \qquad [4.27]$$

It is easy to show that within the limit of small deformations (at draw ratio $\lambda \to 1 \text{or} \varepsilon << 1$), Eq 4.26 becomes

$$\sigma_E = 3G_\infty \varepsilon \qquad [4.28]$$

It means that, within the limit of small deformations, the Hooke Law is valid, and the Young modulus equals $3G_\infty$.

The divergence from linearity of $\sigma(\varepsilon)$ dependence, predicted by Eq 4.26, is illustrated in Figure 4.20. It is quite evident that non-linear effects appear at rather large deformations. Initial slope of the curve (dotted line in Figure 4.20) equals $3(\lambda - 1)$, corresponding to Eq 4.28.

It is important to emphasize that Eq 4.26 is a single-constant equation (contains only one parameter G_∞). Another single-constant equation for large deformation was proposed by Bartenev and Khazanovitch.[38] For uniaxial extension it has the following form

$$\sigma_E = A(\lambda - \lambda^{-1/2})$$

where A is an empirical constant.

Numerous other equations for large deformations, discussed in scientific literature and used in practice, are multi-parametric. Among them is the **Mooney - Rivlin equation,**[39] which is the most popular equation. For uniaxial extension, this equation is written in the following form

$$\sigma_E = 2[C_1(\lambda^2 - \lambda^{-1}) + C_2(\lambda - \lambda^{-2})] \quad [4.29]$$

where C_1 and C_2 are empirical <%-5>constants (parameters).

Quite different two-parameter equation of power type, for large deformations, was proposed.[40] For uniaxial extension it has the following form:

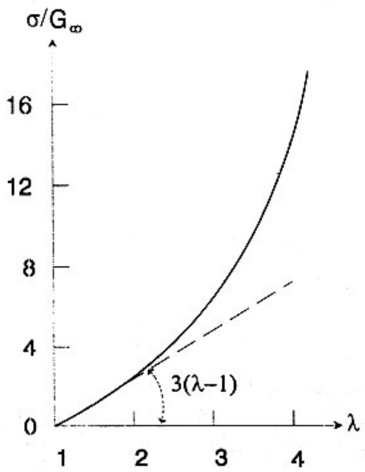

Figure 4.20. Stress versus deformation dependence predicted by the Kuhn-Guth-Mark equation. Dotted line is linear stress versus deformation dependence.

$$\sigma_E = 2B(\lambda^n \ \backslash \lambda^{\backslash n/2}) \quad [4.30]$$

where B and n are empirical constants. Eq 4.30 is close to the equation earlier discussed by Ogden[41] and can be treated as an analogue to the power law for non-Newtonian liquids (Eq 4.5).

Certainly, experimental data on uniaxial extension at large deformations (like any other set of experimental data) can be described in many different ways by means of equations of various mathematical structure. It seems that there is only one formal limitation: existence of a linear region in the limit of small deformations. There are some other inevitable limitations for use of arbitrary stress versus deformation equations and they will be discussed below on the basis of general principles for constructing rheological equations of state. That is why other possibilities for describing large deformation will be discussed below within the frame of a general theory of elastic bodies (Chapter 6).

Large elastic deformations lead to numerous macro-effects and they can be a source of some effects which might be treated as independent rheological effects; for example, large elastic deformations during shear are intimately related to the Weissenberg effect, and perhaps, at least in some cases, they correspond to non-Newtonian flow of "elastic" (i.e., capable of superposition of flow and recoverable deformations) liquids.

There are some direct consequences of large elastic deformations in different media. For solids, it includes the so-called **Poynting effect**.[42] It consists of extension of a body when sheared. It leads to an increase of its length, even though in a classical Hookean solid the deformation of one type (twisting) must not influence deformation of another (longitudinal extension). It is interesting to mention that, according to original experimental data, axial deformations observed in the Poynting effect are proportional to the squared angle of twisting. That is why the Poynting effect and some other related manifestations of large elastic deformations are sometimes called effects of the second order.

An increase of a diameter (swelling) of liquid streams is another manifestation of large elastic deformations. When an elastic liquid leaves a capillary (or a die), its diameter increases above a diameter of a channel, though a diameter of stream in flow of classic Newtonian liquid must decrease. The origin of this effect, called **die swelling** or the **Barus effect**,[43] is also related to large elastic deformations developed during the flow through a channel.[44]

Large elastic deformations can act in combination with other rheological effects. One of the most interesting cases includes superposition of large elastic deformations and thixotropy, when large deformations destroy the inherent structure of a material. This situation is typical, for example, for filled rubbers (rubbers containing reinforcing filler such as carbon black) or crystalline solid plastics. In this case, repeated deformations (stretching - compression cycle or periodic large amplitude shearing) lead to change of observed stress versus deformation dependence which approach some "equilibrium" shape only after several loading-unloading cycles. The phenomenon is called the **Mullins effect**.[45]

In discussion of the theory of deformations (Chapter 3), it was shown that some non-linear effects may occur purely for geometrical reasons and can be explained and described if we want to use "correct" (or corrected) measures of the effect. For example, introduction of Hencky's measure of deformations allows one to "linearize" the behavior of a material because deformations are summarized in accordance with a linear rule. That is why corresponding phenomena, which are only due to geometrical transformations of a body and can be excluded by introducing "proper" quantitative measures of an effect, can be treated as **geometrical non-linearity** in rheological behavior.

4.1.9 VISCOELASTIC BEHAVIOR
(TIME EFFECTS AND SUPERPOSITION OF FLOW AND ELASTIC DEFORMATIONS)

Superposition of viscous and elastic behavior is a typical and important rheological effect characteristic of real materials. This phenomenon is called **viscoelasticity**. It can be observed in deformation of all materials, even such as metals and stones, on the one hand, and water and oil, on the other. The difference is only in the relative participation of elastic and plastic components and the sensitivity of the method used for their investigation.

The idea of viscoelasticity of solids was introduced into scientific discussions by Lord Kelvin (W. Thomson), who applied this concept to deformation of the Earth.[46] Long-term, very slow deformations of metals under stress, damping of vibrations of bells, and many other phenomena of this type are all consequences of viscoelastic properties of real materials.[47] However, the most important class of materials possessing viscoelastic properties include polymers (rubbers, plastics, solutions) because viscoelastic phenomena are observed in deformations of these materials in ordinary time-scale (seconds, minutes, and hours), while observation of viscoelastic effects for other materials requires either very short (fraction of a second) or very long (years) time-scales.

There are two main phenomena related to viscoelastic properties of a material. They are **creep** and **relaxation**, though viscoelastic behavior of a material can be observed in numerous other experiments and applied situations.

Creep is slow development of deformations at a constant stress. For a Hookean elastic body, application of a constant stress creates constant deformation, which appears (practically) instantaneously and does not change as long as stress continues to be constant. For a Newtonian liquid, application of constant stress leads to flow with a constant rate of deformation. The behavior, called creep, is illustrated in Figure 4.21. We can distinguish three different cases:

- limited creep - deformation reaches its maximum level and after that does not change; this behavior reflects viscoelastic properties of solids

- limited rate of deformation - after a transient period, constant rate of deformation is set. This constant value of deformation rate is given by the curve 2, the behavior reflects visco-elastic properties of liquids which flow at constant rate of deformation
- accelerated creep - not only deformation but also the rate of deformation show limitless increase until the rupture of a body; this situation is typical for both liquids and solids, if stresses are sufficiently high and exceed cohesive strength of material.

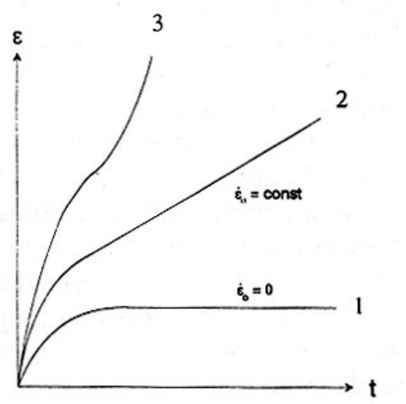

Figure 4.21. Different types of creep: limited deformation (curve 1), limited constant rate of deformation - marked at the curve (curve 2), and accelerated creep (curve 3).

In the first case shown in Figure 4.21, full deformation is completely elastic (or reversible). It means that, if an external force is removed, the initial dimensions of a body are completely restored. In two other cases, full deformation consists of elastic (reversible) and plastic (irreversible) components. It means that after removal of an external force, the initial dimensions of a body are only partially be restored. This difference is demonstrated in Figure 4.22, which can be treated as a continuation of first two curves in Figure 4.21. The portions of curves, after the dotted line x-x, reflect behavior of a material after removal of an external force; the resulting deformation is zero in the first case and there is a residual deformation, ε_f, in the second case (the third case in Figure 4.21 gives similar picture as the second case).

Creep is an important property of many materials which are not very "rigid" or/and fragile. Creep is practically non-existing in metals at room temperature but it becomes a very serious problem if a metal is used close to its melting temperature, as characteristic, for example, for high-temperature steels used in gas turbines. Creep is also important for parts working under high stresses for a long time, for example, pipes under internal pressure. Creep is of special importance in different types of plastics, including reinforced plastics, highly filled polymers (for example, solid propellants), because they are used at temperatures not far below their melting temperature. That is why measurement of creep is very popular in polymer material science.

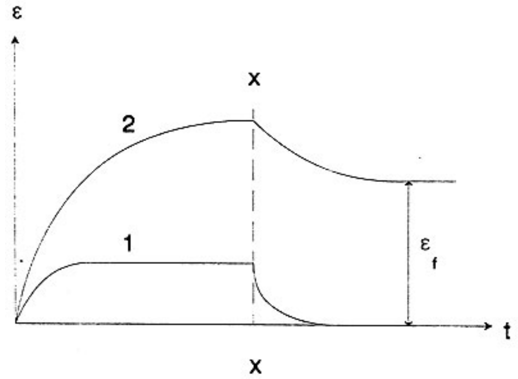

Figure 4.22. Elastic recovery of deformation after removal of stress for a visco-elastic solid body with residual deformation, ε_f, (curve 1) and visco-elastic liquid (curve 2).

Relaxation is a slow decay of stresses at constant deformation. For a Hookean body, stress continues to remain constant during preservation of deformation. For a Newtonian liquid, stress cannot act if rate of deformation is absent (it is absent at constant deformation, because the derivative of a constant is zero). In real bodies, stress decay is not instantaneous but requires time as shown in Figure 4.23. One can distinguish two possible situations, as illustrated in Figure 4.23:

- stress may dissipate and completely disappear - this is a case of stress relaxation in a visco-elastic liquid
- part of an initial stress, σ_∞, can be stored in a material for unlimited time, in the case of a visco-elastic solid.

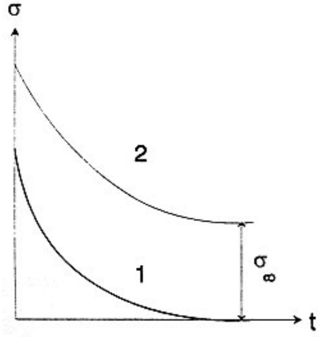

Figure 4.23. Relaxation in visco-elastic liquids (curve 1) and solids (curve 2). Residual stress equals σ_∞.

Both basic visco-elastic phenomena can be considered as a mutual delay in change of stress and deformation. Thus, it is necessary to introduce time as a factor determining the stress versus deformation relationship and accept that an unambiguous correlation between stress and deformation does not exist.

In fact, the concept of relaxation is much wider than only slow decay of stresses. Maxwell, who introduced an idea of relaxation in physics,[48] used this term to designate delayed restoration of a molecular structure of matter distorted by any external factor or (maybe) simply by a statistical fluctuation. Then we can understand relaxation as restoration of an equilibrium state, disturbed for any reason.

Any time effect is a consequence of various transformations of inherent structure of a material and kinetic processes of this restoration. In this line of thought, the visco-elastic behavior can be treated as a thixotropic effect of some kind. At least in some cases, both phenomena are intimately related to each other. However, as a general rule, visco-elasticity is considered as an independent phenomenon and the theory of this effect (Chapter 7 is devoted to the complete discussion of this theory) is constructed regardless of analysis of structural and/or kinetic processes which may take place in a body.

In practical applications, relaxation is always considered when a material or a structure as a whole is deformed. A rather obvious example of relaxation is offered by damping of vibrations by shock-absorbers in cars and other transport devices. Exploitation of seals in pressure vessels is another example. In initial state, seals can be very tightly pressed by screws. The relative positions of a cover and a vessel are not changed during work (i.e., deformation of a seal continues to be constant) but due to relaxation; a material becomes unstressed and sealing becomes not as tight as it was in the beginning.

4.1.10 FLOW AROUND SOLID OBSTACLES

Flow of liquid around a solid body (obstacle) is an interesting and important example from hydrodynamics. The effect is the same when a stream flows around a solid body or a body moves through a liquid medium, similar to river flow under the bridge or a ship moving in a sea. In both situations, the hydrodynamic resistance to movement is of interest.

Classical experimental and theoretical investigations (initiated by A. Eiffel in the 19th century) showed that the general hydrodynamic picture can be demonstrated as in Figure 4.24, and there are two characteristic effects observed:

- existence of a point at which a stream is diverted by a body, and this point is characterized by the value of an azimuthal angle, β^*
- formation of vortices after passing the point of first contact between a body and a stream; they appear even in laminar flow and remain stable after passing a solid body in the form of so-called **Karman's strip**.

These effects are observed in flow around any solid body with smooth curvature (spheres, cylinders, ovals, and so on). It is worth mentioning that the hydro-

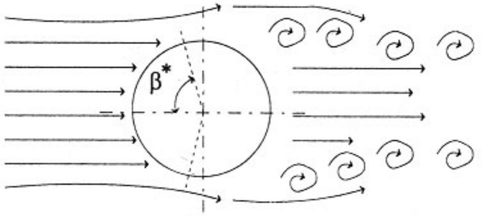

Figure 4.24. The picture observed when a liquid flows around a solid body at transient range of the Reynolds Numbers between laminar and turbulent regions.

dynamic resistance in all cases is primarily determined by the pressure of a stream before the point of contact, and contribution of viscous friction does not exceed 2% of the total resistance. Heat and mass exchange processes between a liquid and a solid body during these process is of special significance in the design of heat exchange equipment.

It is important to emphasize that the value of the azimuthal angle, β*, found in flow of numerous Newtonian liquids is rather constant and close to 82° in the range of the Reynolds Number from 3×10^2 to 3×10^5. This range covers the transition zone from laminar to turbulent flow, typical of real technological application.

Experiments and some theoretical studies showed that the azimuthal angle, β*, is lower than 82° for non-Newtonian liquids. A more pronounced effect is observed if liquid is not purely viscous but also has elastic properties (for example, polymer solutions, some biological liquids, etc.). The following new effects are observed here: the position of the point of stream diversion becomes variable and moves upstream. The shift can be so large that β* reaches 180° and flow approaches an undisturbed pattern flowing around a body in the range of the Reynolds Numbers mentioned above.

This is a consequence of rheological properties of a medium, namely, elasticity of a liquid. This effect is frequently used in technology where liquids are modified to impart elastic properties.

4.1.11 PHASE TRANSITIONS INDUCED BY DEFORMATIONS

Deformations of some materials can lead to phase (or at least to relaxation) transition under isothermal conditions. Treating this phenomenon as a rheological effect (though one may think that there is some conditionality in such treatment) has the following reasons:

- it happens with materials which manifest many other rheological effects discussed above

- it leads to a very strong change in rheological properties of matter during its deformation
- at least in some cases, several rheological effects discussed above can be explained based on the idea of phase or relaxational transition occurring as a consequence of deformation.

There are some very typical and practically important situations observed in deformation of polymer solutions and melts related to transitions caused by deformations and therefore treated as rheological effects. They are:

- **necking** - formation of a sharp contraction in uniaxial stretching of many amorphous and crystalline polymers at some critical deformation; further stretching occurs through transition of an initial width into a uniform narrow "neck"
- **orientational dewetting** (or phase separation) - at very high rates of extension of some polymer solutions, polymer becomes insoluble (it means that transition into a two-phase system takes place) and polymer precipitates from solution; similar effects were observed in shear when phase transition shifted along the temperature scale on increase in shear rate
- **spurt in flow** - at high stresses, polymer, moving along a channel, loses its fluidity and begins to slip from a solid wall of a channel. This phenomenon is caused by flow-to-rubbery state transition
- **orientational crystallization** - deformation can shift temperature of equilibrium crystallization and thus it influences kinetics of isothermal phase transition; this effect is well known in stressed rubbers. Crystallization under deformation in loaded parts radically changes their mechanical properties and can lead to an unexpected breakage during operation.

Phase and relaxational transitions caused by deformations lead to very sharp changes in rheological properties of a material. That is why effects related to transitions can be classified as **phase non-linearity** in rheological behavior.

4.2 GENERAL PRINCIPLES

Formulation of rheological equation of state requires answers to the following questions:

- rheological effects are observed (as a rule) in rather simple unidimensional deformations - how to describe them in three-dimensional space?
- many different effects coexist - can they be considered as independent or are at least some of them a consequence of the same inherent mechanism?

- rheological properties of a material are measured under some chosen conditions - is it possible to predict behavior of a material in other situations? What is the minimal range of experiments necessary to make a valid prediction for a full set of different stress states?
- are the empirical methods, used to generalize different experimental results, not contradictive?

Let us assume that sets of experimental data were obtained for different conditions of deformation; for example, in uniaxial extension and simple shear. Each such set of data can be described by an empirical equation. The final interpretation would be simple if both observed cases of rheological behavior of the same material would not offer two different manifestations of inherent properties of matter. Then both stress versus deformation equations must be considered as consequences of a general rheological equation of state of a material. In other words, equations for different geometrical modes of deformation must be compatible.

There are some general limitations for rheological equations of state to produce compatible stress versus deformation relationships for different geometrical modes of deformation. The limitations will be discussed below, whereas rheological equations of state for main groups (types) of materials will be analyzed in Chapters 5 and 6. In particular, it will be demonstrated that stress versus deformation (or rate of deformation) equations written above can be treated as consequences of some general rheological equations of state. Moreover, the same equations for one-dimensional deformation can be obtained from quite different rheological equations of state, i.e., the same experimental data can be generalized in a different way. These different equations of state give non-equivalent predictions for other deformation modes. That is why, in order to establish the correctness of the equation of state, it is necessary to have experimental data from several different geometrical modes of deformation.

Let us discuss characteristic and important cases, illustrating the above problem in regard to properties of anisotropic materials. It has been known for years that mechanical properties of even such old and popular material as cast iron are different in extension and compression. This means that it is incorrect to predict behavior of this material in engineering application based on results of measurement of its properties in extension if material actually works in compression mode.

The situation becomes even more complex if one considers properties of monocrystals or reinforced plastics. Modulus of elasticity (and in fact all other physical properties) of monocrystals depend on orientation of an applied force in respect to crystallographic axes and it is quite possible to find some different values of modulus which depend on a type of crystal symmetry. In real polycrystalline material, this effect is averaged, but it is not for monocrystals.

In reinforced plastics, modulus and all other mechanical properties depend on orientation of a force in relation to orientation of reinforcing fibers and their arrangement. All this means that attempts to build the rheological equation of state of such anisotropic materials, based on results of one-dimensional experimental data, are absolutely futile. Instead, it is necessary to carry out a set of different experiments for various geometries of deformation.

Anisotropic properties of material can be considered, within the limit of small deformations, and in such a case, interpretation is a part of classical linear theory of elasticity. But modulus of elasticity of anisotropic materials must be treated as a tensor by itself. Anisotropy of material properties is a particular kind of rheological behavior of a material and it certainly does not exclude any particular direction of all other rheological effects (for example, visco-elastic behavior or thixotropy).

General principles of constructing rheological equations of state were introduced in modern rheological literature in some fundamental works, primarily by Oldroyd,[49] Truesdell,[50] and Coleman *et al*.[51] The principles must be followed to assure that at least some of the equations used for describing rheological effects in deformation of real materials have physical meaning and the above-formulated questions receive proper answers.

First of all, it is necessary to limit the use of tensor components for formulating rheological equations of state because physical laws must not depend on choice of coordinate system. This idea, which can be called the **principle of coordinate invariance**, requires all rheological relationships to be formulated through invariants of an appropriate tensor but not through their components. If the equation is written in invariants, it is still possible to discuss observed or predicted effects in a convenient coordinate system using tensor components as compounded variables.

In order to pursue this principle, it is convenient to introduce two fundamental physical concepts related to deformations. They should describe the most general result of action of force. The first result of deformation can be accumulation of work of external forces in the form of elastic energy. This stored energy is characterized by the value of **elastic potential**, W, which is a specific stored energy (energy related to the unit volume). The second possible result of deformation is dissipation of work of external forces, i.e., its irreversible transition to heat. This effect is characterized by **intensity of heat dissipation**, A, which is a quantity of heat produced in a unitary volume of a material.

Introduction of the concept of elastic potential and intensity of heat dissipation gives grounds for a very general classification of different materials:

- If during deformation, $W \neq 0$ and $A = 0$, a material has pure elastic response, and it can be called an elastic body.
- If during deformation, $A \neq 0$ and $W = 0$, a material is a pure viscous liquid.
- Finally, if during deformation only part of the work produced by external forces is stored in a material and the other part dissipates, i.e., $W \neq 0$ and $A \neq 0$, a material is a visco-elastic body.

These three types of rheological behavior will be discussed in the three subsequent Chapters of the book.

The concepts of elastic potential and heat dissipation are very fruitful for formulating rheological equations of state, because both values are physical objects not connected to any coordinate system. When these concepts are used in rheological equations of state, they must be represented as functions of invariants to follow the principle of coordinate invariance. This can be invariants of kinematic (deformation or rate of deformation) or dynamic (stress) tensors but not their arbitrary components. Certainly, if the equation of state is formulated as a dependencies of W and A on invariants of kinematic or/and dynamic tensors, it is always possible to arrive at the relationship between their components.

The direct consequence of the principle of coordinate invariance is the necessity to express scalar values, met in rheological equations of state, as functional invariants of kinematic and/or dynamic tensors, but not of their components. These scalar values are physical properties of an individual material. For example, it can be viscosity or modulus of elasticity. They can change under deformation, but dependencies of the constants characterizing conditions of deformation must enter into rheological equations of state only in the form of functions of tensor invariants.

In the next step, physical laws should be related to the definite site (point) of a material in a form that allows one to follow material moving in space. It means that a rheological equation of state must describe behavior of a material, regardless of the possible motions of an observer. This approach has already been mentioned in Chapter 3 in our discussion of large deformations and is called the **principle of material objectivity**. The direct consequence of this principle is the requirement of transformations of deformation and stress tensor from moving to a fixed coordinate system (according to the rules of tensor transformations) in order to give an observer the possibility to see what happens with a material.

There are some other ideas which are also accepted in constructing rheological equations of state. There is an easily grasped idea, stating that material has memory of its prehistory (i.e., the manner of stress and deformation changes can influence the current state of material) but material cannot predict future events. This is called a **principle of determinism**.

Also, it is considered as a general rule that only short-range interactions are important, i.e., stress and deformation behavior at some point are influenced only by the nearest neighbors of this point, which is called a **principle of local action**.

Although the above-cited principles are a general basis for formulating rheological equations of state (constitutive equations) of various materials and are considered as objective laws, it is possible to find real physical examples which do not obey some of them. For example, for liquid crystals and other materials possessing inner macrostructure, which cannot be neglected, the idea of local action can be invalid.

Rheological equations of state must describe mechanical behavior of all possible real materials. It is therefore important to answer the following question: where is the place of individual properties of a material? There are two levels in answering this question. First, the difference between behavior of various media is reflected in the form of a rheological equation of state used to describe peculiarities of their deformational properties. Second, the difference of two materials with similar rheological properties (i.e., expressed by the equivalent rheological equations of state) is reflected in absolute values of scalar coefficient entering the equation.

For example, water and steel are different materials, one of them is a liquid and the second is a solid, and the difference in their properties is reflected by the necessity to use quite different rheological equations of state for description of their mechanical behavior, i.e., the Newton or Hooke Laws. Water and paint are both liquids but with different specific behavior at various levels of stress; that is why we need to use different rheological equations of state for these two forms of matter, though both of them are liquids. Finally, water and oil are both Newtonian liquids and the distinction of their behavior is hidden in the difference of their coefficient of viscosity.

4.3 CONCLUDING REMARKS

Investigating deformational properties of real materials, one encounters many "new" effects compared with "ideal" models of a linear liquid (Newtonian liquid) or a linear solid (Hookean solid). These effects must be treated as special **rheological phenomena**. Understanding their origin, correlation with inherent structure of matter, and quantitative description are the main problems discussed in theoretical, experimental, and applied rheology.

The most important and evident rheological effects are:

- **non-Newtonian viscosity** - dependence of apparent viscosity calculated as for Newtonian liquids for a particular geometry and flow conditions for different rates of flow
- **plastic behavior** - lack of deformation if stress does not exceed some critical level
- **Weissenberg effect** - existence of normal stresses in shear flow, or appearance of a three-dimensional stress state in uni-dimensional deformation
- **transient** (or time-dependent) **behavior**. It can have numerous and interpenetrating manifestations: **thixotropy** and **rheopexy**, i.e., reversible change of inherent structure of matter, its destruction or building, under applied stresses; dilatancy, i.e., reversible volume changes under shearing; **visco-elastic behavior**, i.e., delayed deformation after stress application (**creep**) or remaining stress after applying deformation (**relaxation**)
- anomalies in **uniaxial extension** - probability of uniform stretching at large extension ratio, increase of longitudinal (extensional) viscosity as a function of deformation and rate of extension
- **flow instability**, particularly **melt fracture**, which is not related to the classical Reynolds inertial turbulence but connected with elasticity of a flowing liquid; appearance of **secondary flows**, and so on
- **non-linear elasticity** as a result of **large elastic deformations** - complicated stress versus deformation dependence and consequences of geometrical non-linearity, particularly the **Poynting effect** - extension of twisted wires.

Generally speaking, all rheological phenomena can be treated as **non-linear effects**, bearing in mind that they manifest themselves as a departure of mechanical behavior of real material from the prediction of linear models, represented by the Newton and Hooke Laws.

It is reasonable to distinguish between different "degrees" of non-linear behavior. Different rheological effects which are non-linear phenomena originate from three general principle causes:[52]

- Non-linear effects can be caused by geometrical reasons and can be nothing more than a direct consequence of large elastic deformation. Typical results of such effects were discussed in Chapter 3, concluding that it is necessary to introduce other measures of deformation to characterize the deformed state of material. Such an approach allows one to exclude non-linearity. It is reasonable to think that the Weissenberg effect (at least within the limit of very low rates of deformation) and the Poynting effect are two main consequences of **geometrical non-linearity**, or large elastic deformation. Non-linear effects of such kind are observed in static (or equilibrium) conditions or in slow flows.
- Non-linear effects can be related to changes (or "rupture") of the inherent structure of material. At different stresses available at various rates of deformation, incomparable materials are encountered, having new values of essential parameters, such as viscosity or elastic modulus. This type of non-linearity is the most typical for colloidal systems and filled polymeric materials. **Structural non-linearity** can be one of the reasons for non-Newtonian viscous flow, and it is the cause of the **Mullins effect**. It is worth noting that in discussion of structural non-linearity, it is useful to add kinetic arguments to rheological considerations.
- Strong non-linear effect can be observed if material transits into a new relaxational or phase state due to the action of deformation. Rheological properties of material in different phase or relaxational state are quite different because of changes along the transition. This type of rheological behavior, which can be called **phase non-linearity**, is encountered, for example, during polymer crystallization in extension. Amorphous phase separation is observed in flowing polymer solution or rupture of visco-elastic stream ("melt fracture") which occur at high rates of deformation. It is worth mentioning that in discussion of phase non-linearity, it is useful to add thermodynamic arguments to rheological considerations.

Based on the above discussion, it is possible to build a hierarchy of non-linear rheological effects, characterized by the following terms:

geometrical	*structural*	*phase*
weak	*strong*	*breaking*
static	*kinetic*	*thermodynamic*

Many real materials are multi-component compositions. Different components of material can behave differently at the same rates of deformation, i.e., above-mentioned types of non-linearity can appear at different conditions of deformation. For example, any real polymer is polydisperse, i.e., it consists of components of different rheological properties. Thus, a certain level of deformation rate is sufficient for appearance of non-linear behavior for a part of a material, but this level of deformation rate might not be adequate to cause non-linear behavior of other components of the same system. It is also possible that different modes of non-linearity are characteristic for various components of complex material. For example, filled polymer melt can manifest non-linear behavior of one type, due to particular properties of a visco-elastic polymeric matrix, and the other type due to rupture of the structure of a filler. It means that in real practical application, superposition of various non-linear effects of different types can be expected.

As a general rule, rheological phenomena are observed in analysis of one-dimensional deformation, although one of the most interesting characteristic rheological effects is a limited probability of maintaining one-dimensional stress state for some materials.

Experimental points obtained under different conditions of measurement (stress versus deformation or/and versus time) can be approximated by different equations. Thus, the central problem in rheology is the compatibility of equations used for quantitative description of various rheological phenomena.

There are two sides to the problem:

- it is important to relate the explanations to analogous phenomena, but observed for different geometrical modes of deformation (for example, flow in shear and extension must correlate - but how?), they need to be treated as related consequences of the single relationship between forces and deformations

- it is of importance to correlate different rheological effects; for example, non-Newtonian flow, normal stresses in shear, and large elastic deformations in the quest to understand their common source.

In this aspect, the concepts of **rheological equation of state** occupy the central position in the description and generalization of experimental data. There are some important (physical) limitations, determining the fact that not every analytical equation can be used as a rheological equation of state. These limitations are expressed as the following principles:

- **coordinate invariance** - behavior of a medium does not depend on choice of a coordinate system; that is why the rheological equation of state must be formulated, not in the form of components of stress and deformation tensors, but as their invariants
- **material objectivity** - behavior of a medium does not depend on movement of an observer or a body as a whole
- **determinism** - a material can remember its past, which influences its behavior in a current moment, but does not know future events
- **local action** - only the nearest surrounding may influence behavior of a body at a point not the events happening far from this point.

In spite of all these limitations, freedom in constructing rheological equations of state is rather wide. Therefore, it is very important to choose equations which are not too complicated to be used for practical calculations and which can be correlated with the physical structure (or content) of matter. The first is necessary for industrial and technological application of rheology, and the second is of basic value if one considers rheology as one of the fields of physical chemistry offering background for objective quantitative characterization of the properties of matter.

There are two possible general types of body reaction on the action of external forces:

- storing the work in the form of **elastic potential**
- irreversible loss of this work by **heat dissipation**.

In accordance with these fates of energy which was delivered by the work of external forces, we can distinguish between elastic (solid) bodies and viscous liquids. The intermediate situation when the work done is partly stored and partly dissipated is also possible, and this is the case of visco-elastic materials.

In construction of rheological equations of state, the elastic potential and intensity of heat dissipation must be expressed as functions of invariants of kinematic and/or dynamic tensors. The difference in mechanical behavior of various materials is reflected in the form of the rheological equation used, and the values of scalar coefficients ("material constants") which are parameters of this equation, customizing properties of a material.

The last general remark is rather evident for a rheologist but may look strange for a non-professional or even for an engineer. From practical or technological point of view, in the great majority of cases, one can definitely distinguish between solid bodies and fluids, i.e., they are qualitatively different entities. For rheology, the difference between them is quantitative rather than qualitative, and it is preferable to qualify them, not into solids and liquids but as materials with dominating solid-like and liquid-like behavior under real conditions. The difference appears as a consequence of the ratio of the time scale (duration) of observation and the inherent (characteristic) time scale of a material.

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5

RHEOLOGICAL VISCOUS FLUIDS

5.1 DEFINITIONS

The concept of a **liquid** seems rather evident. Nobody doubts that water or gasoline are liquids. But what about tooth paste or adhesive? These simple examples show that it is not sufficient to imply that a liquid is a material which can flow. It is necessary to introduce a more rigorous definition and compare behavior of real materials with such a definition.

We may think that a liquid is a material which undergoes **unrecoverable (irreversible) deformations**, i.e., changes in shape remain after the action of external forces is removed. It should be noted that the definition must encompass all real materials. For example, one would need to consider metals as liquids because during some technological operations, e.g., punching of golden articles, wire-drawing of silver or rolling steel ingots, we undoubtedly create unrecoverable deformations. These examples show that the above definition is too wide. Indeed, it covers two types of behavior: **viscous** and **visco-plastic**. In the first case, unrecoverable deformations (or **flow**) can be detected at any stress, regardless how small it may be. In the second case, unrecoverable deformations appear only when stress overcomes some definite level, which is called **yield stress** or **yield point**. It means that a visco-plastic medium can be called a “liquid” only with some precautions. Nevertheless, treating deformation of visco-plastic materials, at stress exceeding yield stress as a flow, looks quite reasonable.

We can also define a liquid as a material which can flow (or is capable of unrecoverable deformations) under the action of infinitesimal (small) stress. Formally, this definition looks quite acceptable. But an experimentator may ask two questions:

First: Perhaps if stress is decreased by one (two, three, etc.) orders of magnitude, it is possible to reach the yield point at which flow, at very low stress, does not occur, i.e., in the case of any liquid, one deals with a visco-plastic liquid, but the yield stress is so small that it cannot be observed under experimental conditions but can be attained if conditions change. This assumption may have rather serious consequences. Doubt was expressed even for such a classical liquid as water. Indeed, it is never certain that the level of stress attained in an experiment is sufficiently low to assume that a material is a liquid **from an experimental point of view**.

The possibility to flow under infinitesimal stress means that a liquid at rest cannot store any stress. Indeed, if outer boundaries of body (treated as a liquid) are motionless, no stress should exist in the whole volume of the body. This is true with some reservations only. For example, flow inside a body having motionless boundaries can appear as a result of temperature gradient in a liquid. Nevertheless, this idea can also be considered as a definition of a liquid state. Contrary to such behavior, liquid visco-plastic media ("liquids") can store residual stresses equal to the yield stress.

Second: Perhaps during the period of observation (or experiment) unrecoverable deformations are so small that they cannot be detected, even though they exist. If an experiment is prolonged, flow of a material under investigation should occur.

Rheologists like to cite a famous exclamation by the Bible's Deborah: *"The mountains melted from before the Lord"*, bearing in mind that in the scale of eternity, the Lord really can observe flow of rocks (mountains). That is true, and the general answer to the problem raised by the theoretician lies in the comparison of "inherent" time scale of a material, t_{inh}, and time of observation, t_{obs}. This characteristic inherent time, t_{inh}, can be treated as time of relaxation, i.e., time necessary for recovery of a stable structure state after removal of external forces. Then, we can introduce the dimensionless criterion t_{obs}/t_{inh} (see also Eq 4.17), called the Deborah Number, De:

$$De = t_{obs}/t_{inh}$$

If De > 1, material behaves like a liquid, which occurs when t_{inh} is small and relaxation happens very quickly (in comparison with time of observation). In the opposite time scale (when De < 1), unrecoverable deformations cannot be detected and we cannot discover flow and treat a material as a liquid.

We then can define liquid as a material which **relaxes** very quickly, and this definition gives the concept of liquid, not as a state of a matter, but as a kind of behavior. Therefore, one should consider **liquid-like behavior** of a material, which answers the second question regarding rigorous definition of a liquid.

Finally, a very general definition of a liquid might be constructed on the basis of energy concept (see Section 4.2). Any action is connected with energy consumption. Two types of energy used for material deformation might be considered: the energy stored in the material and its return after the removal of external forces. Storage of energy is characteristic for an elastic medium (elastic behavior in rheological media is discussed in Chapter 6). The second reaction consists of energy dissipation by its conversion to heat, which is characteristic for viscous liquids, because viscous resistance to movement means heat dissipation of the work produced by the forces applied.

A viscous liquid then, can be defined as a medium deformed in such a manner that **energy needed for deforming completely dissipates** in the process of deformation. In essence, it means that no energy source for further deformation exists in the material after the action of external forces ceases and that is why deformation cannot be recovered (no driving force exists for the process).

Certainly, intermediate cases may exist when energy of deformation is partly stored in a material and only part of this energy can be dissipated. Such is the case of a viscoelastic body, in particular, of a viscoelastic liquid. We shall not consider such liquids here, only a viscous liquids, without any elastic effects, since all of Chapter 7 is specifically devoted to media properties having a combination of viscosity and elasticity.

The energy concept dividing materials according to their reaction to the work of deformation is the most general approach of characterization of a material type. Such a concept is not related to any considerations of local values of stresses and deformations and does not need to be related to observation of material behavior in coordinate axis. In this sense, the energy approach is invariant to a coordinate transformations and satisfies general requirements of rheological equations of state.

5.2 NEWTONIAN LIQUID

The idea of **Newtonian** and **non-Newtonian behavior** of liquids was introduced in discussion of rheological effects describing the development of rheology as a separate branch of natural science (Chapter 4). We shall now discuss a general approach to the concept of Newtonian liquid, bearing in mind the common principles of rheology formulated in Chapter 4.

One-dimensional (trivial) definition of Newtonian (or Newton-Stokes) liquid is given in Eq 1.1 for simple shear. It is very easy to convert this equation, using tensor notation:

$$\sigma_{ij} = 2\eta D_{ij} \qquad [5.1]$$

and for simple shear

$$\dot{\gamma} = 2D_{ij} = \frac{\partial u_1}{\partial x_2} \qquad [5.2]$$

which refers to the standard definition, Eq 1.1. Further discussion concerns the concept of a Newtonian liquid in an invariant form.

In order to apply the definition of a liquid as a material for which all work done in deformation dissipates, one needs to express the intensity of dissipation, A, as a function of deformation rate in a rheological definition of a liquid. The A is a physical object invariant to the choice of a coordinate system, which is why the rate of deformation also must be represented through its invariants.

This general approach allows for the following definition of the Newtonian liquid:

$$A = -4\eta D_2 \qquad [5.3]$$

where D_2 is the second invariant of the rate of deformation tensor.

Intensity of dissipation, A, is expressed as

$$A = \sum \sigma_{ij}\dot{\gamma}_{ij}$$

where σ_{ij} are components of the stress tensor, $\dot{\gamma}_{ij}$ are components of the rate of deformation tensor, and η is (Newtonian) viscosity.

The second invariant of the rate of deformation tensor is

$$D_2 = \dot{\gamma}_{11}\dot{\gamma}_{22} + \dot{\gamma}_{11}\dot{\gamma}_{33} + \dot{\gamma}_{22}\dot{\gamma}_{33} - (\dot{\gamma}_{12}^2 + \dot{\gamma}_{13}^2 + \dot{\gamma}_{23}^2)$$

Combining the expressions for A and D_2 with the definition, Eq 5.3, and considering coefficients in tensor notations, one comes to the starting formula of the Newton-Stokes liquid, Eq 1.1.

It is interesting and instructive to draw the relationship between stress and rate of deformation for uniaxial elongation based on the general (invariant) definition, Eq 5.3.

Stress tensor for uniaxial extension is expressed as

$$\sigma_{11} = \sigma_E$$

where σ_E is the drawing stress and all other components of the stress tensor are absent (equal to zero).

The rate of deformation tensor has only diagonal non-vanishing terms. It should be assumed that a liquid is incompressible. In this case (see Chapter 2), the first invariant of the deformation tensor equals zero. Thus, its time derivative (i.e., the first invariant of the rate of deformation tensor) also equals zero and we have

$$D_1 = \dot{\gamma}_{11} + \dot{\gamma}_{22} + \dot{\gamma}_{33} = 0 \qquad [5.4]$$

For an axially symmetrical body, for example, for a cylinder,

$$\dot{\gamma}_{22} = \dot{\gamma}_{33} = -\frac{1}{2}\dot{\gamma}_{11}$$

Therefore, A is evidently equal to

$$A = \sigma_{11}\dot{\gamma}_{11}$$

For uniaxial extension, considering relationship between components of the rate of deformation tensor, we have

$$D_2 = -\frac{3}{4}\dot{\gamma}_{11}$$

which leads to the following relationship between drawing stress and rate of deformation in uniaxial extension

$$\sigma_E = 3\eta\dot{\gamma}_{11} \tag{5.5}$$

The coefficient between normal stress, σ_E, and the rate of deformation is called elongational viscosity, λ, and according to Eq 5.5

$$\lambda = 3\eta$$

which is Trouton equation, discussed above. In fact, it demonstrates that both equations (Newton and Trouton equations) represent *the same type of rheological behavior*, i.e., the Newtonian liquid (liquid obeying the Newton Law in shear) will obey the Trouton Law in uniaxial extension and *vice versa*.

The same result can be obtained, not only by using the idea of intensity of dissipation, but also by exploring the decomposition of stress and the rate of deformation tensors into spherical and deviatoric parts.

The stress tensor can be decomposed into spherical and deviatoric parts in the following manner:

$$\sigma = \begin{vmatrix} \sigma_E & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} = \frac{\sigma_E}{3}\delta_{ij} + \frac{\sigma_E}{3}\begin{vmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

where the first member is a spherical part (negative hydrostatic pressure) and the second term is a deviator of the stress tensor.

For uniaxial stretching of a symmetric body, using the above mentioned relationship between components of the rate of deformation tensor, we can write:

$$\dot{\gamma} = \begin{vmatrix} \dot{\gamma}_{11} & 0 & 0 \\ 0 & \dot{\gamma}_{22} & 0 \\ 0 & 0 & \dot{\gamma}_{33} \end{vmatrix} = \frac{1}{2}\dot{\gamma}_{11} \begin{vmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

The spherical component in the rate of deformation tensor is absent which is the consequence of the incompressibility of liquid. The spherical part in the stress tensor is present but its value is immaterial for rheological behavior of liquid (regardless of the hydrostatic pressure, the volume of liquid remains unchanged). If we compare deviatoric parts of both tensors, we again come to the **Trouton equation** for elongational viscosity, which equals 3η.

The general definition (Eq 5.3) of the Newtonian liquid also allows one to calculate elongational "viscosity", now measured in biaxial extension.

Let us find the relationship between drawing (normal) stresses, $\sigma_E = \sigma_{11} = \sigma_{22}$, ($\sigma_{33}$ equals zero) and rate of deformation, $\dot{\varepsilon} = \dot{\varepsilon}_{11} = \dot{\varepsilon}_{22}$. According to Eq 5.4, in this case, $\dot{\varepsilon}_{33} = 0$.

For biaxial extension

$$A = 2\sigma_E\dot{\varepsilon}; \quad D_2 = -3\dot{\varepsilon}^2$$

and then in accordance with fundamental Eq 5.3, we have

$$\sigma_E = 6\eta\dot{\varepsilon} \qquad [5.6]$$

It is possible to treat the coefficient of this Equation (i.e., the coefficient of proportionality between stress and rate of deformation) as elongational viscosity, in the same manner as done for the Newton and Trouton Laws. Then, the **biaxial "elongational viscosity"** equals 6η (not 3η as in uniaxial extension). These two examples (uniaxial and biaxial extension) show that "viscosity" of a liquid can be different, depending on its definition.

These simple examples demonstrate that results of different experiments can be considered as consequences of the same rheological equation of state (constitutive equation) if formulated in a generalized (tensor) form. Also, it is clear that invariants must be used in the formulation of rheological equations of state for liquids in relationships between components of stress and rate of deformation tensors.

A Newtonian liquid is the simplest incompressible **linear liquid** and its rheological properties are completely described by a single parameter, its shear viscosity. In fact, it implies that a liquid is isotropic. But **anisotropic liquids**, i.e., liquids with properties dissimilar in different directions, can also exist (for example, in liquid crystals). Even if such liquid is linear, a single coefficient of viscosity is not sufficient for complete representation of its viscous properties. If we measure viscosity by creating shear at different planes, we will obtain dissimilar values of "viscosity".[1] For such anisotropic liquids, it appears necessary to characterize their properties by a **tensor of viscosities**,[1] though practical determination of components of this tensor can appear a very complex problem.

In order to give an impression of the possible range of changes of viscosity for real liquids let us list some typical values:

Gases	*0.1 mPa·s*
Water (at 20°C)	*1 mPa·s*
Sulphuric acid	*30 mPa·s*
Lubricating oils	*0.1 - 3 Pa·s*
Glycerin	*2 Pa·s*
Oligomers	*10 mPas - 10 Pa·s*
Glues, paints	*1 - 200 Pa·s*
Melts of thermoplasts	*100 Pas - 100 kPa·s*
Rubbers and rubber compounds	*10 kPas - 10 MPa·s*
Bitumens	*100 kPas - 100 MPa·s*
Melted inorganic glasses	*1 MPas - 100 GPa·s*
Glassy liquids	*100 GPa·s*

The viscosity of liquids can vary in a wide range of values exceeding 15 decimal orders.

5.3 NON-NEWTONIAN LIQUIDS

According to the discussion in Chapter 4, any viscous liquid is a medium for which intensity of heat dissipation in deformation is expressed as a function of kinematic and/or dynamic invariants. The simplest equation representing the idea is the Newton Law written as Eq 5.3. Certainly this equation does not describe other effects characteristic for non-Newtonian liquids.

The formal way of generalization was proposed by Rivlin[2,3] who advanced the idea that intensity of energy dissipation is a linear function of the second and third invariant of the deformation rate tensor. This assumption can be written as

$$A = -4\eta D_2 + \eta_c D_3 \tag{5.7}$$

where the first member is Newtonian input to stress tensor and the second one is a non-Newtonian addition. The coefficient of proportionality, η_c, is called "cross-viscosity".

The dissipative function (Eq 5.5), describing behavior of the **Reiner liquid**, predicts the existence of normal stresses (Weissenberg effect) as a second-order phenomenon (normal stresses are proportional to the squared shear rate) but no other special rheological effects, including non-Newtonian viscosity. Moreover, the predicted sign of a normal stress is opposite to experimentally observed values. It is important to emphasize that in the Reiner liquid, normal stress appears for pure viscous medium (stored elastic energy is absent) but is not related to rubbery elasticity of a material. It also contradicts the experimental evidence, because we know that normal stresses always accompany, or are accompanied by large elastic deformations.

The model of the linear Reiner liquid does not reflect the mechanical behavior of any real material known to date; nevertheless, this model is very interesting for two reasons: firstly, it shows the rigorous way of generalizing a rheological equation of state through introducing different invariants of the kinematic tensor; secondly, it shows that not every formal way of constructing rheological equations of state leads to realistic results. Bearing this conclusion in mind, the Reiner viscous liquid model mostly has historical relevance.

Development of ideas concerning construction of rheological models of non-Newtonian behavior takes various routes. First of all, the third invariant was not used as an argument in rheological equations of state. Then the second invariant of the rate of deformation tensor was used as an argument for a scalar material constant, identifying properties of a material. It reflects the idea that deformation influences the inherent properties of a medium, and this is the reason for non-Newtonian behavior.

For one-dimensional deformation, this concept can be written in the following form

$$\sigma_{ij} = 2\eta(D_2)\dot{\gamma}_{ij} \qquad [5.8]$$

According to this equation, we assume that rate of deformation (expressed through its second invariant) influences apparent viscosity of a liquid. The form of the function $\eta(D_2)$ can vary, depending on individual properties of material.

Certainly, this equation can be treated as a generalization of Eq 5.3, and in this case, it is written as

$$A = -4\eta(D_2)D_2 \qquad [5.9]$$

One of the most popular (widely used for various applied calculations) models of non-Newtonian flow is a **power law**, written as

$$\sigma = K\dot{\gamma}^n$$

Apparent viscosity in this model is a decreasing function of shear rate or shear stress

$$\eta = \frac{\sigma}{\dot{\gamma}} = K\dot{\gamma}^{n-1} = K\frac{1}{n}\sigma^{\frac{n-1}{n}} \qquad [5.10]$$

and as a rule n < 1. A generalized (three-dimensional) form of the power law takes the following form

$$\sigma_{ij} = 2K\left(\frac{1}{2}D_2^{\frac{n-1}{n}}\right)\dot{\gamma}_{ij} \qquad [5.11]$$

For one-dimensional shear flow this equation can be written as

$$\sigma = K\dot{\gamma}^{n-1}\dot{\gamma}$$

where apparent viscosity is expressed as in Eq 7.10.

Eq 5.10 can be applied to unidimensional axial extension of a liquid cylindrical stream. In this case, components of the rate of deformation tensor are

$$\dot{\gamma}_{11} = \dot{\lambda};\ \dot{\gamma}_{22} = \dot{\gamma}_{33} = -\frac{1}{2}\dot{\lambda};\ \dot{\gamma}_{ij} = 0 \text{ for } i \neq j$$

where the first component of the rate of deformation tensor is the rate of extension. The D_2 can be found from equation

$$D_2 = -\frac{3}{4}\dot{\lambda}^2$$

Let us suppose that, as usual, apparent viscosity is a decreasing function of shear rate (and of D_2). It means that in a three-dimensional generalization of the power law, one may expect that the function $\eta(D_2)$, as the invariant characteristic of a material, must be decreasing as well. This leads to the conclusion that the increase of rate of extensional deformation must cause the decrease in apparent viscosity, measured in uniaxial extension. Moreover, one can see that if we take the condition between shear and extensional rate of deformation as

$$\dot{\lambda} = \frac{1}{\sqrt{3}}\dot{\gamma}$$

we arrive at the Trouton Law, which becomes true for any viscous liquid at appropriate condition of comparison between shear and extension.

On the other hand, we know that for many “rheological” liquids the Trouton Law is not correct, which is apparently not related to non-Newtonian behavior of a purely viscous liquid but is hidden in its other rheological properties, in fact, in its elasticity. The divergence from the Trouton Law in properties of some liquids demonstrates that the possibility of describing properties of a liquid by equation in one geometrical mode of deformation does not automatically lead to correctness of its three-dimensional generalization and its application to another mode of deformation. Indeed, viscous properties of two liquids can be the same in shear but quite different in uniaxial extension.

5.4 VISCO-PLASTIC LIQUIDS

Rheological equation of state for a visco-plastic liquid was introduced in Chapter 4. One-dimensional rheological properties of a **Bingham visco-plastic medium** are expressed by Eq 4.7. The main problem in generalization of the Bingham equation is the formulation of a three-dimensional **criterion of yielding**. This problem is typical in finding the three-dimensional criterion of strength in mechanics of rupture of solids or plasticity for solid plastic materials. The common question is: how to write the condition of rupture in a complicated (three-dimensional) scheme of loading, if the strength of material was measured in unidimensional extension.

Certainly, the answer to both analogous questions (regarding the strength and the yield stress) lies in the use of invariants of the stress tensor, and this criterion must be formulated through invariants of the stress tensor.

As a general rule, the influence of the hydrostatic pressure (or the first invariant of the stress tensor) is immaterial in a rheological problem, if pressure is not very high. This fact has been already mentioned in discussion of the Weissenberg effect in Chapter 4. The criterion of yielding for different main stresses must be found, and the yield stress, σ_{yE}, should be a function of the second invariant of the stress tensor. This approach is equivalent to the one used in the theories of strength of solids. Moreover, the main analytical approximations used in these theories also are used for the yield stress.

Different conditions (criteria) of the threshold of yielding (strength, plasticity) in multi-dimensional loading were proposed and used. The most popular and simple equation for the yield stress is based on the old idea which determines the meaning of the critical value of the maximal shear stress (the **Treska - Saint-Venant criterion**). It assumes that if the yield stress in simple shear is σ_{yE}, the same material being stretched in one direction begins to flow at normal stress, σ_E, calculated as (see relationships between normal and shear stresses in Chapter 2):

$$\sigma_E = 2\sigma_{yE}; \quad \sigma_{yE} = 0.5\sigma_E \qquad [5.12]$$

Then, if the principle stresses in a multi-dimensional stress field are σ_1, σ_2, and σ_3, the Treska - Saint-Venant criterion of yielding is given by

$$\frac{|\sigma_1 - \sigma_2|}{2} \le \sigma_{yE};\ \frac{|\sigma_1 - \sigma_3|}{2} \le \sigma_{yE};\ \frac{|\sigma_2 - \sigma_3|}{2} \le \sigma_{yE}$$

An alternative approach used for determination of the threshold of yielding is known as the **von Mises criterion** and is assumed as a condition of reaching some critical value of the intensity of shear stresses. It is formulated through principle stresses as

$$(\sigma_1 - \sigma_2)^2 + (\sigma_1 - \sigma_3)^2 + (\sigma_2 - \sigma_3) = 2\sigma_{yE}^2 \qquad [5.13]$$

where σ_E is the yield stress in uniaxial extension.

It is interesting to note that the von Mises criterion of yielding can be called an energetic criterion, because it is possible to show that the left side of Eq 5.13 represents (for the Hookean solid) specific energy of elastic deformation required to change the form of a body (calculated for a point). It means that the material begins to flow when it has stored a critical amount of elastic energy while changing its form (not volume, since we do not take into account the first invariant of the stress tensor).

The correspondence between the shear yield stress and the critical normal stress, according to the von Mises criterion, can be written as

$$\sigma_{yE} = \frac{\sigma_E}{\sqrt{3}} \approx 0.577\sigma_E \qquad [5.14]$$

Comparing Eqs 5.12 and 5.14, one can see that Treska - Saint-Venant and von Mises criteria are rather close to each other.

5.5 SOME BASIC PROBLEMS

5.5.1 INTRODUCTION

Some basic problems of hydrodynamics are discussed below in order to demonstrate typical examples of application of rheological equations of state for main types of “rheological” liquids. The term “**hydro**dynamic” should not lead to confusion. Use of this term does not imply that it is related specifically to water (“hydro-”) but to any viscous fluid.

The transition from rheological equation of state (or constitutive equation) of a liquid to a hydrodynamic problem is equivalent to the transition from discussing the situation "at a point" to considering flow of a liquid in a volume. It requires one to combine the following elements:

- rheological equation of state (see Chapter 4)
- equilibrium (balance) equations (see Chapter 2); in the isothermal case, it is an equation of force balance only
- boundary conditions.

The last element is yet to be defined. The use of *boundary conditions* is very typical and common for solving any differential equation. Below, we shall demonstrate the importance of this factor for hydrodynamic problem-solving in a volume.

In the subsequent sections, we shall discuss basic hydrodynamic patterns which are most frequently observed in applications. Real situations can be very complex; at the same time, they can be expressed by relatively simple models.

The choice of examples discussed below is determined by the possibility to integrate differential equations of flow to obtain a solution in analytical form. It is done only for illustrative purposes, because equations of flow for practically any geometrical pattern (even very complex) can be solved numerically, with desirable accuracy, by computer calculations. This is also true for different rheological equations of state which are used for investigation of various hydrodynamic situations. In this respect the majority of solutions discussed below are exact solutions, contrary to their solutions obtained by computational methods, which are approximate solutions, even though their divergence from an exact solution can be as small as required.

All examples discussed in this Section are related to laminar flow and are not applicable to turbulent flow. Meanwhile, turbulence can be considered as non-Newtonian ("rheological") flow of some special kind, because in a turbulent regime the Newton-Stokes relationship between shear stress and shear rate is not valid, and as a consequence, for example, the relationship between flow rate and pressure in flow through a channel appears to be different than predicted for a Newtonian liquid.

The **solution** of different hydrodynamic problems includes understanding of:

- distribution of hydrostatic pressure and components of the velocity vector in space in which flow takes place; four variables are functions of four basic hydrodynamic equations (three balance equations and an equation of conservation of mass)

- integral characteristics of stream, such as complete force applied to a moving body, output (or flow rate) of a liquid flowing through a channel, and pressure which must be applied to create predetermined flow rate.

Flow in different geometrical forms is used for numerous applications. Among them are:

- problems of transportation of different liquids (so-called **inner problems** - flow of liquids inside channels with solid external boundaries)
- movement of solid bodies in liquids (so-called **outer problems** - a liquid flow around solid boundaries)
- purely rheological problems, such as comparison of theoretical predictions with experimental observations (cannot be solved "at a point" but only for volumetric flow) or determination of constants in rheological equations of state.

First, two items on the list can be formulated for any space situation and arbitrary geometry of solid boundaries of a channel or moving solid body, because they are determined by the practical value of the situation under discussion. The problems of the third group are considered, as a general rule, for rather simple geometrical forms of solid boundaries, because only for such simple forms is it possible to build an apparatus for comparison of theoretical prediction and experimental observation resulting in an evident and easy-to-grasp result.

5.5.2 PLANE UNIDIMENSIONAL FLOW

Figure 5.1 explains the example. Let us consider flow along the z-axis, then assume that the size of parallel planes in x-direction is unlimited (at least much larger than the distance between planes equal to H), which allows one to neglect all changes which can happen along the x-coordinate. It means in particular that

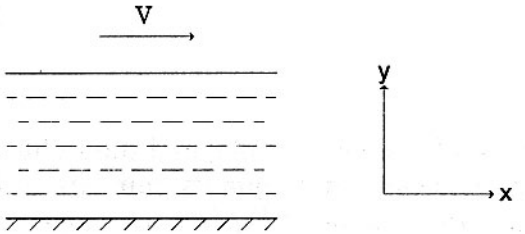

Figure 5.1. Scheme of plane unidimensional flow and system of coordinates used for formulating basic hydrodynamic equations.

$$V_x = 0; \quad \frac{\partial V}{\partial x} = 0; \quad \frac{\partial p}{\partial x} = 0$$

Besides

$$\frac{\partial V}{\partial z} = 0; \quad \frac{\partial p}{\partial y} = 0$$

This shows that there is only one component of velocity, V_z, different from zero (therefore, below we shall use the symbol V without subscript index). V can be a function of the y-coordinate only. Pressure can be a function of the z-coordinate only, i.e.,

$$V = V(y); \quad p = p(z)$$

Steady flow is considered, and therefore any inertial effect does not need to be taken into account and inertial members in the equilibrium equations can be omitted.

Consequently, there is a need for only one balance equation:

$$\frac{dp}{dz} = -\frac{d\sigma}{dy} \tag{5.15}$$

where

$$\sigma \equiv \sigma_{yz} = \sigma_{zy}$$

The left-hand side of this equation is a function of z only, and the right-hand side member is a function of y only. It means that equality can exist if both members are constant. Then, the general solution of Eq 5.15, considering the boundary conditions, can be written as

$$\sigma = \sigma_w - \frac{dp}{dz} y \tag{5.16}$$

where σ_w is the shear stress acting (or applied) at the solid boundary (at the plane). If the area of planes is S and total tangential force F, then

$$\sigma_w = \frac{F}{S}$$

It is important to emphasize that the general solution (Eq 5.16) is not related to any rheological model, i.e., it is valid for any material. It is true because as long as stress, but not velocity distribution, is discussed, it does not involve any rheological equation of state.

The last general postulate should include the gradient of pressure. Assuming that

$$\frac{dp}{dz} = \text{const}$$

one can write

$$\frac{dp}{dz} = \frac{\Delta P}{L}$$

where ΔP is the pressure drop (difference of pressures at the ends) in a channel where flow takes place, and L is the length of this channel.

(i) Drag flow. The important case of Eq 5.16 includes flow in the absence of a pressure gradient: $dp/dz = 0$, when

$$\sigma = \sigma_w = \text{const}$$

In this case, shear stress is uniform throughout the whole volume between planes, regardless of rheological properties of a liquid. This type of flow is possible when one plane is moved relative to the other and “drags” a liquid. This type of behavior is called **drag flow**. Because shear stress is constant throughout a gap between planes, the shear rate must be also constant (in steady flow), since, for any non-Newtonian liquid, shear rate is an unambiguous function of shear stress

$$\frac{dV}{dt} = \text{const}$$

which gives a linear velocity profile through a gap between planes:

$$V = V_w \frac{y}{H}$$

where V_w is the velocity of a moving plane (velocity of the other plane is assumed to be equal zero).

The last equation can be rewritten in dimensionless form

$$\frac{V}{V_z} = \beta \qquad [5.17]$$

where β is a dimensionless coordinate

$$\beta = \frac{y}{H}$$

The solution (Eq 5.17) is represented in Figure 5.2. The presence of linear velocity profile and constant shear rate in the gap is evident. Constant shear stress leads to a constant rate of shear. The volumetric output, Q, in drag flow is calculated as

$$Q = \frac{V_w}{2} BH \qquad [5.18]$$

where B is the size of planes in the x-direction.

The possibility to realize flow with constant shear stress is an unique method of constructing flow curves. Varying shear stress (changing total force), the shear rate is determined by the ratio

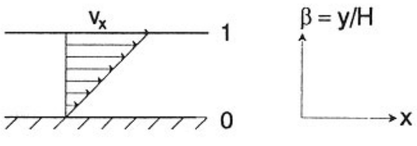

Figure 5.2. Velocity profiles in flow between two parallel planes without pressure gradient.

$$\dot{\gamma} = \frac{V_w}{H} \qquad [5.19]$$

Then, the pairs of values "shear stress - shear rate" are obtained.

The experiment can be reversed: we can set velocity, V_w, of a moving plane, measure total force, F, and calculate shear stress as the ratio of F/S.

In practical realization, it is not necessary to have flat planes; they can be curved into cylinders. Circular drag flow between two coaxial cylinders was investigated by Couette,[1] and thus the problem is called the **Couette problem**. Also, other drag flows (not only circular) are often called the Couette problem. If the gap between two coaxial cylinders is much smaller than their radii, one can neglect their curvature and treat them as parallel plates.

Let the radius of the outer cylinder be R_o, the radius of the inner cylinder R_i, and the condition

$$\frac{R_o - R_i}{R_o} << 1 \qquad [5.20]$$

is fulfilled. The system of two coaxial cylinders is then treated as parallel planes

$$H = R_o - R_i\,; \quad S = 2\pi \frac{R_o + R_i}{2} L$$

where L is the height of the cylinders.

Linear velocity is expressed as

$$V = \omega R$$

where ωis angular velocity (measured in rad/s), R is the radius of an outer or inner cylinder which are almost the same if the condition 5.20 is valid.

The shear rate in the gap is

$$\dot{\gamma} = \frac{\omega R}{R_o - R_i} \qquad [5.21]$$

The existence of shear stresses leads to torque, M, expressed as

$$M = 2\pi R_o^2 H\sigma_o = 2\pi R_i^2 H\sigma_i \tag{5.22}$$

where H is the height of cylinders (more exact: height of a gap filled with flowing liquid).

The last equation allows one to estimate the inhomogeneity of stress field in the gap between two coaxial cylinders. Since M = const,

$$\frac{\sigma_i}{\sigma_o} = \left(\frac{R_o}{R_i}\right)^2 \equiv \alpha$$

If R_o/R_i is close to 1, then we have an "almost" homogeneous stress field.

This configuration is often used in viscometric practice in so-called rotational viscometers. The most important point here is the possibility to find shear stress and shear rate independently and regardless of any rheological model, i.e., this configuration can be treated as an absolute method of determining a flow curve of a non-Newtonian liquid with unknown rheological properties. Certainly, this method works when the condition 5.20 is fulfilled. If we know shear stress from the torque (Eq 5.22) and shear rate from angular velocity (Eq 5.21), we can easily find apparent viscosity in accordance with the Newton-Stokes definition of "viscosity":

$$\eta \equiv \frac{\sigma}{\dot{\gamma}} = \frac{M(R_o - R_I)}{2\pi R_o^3 H\omega} \tag{5.23}$$

where it is assumed that an outer cylinder is rotating and M is the torque measured also for an outer cylinder. Changes in Eq 5.23 must be introduced if an inner cylinder is rotating, or if we measure the torque applied to an inner cylinder.

If the gap between cylinders is not small in relation to the radius of the inner cylinder, the general solution for a liquid with arbitrary rheological properties does not exist. Indeed, velocity distribution in circular flow between two coaxial cylinders with an arbitrary (not an obligatory small) gap between them depends on rheological properties of a liquid. The exact solutions can be found for some shear rate versus shear stress laws. The simplest case is surely a Newtonian liquid. In this case, when an outer cylinder is rotating with angular velocity, ω_o, and angular velocity of an inner cylinder is ω_i, velocity distribution is expressed by a formula

$$V(r) = \frac{(\omega_o R_o^2 - \omega_i R_i^2)r^2 + (\omega_o - \omega_i)R_i^2 R_o^2}{(R_o^2 - r_i^2)r} \qquad [5.24]$$

where V is the V_φ (circular) component of the velocity vector and r is a current radius ($R_o > r > R_i$). Special cases, when $\omega_o = 0$ or $\omega_i = 0$, are formally included in Eq 5.24.

The distribution of shear stress is

$$\sigma = \frac{2\eta(\omega_o - \omega_i)R_o^2 R_i^2}{(R_o^2 - R_i^2)r^2} \qquad [5.25]$$

where η is viscosity of a Newtonian liquid.

The torque in flow of a Newtonian liquid is expressed as

$$M = \frac{4\pi\eta L(\omega_o - \omega_i)R_i^2 R_o^2}{R_o^2 - R_i^2} \qquad [5.26]$$

The torque is the same for any value of radius, which is why the current radius, r, does not enter Eq 5.26.

Eq 5.26 is the basic equation for determination of viscosity of Newtonian liquids. If two parameters, torque, M, and difference of angular velocities, $\omega_o - \omega_i$, are measured (in practice, as a general rule, one of the velocities equals zero), viscosity can be calculated as a measure of the ratio of these parameters:

$$\eta = \frac{KM}{\omega_o - \omega_i} \qquad [5.27]$$

where K is a geometrical factor, i.e., the value determined by geometrical sizes of an instrument used for measurement. In a cylinder - cylinder rotational viscometer

$$K = \frac{R_o^2 - R_i^2}{4\pi H R_i^2 R_o^2}$$

When a rotational viscometer is used as an instrument for absolute measurements, the value of a geometrical factor, K, is found from the sizes of instrument elements. If this apparatus is used for comparative measurement, the value of K is found from a calibration experiment in which the torque and angular velocity are measured for a liquid with known viscosity. Then Eq 5.27 is used in order to find the K-value for the instrument.

The rotation of a cylinder in an infinite volume is an interesting limiting case ($R_o \therefore \chi 4 \infty$). Velocity distribution in flow of a Newtonian liquid in an infinite volume is expressed by the equation

$$V = \frac{\omega R^2}{r} \qquad [5.28]$$

where $\omega$is an angular velocity of cylinder rotation, R a radius of cylinder, and r a current radius (distance from the axis of a rotating cylinder). Eq 5.28 shows that velocity decreases to zero "at infinity", i.e., sufficiently far from a rotating cylinder.

The torque applied to rotate a cylinder in an infinite volume is calculated according to the equation

$$M = 4\pi\eta\omega H R^2$$

Rotation of a cylinder in an unlimited volume is a model case used in many real situations when a size of a rotating body is much smaller than the size of a sample (for example, rotation of a screw propeller in a sea).

Numerous experiments were carried out to confirm theoretical predictions on the relationship of torque, rate of rotation, and geometrical sizes of rotating bodies. All of them demonstrated good correlation between theory and experimental results in limits of a laminar flow. It proves the basic assumptions used in building the theory, and in particular, the validity of the Newton-Stokes rheological equation for many real liquids.

It is interesting to investigate the situation when a gap between cylinders is filled with visco-plastic liquid. Let the shear stress at an inner cylinder be calculated in usual manner as

$$\sigma_i = \frac{M}{2\pi R_i H} \qquad [5.29]$$

and shear stress at an outer cylinder is

$$\sigma_o = \sigma_i \alpha^{-1}$$

It is evident that

$$\sigma_o < \sigma_i$$

The whole volume of a material flows if

$$\sigma_o > \sigma_y$$

i.e., stress at any point of a material exceeds the yield point. If this condition is not valid, we have a situation when a solid (non-fluid) layer exists near an outer cylinder (up to the value of a radius where shear stress becomes equal to yield stress), and this solid layer rotates together with an outer cylinder.

(ii) Flow under pressure. Let us assume that both boundary surfaces are motionless and flow between planes along the y-axis is provoked by the pressure gradient gradP = ΔP/L. The shear stress profile is given by Eq 5.16, which can be written as

$$\sigma = \sigma_w - \frac{\Delta P}{L} y \qquad [5.30]$$

It is convenient to draw a coordinate system in such a manner that the plane y = 0 would coincide with a middle section of a gap (plane of symmetry). Then coordinates of the boundary parallel planes are +H/2 and -H/2. It is easy to understand that the flow through a channel is symmetrical and

$$\frac{dv}{dy} = 0 \quad \text{at } y = 0$$

i.e., the velocity profile has a maximum at the middle plane (or at y = 0). If dV/dy = 0, then shear stress also equals zero, which means that

$$\sigma_w = \frac{\Delta P}{L} \qquad [5.31]$$

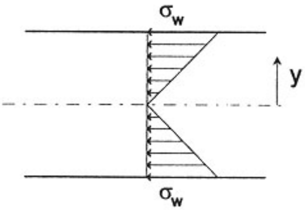

Figure 5.3. Profile of shear stresses in flow between two parallel planes under pressure gradient.

The shear stresses, shown in Figure 5.3, have a linear profile. The shear stress is zero at the axis of a stream, and maximal at the wall, as calculated from Eq 5.31.

The last two conclusions (existence of the maximum in velocity profile at the axis of a stream and linear profile of shear stresses) are valid for any liquid. The velocity profile must be different because linear change in shear stress leads to linear change of shear rate only for a Newtonian liquid; in all other cases, velocity profiles for "rheological" liquids will be non-linear.

Figure 5.4 demonstrates three typical situations:

- velocity profiles for Newtonian liquid (a)
- non-Newtonian liquid (b)
- visco-plastic liquid (c).

The first case (flow of a Newtonian liquid) is the simplest case. The linear profile of stress is automatically reflected by a linear profile of shear rate and thus a parabolic profile of velocity. It looks like this:

$$V(y) = -\frac{H^2}{8\eta}\frac{\Delta P}{L}\left[1-(2\beta)^2\right] \qquad [5.32]$$

The "minus" sign before the right-hand side of this equation shows that flow occurs in a direction opposite to the gradient of pressure, and β is a dimensionless distance from the axis of a channel: β = y/H.

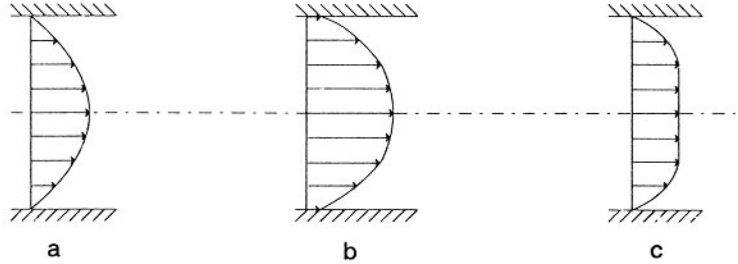

Figure 5.4. Velocity profiles for Newtonian (a), non-Newtonian (b), and visco-plastic (c) liquids in flow under pressure.

The volumetric output in the flow of a Newtonian liquid under a pressure gradient is expressed in the following manner:

$$Q = -\frac{BH^3}{12\eta}\frac{\Delta P}{L} \qquad [5.33]$$

Shear rate profile and the value of the shear rate at the wall (maximal shear rate) can be calculated as often required in applications, especially in the theory of viscometry:

$$\dot{\gamma}_o = \frac{6Q}{BH^2} \qquad [5.34]$$

It is useful to introduce a value of the average velocity, V_o, determined as

$$V_o = \frac{Q}{BH}$$

i.e., volumetric output divided by the area of the cross-section. Then

$$V_o = -\frac{H^2}{12\eta}\frac{\Delta P}{L}$$

It is interesting to note that the maximal velocity at the axis of a channel, V_{max}, equals

$$V_{max} = \frac{3}{2}V_o$$

Now, we can write the equation for the velocity distribution in a dimensionless form

$$V^* \equiv \frac{V}{V_o} = \frac{3}{2}[1-(2\beta)^2] \qquad [5.35]$$

where V^* is dimensionless velocity.

Finally, if pressure, which must be created to produce some average velocity of a stream in a plane tube of the length, L, is of interest, it can be calculated as

$$\Delta P = 12\eta V_o \frac{L}{H^2} \qquad [5.36]$$

Let us carry out a similar analysis for non-Newtonian liquids. First of all, we can see that non-linear relationship between shear stress and shear rate results in the rate of shear profile, though its value at the axis is zero as before. Then the velocity profile becomes non-parabolic (but with the maximum at the axis of a stream).

Let us assume that the rheological properties of a liquid are expressed by a power law often used in the theory of polymer processing. This relationship can be written as follows

$$\sigma = K\left|\frac{dV}{dy}\right|^{n-1} \frac{dV}{dy}$$

where K and n are constants of the rheological equation and the segment written before rate of shear can be treated as apparent viscosity depending on shear rate.

Such "power" liquid velocity profile is expressed by the equation

$$V(y) = \frac{n}{n+1}\left(\frac{|\Delta P|}{KL}\right)^{\frac{1}{n}}\left(\frac{H}{2}\right)^{\frac{n+1}{n}}\left(1-2\beta^{\frac{n+1}{n}}\right) \qquad [5.37]$$

where $\beta = y/H$ as before.

Maximal velocity (at the axis of a channel) is

$$V_{max} = \frac{n}{n+1}\left(\frac{H}{2}\right)^{\frac{n+1}{n}}\left(\frac{|\Delta P|}{KL}\right)^{\frac{1}{n}}$$

and it is easy to find an average velocity

$$V_o = \frac{1+n}{1+2n}V_{max}$$

For n = 1, these relationships take the form of the above-written expressions for a Newtonian liquid; therefore, the rheological effects cause modification in the velocity profile, with all the evident consequences of this phenomenon.

Shear rate profile is easily calculated as a derivative of velocity. Two points are of particular interest. The first is the zero value at the axis, although it does not give useful information, because shear stress is also zero, giving a quite trivial relationship between these variables. The second point is much more interesting. It is a point at the wall. We can calculate shear stress at this point according to Eq 5.31 to find shear rate at the wall as

$$\dot{\gamma}_w = \frac{2(2n+1)Q}{nBH^2} \qquad [5.38]$$

Shear rate at a wall, in flow of a "power" liquid, can be expressed through the corresponding value of a Newtonian liquid

$$\dot{\gamma}_w = \frac{2n+1}{3n}\dot{\gamma}_o$$

where the value $\dot{\gamma}_o$ is calculated from Eq 5.34.

It is then possible to construct a flow curve "point-by-point", changing volumetric output or pressure gradient and thus changing shear rate and shear stress.

The relationship between pressure drop and volumetric output in flow of a "power" liquid is given by:

$$\Delta P = 2^{n+1} LB \left(\frac{2n+1}{n} \right)^n K \frac{Q^n}{H^{2n+1}} \tag{5.39}$$

It is evident that the last equation can be written as

$$\Delta P = K_n Q^n \tag{5.40}$$

where K_n is the geometrical factor which is evidently calculated as

$$K_n = 2^{n+1} \left(\frac{2n+1}{n} \right)^n \frac{LB}{H^{2n+1}}$$

It is worth mentioning that the power-type relationship between pressure gradient and volume output reflects the power law for the relationship between shear stress and shear rate. For the Newtonian liquid, the same relationship is also true and n = 1, i.e., the linear relationship exists between volume output and pressure gradient.

Let us now discuss the main peculiarities of flow of visco-plastic liquid in a plane channel under pressure. If the shear stress at the wall, calculated from Eq 5.31, is lower than the yield stress, no movement through a channel occurs, and the material behaves like a solid body. If shear stress at the wall and layers near the wall exceed the yield point, then flow becomes possible in this layer but not in the central zone of a channel, and the velocity profile appears as shown in Figure 5.4c.

(iii) Superposition. In some applications (for example, in theoretical analysis of processing of polymeric materials in extruders), it is important to understand velocity profiles, when flow is generated by superposition of drag due to the movement of a boundary plane and pressure gradient, and observe superposition of effects discussed above.

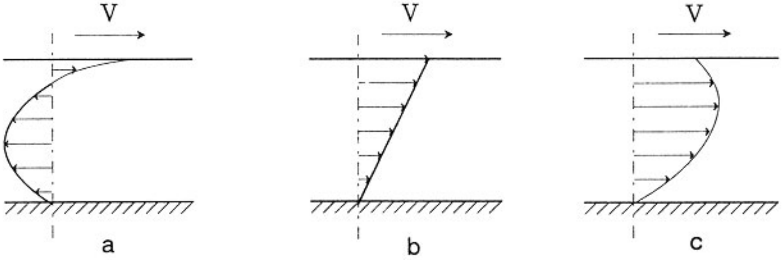

Figure 5.5. Velocity profiles in flow of a Newtonian liquid between two parallel planes when there is superposition of drag and flow under pressure: (a) exit closed; (b) pure drag flow; (c) superposition of drag and pressure flow.

The general picture, illustrating velocity profiles, is shown in Figure 5.5. The middle picture shows a pure drag flow. The left picture illustrates a very interesting situation when an exit is closed so that the net output is zero. In this case, the areas between velocity profile and a vertical (zero) line are equal on positive and negative sides. It means that output created by drag of a boundary plane is compensated by negative (or "back") flow under pressure. The right picture represents typical superposition of drag and pressure streams oriented in the same direction. The existence of the drag component of flow is proven by the non-zero value of velocity at the upper boundary plane.

Now, let us analyze an analytical expression for velocity profiles in superposition of drag and pressure flow. Such analysis is easy for a Newtonian liquid because we can simply summarize velocity profiles for both components of a stream. The result of calculations in dimensionless variables is as follows:

$$\frac{V(y)}{V_w} = \frac{\beta - 3\beta(1-\beta)H^3}{6\eta V_w}\frac{\Delta P}{L} \qquad [5.41]$$

where $\beta = y/H$ is a dimensionless coordinate, as before.

It is quite evident that Eq 5.41 contains two members. The first is a reflection of drag flow, and the second represents flow under a pressure gradient. The same is true for integral characteristics of flow, i.e., volumetric output:

$$Q = \frac{V_w H}{2} - \frac{H^3}{12\eta}\frac{\Delta P}{L} \qquad [5.42]$$

(the width of a channel, B, is omitted from both members of Eq 5.42).

Again, we see that volume output consists of two components: the first is related to drag flow, and the second originates from existence of a pressure gradient along a channel.

It is especially interesting to separate the case of zero output represented by the left picture in Figure 5.5. If Q = 0, we can calculate the pressure created by a movement of a boundary plane. This pressure is

$$\Delta P = \frac{6V_w \eta}{H^2} L$$

The structure of this equation demonstrates that the pressure created is proportional to the viscosity of a liquid (i.e., high pressures can appear only for highly viscous liquids) and velocity of a moving boundary plane.

We can introduce a value of volume output due to pressure gradient, Q_P, and volume output due to drag, Q_D. Then, a dimensionless ratio is a measure of mutual inputs of pressure and drag:

$$\xi \equiv \frac{Q_P}{Q_D} = \frac{H^2}{6\eta V_w}\frac{\Delta P}{L} \qquad [5.43]$$

Two particular cases are of primary interest:

at $\xi = -1$, output is zero (the exit is closed)
at $\xi = 0$, there is a pure drag flow and pressure gradient is absent.

All other cases reflect superposition of both factors and their relative “weight” is determined by the value of ξ.

If a flowing liquid is characterized by non-Newtonian properties, the general physical idea of superposition of drag and pressure flow remains valid. Moreover, characteristic pictures drawn in Figure 5.5 are also valid. That is why in discussion of Figure 5.5 we did not mention what “rheological” kind of a liquid it represents. Depending on rheological character of liquid, the analytical expressions for velocity profiles and output must be modified. Besides, the method of calculation of net output, as an arithmetic sum of drag and pressure outputs calculated separately, which has been used above, may become invalid. There is no simple method for calculating inputs of both components. It appears necessary to solve the balance equations for any new type of rheological liquid and analyze a solution on an individual basis. Such solutions are not of general value, which is the main point in discussion of superposition of drag and pressure flow of non-Newtonian liquids.

5.5.3 FLOW THROUGH STRAIGHT TUBES UNDER PRESSURE

Flow through a straight channel (tube), with arbitrarily chosen cross-section, under pressure gradient, is a classical hydrodynamic problem. It is often called the **Poisseuille problem**, though Poisseuille himself studied flow in channels with round cross-section only. The importance of this problem is determined by the fact that flow in straight tubes is a very realistic model for numerous applications, such as transport of oil and oil products, pumping water in city networks, and many others.

The example of flow through straight tubes under a pressure gradient has been already discussed in the case of flow between two parallel plates (Figure 5.4).This discussion concentrates on the situation when the cross-section of a tube is circular with a radius, R.

We can immediately state that the relationship between pressure gradient and volume output is expressed by Eq 5.40 and for a Newtonian liquid (n = 1)

$$Q = K|\Delta P|$$

The value of the geometrical factor, K, depends on the form of a cross-section of a channel. In flow of a Newtonian liquid through a channel, with a round cross-section, the geometrical factor is

$$K = \frac{\pi R^4}{8\eta L}$$

and the solution of the Poisseuille problem is the very well-known **Hagen-Poisseuille equation**:

$$Q = \frac{\pi R^4}{8\eta}\frac{|\Delta P|}{L} \qquad [5.44]$$

An equation for a velocity profile in the flow of a Newtonian liquid is given by

$$v(r) = \frac{1}{4\eta}\frac{\Delta P}{L}(R^2 - r^2) \qquad [5.45]$$

where r is a current radius.

The average velocity V_o is

$$V_o \equiv \frac{Q}{\pi R^2} = \frac{R^2}{8\eta}\frac{|\Delta P|}{L}$$

Since the pressure gradient is proportional to flow output, it is easy to write the velocity distribution along a radius through output:

$$v(r) = \frac{2Q}{\pi R^4}(R^2 - r^2)$$

The velocity profile is parabolic and the maximal velocity, V_{max}, at the axis of a tube is

$$V_{max} = \frac{\Delta P R^2}{4\eta L} = \frac{2Q}{\pi R^2} = 2V_o \qquad [5.46]$$

Velocity profile can be written in dimensionless form

$$\frac{v}{V_{max}} = \frac{v}{2V_o} = (1 - \beta^2)$$

where $\beta = r/R$ is a dimensionless radius of a tube.

The velocity profile is known and thus it is possible to calculate shear rate distribution along a radius. Two points are of particular interest. The first of them is quite evident: velocity profile is symmetrical and shear rate at the axis is zero. The second point is a position at the wall of a channel. The shear rate at the wall is

$$\dot{\gamma}_{w,N} = \frac{4Q}{\pi R^3} \qquad [5.47]$$

Shear stress distribution along a radius is the same as in a parallel plate configuration, i.e., linear:

$$\sigma = \frac{\Delta P}{2L}(R - r) = \sigma_w (1 - \beta) \qquad [5.48]$$

where σ_w is shear stress at the wall of a tube:

$$\sigma_w = \frac{\Delta PR}{2L} \qquad [5.49]$$

It is evident that the ratio of shear stress to shear rate calculated at the same point (at the wall of a channel) is indeed the viscosity based on Newton - Stokes definition:

$$\eta = \frac{\Delta PR^4}{8QL} \qquad [5.50]$$

In fact, Eq 5.50 is the Hagen - Poisseuille equation, which is widely used for measuring viscosity of various liquids determined from the ratio of pressure gradient to volume output if geometrical sizes of a channel (its radius and length) are known.

Linear relationship between output and pressure gradient, in flow of a Newtonian liquid through straight tubes, is of a general nature, only geometrical factor is varying. For example, if a cross section of a tube is not round but elliptical the geometrical factor is

$$K_{el} = \frac{1}{4\eta L}\frac{\pi a^3 b^3}{a^2 + b^2}$$

where a and b are semi-axes of an ellipsis.

It is quite natural that, if a = b the factor K_{el} becomes the geometrical factor for a round tube. It is also interesting that, if $a \to \infty$ and $b = H/2$, we arrive at the geometrical factor for flow of a Newtonian liquid between two parallel plates.

The next example is flow through a gap between two coaxial round tubes along the axis. Let the radii of the tubes be R_o for an outer tube and R_i for an inner tube and $\beta = R_i/R_o$. The geometrical factor for a Newtonian liquid, in this case, is

$$K_c = \frac{\pi R_o^4}{8\eta L}\left[(1-\beta^4) - \frac{(1-\beta^2)^2}{\ln(1/\beta)}\right]$$

Again, we arrive at the boundary cases: if $R_i = 0$, we return to the flow through a tube with a round cross-section. And if the gap is very narrow and $\beta \to 1$, we arrive at flow between two parallel plates.

The geometrical factors are also calculated and their analytical forms are known for channels with different regular cross-sections, for example for rectangular or triangle channel, for a channel formed by two round tubes with shifted axes, and so on. These solutions are represented by infinite sums of different structure and they will not be reproduced here only because they are too bulky. Moreover analytical expressions of geometrical factors can be obtained for a channel of an arbitrary cross-section without special problems by means of computer calculations. They also can be found experimentally for model or real channels.

The situation becomes more complicated for non-Newtonian liquids because the geometrical factor depends on the kind of a rheological equation of state used for calculation. As an example, let us discuss relationships for a "power" liquid bearing in mind that Eq 5.40 is always valid.

In flow of a "power" liquid through a straight channel with a round cross-section, we have the following velocity profile

$$v(r) = \frac{n}{n+1} R^{\frac{1+n}{n}} \left(\frac{\Delta P}{2L}\right)^{\frac{1}{n}} K^{\frac{1}{n}} \left[1-\left(\frac{r}{R}\right)^{\frac{1+n}{n}}\right]$$

Then,

$$V_{max} = \frac{n}{n+1} R^{\frac{1+n}{n}} K^{-\frac{1}{n}} \left(\frac{\Delta P}{2L}\right)^{\frac{1}{n}}$$

and the average velocity is related to the maximal velocity by

$$V_o = \frac{1+n}{3+n} V_{max}$$

If n = 1, the last equation transits to the above discussed equation for a Newtonian liquid. This is also true for all relationships obtained for a “power” liquid.

Volume output - vs - pressure gradient for a “power” liquid is calculated from the following equation:

$$Q = \frac{n}{1+3n} R^{\frac{1}{1+3n}} K^{-\frac{1}{n}} \left(\frac{\Delta P}{2L}\right)^{\frac{1}{n}}$$

The equation used in the theory of capillary viscometry is an expression for shear rate at the wall:

$$\dot{\gamma}_w = \frac{3+n}{4} \dot{\gamma}_{w,N} \qquad [5.51]$$

i.e., wall shear rate for a “power” liquid is related to the corresponding value calculated for a Newtonian liquid in accordance to Eq 5.47.

Apparent viscosity of a non-Newtonian liquid, η, can be found as a ratio of shear stress to shear rate at the same point - at the wall:

$$\eta = \frac{1}{2(3+n)} \frac{\Delta P}{L} \frac{\pi R^4}{Q} \qquad [5.52]$$

In the case of n = 1, this equation transits to the Hagen - Poisseuille equation and apparent viscosity is constant. For a non-Newtonian liquid, it is not true because apparent viscosity becomes shear rate or pressure dependent. In this case Eq 5.52 allows one to construct the flow curve, i.e., to find the dependence of apparent viscosity and shear rate, calculated by volume output, or shear stress, calculated from pressure gradient.

Analogous equations can be obtained for different non-Newtonian liquids but in real practice only “power” liquid flow curves are used for applications. In this case, Eq 5.40 is used as a basic equation, and the geometrical factors are calculated or found experimentally for channels of a different cross-section.

The other, very important case, thoroughly investigated by many authors, is a flow of visco-plastic, non-Newtonian liquid.

Let us write one-dimensional rheological equation of state of a visco-plastic liquid, similar to Chapter 4 (Eq 4.7), in the form

$$\dot{\gamma} = \frac{1}{\eta_p}(\sigma - \sigma_y)$$

which has correct meaning when $\sigma > \sigma_y$.

The flow of a visco-plastic liquid through a tube occurs only when shear stress at the wall (maximal shear stress existing in a material) exceeds the yield stress, i.e., when

$$\sigma_w > \sigma_y$$

If this condition is fulfilled, a flow occurs in a layer adjacent to wall. It is clear that, at an axis of a symmetrical tube, the shear stress is zero and there is central zone near the axis where stresses are always lower than the yield stress. It means that, in movement of a visco-plastic liquid through a tube, there is two-zone pattern: flowing layer near a wall and non-deformable plug-like zone around an axis. This pattern has been already shown in Figure 5.4c, and it is the same for any cross-section of a straight channel.

Volume output in movement of a visco-plastic liquid is a sum of two components - flow through a near-wall ring and plug movement at the central zone. The solution of the hydrodynamic problem for a visco-plastic liquid is known as the **Buckingham - Reiner equation**

$$Q = \frac{\pi R^4}{8\eta_p}\frac{\Delta P}{L}\left[1 - \frac{4}{3}\beta + \frac{1}{3}\beta^4\right] \qquad [5.53]$$

where

$$\beta = \frac{\sigma_w}{\sigma_y}$$

The equation is written in the form of the classical Hagen - Poisseuille equation (item in the front of the square brackets) and a correction term (inside the square brackets), which reflects the effect of plasticity.

If we have the movement of a visco-plastic liquid, under sufficiently high pressure gradient with developed flow zone, for example if $\beta < 0.5$, then it is possible to use the approximate form of Eq 5.53:

$$Q \approx \frac{\pi R^4}{8\eta_p}\left(1 - \frac{4}{3}\beta\right)$$

The structure of Eq 5.53 allows one to rewrite it with variables used for a Newtonian liquid using shear stress and shear rate values related to a wall:

$$\dot{\gamma}_{w,N} = \frac{\sigma_w}{\eta_p}\left[1 - \frac{4}{3}\beta + \frac{1}{3}\beta^4\right] \qquad [5.54]$$

where as before

$$\sigma_w = \frac{\Delta PR}{2L}; \quad \dot{\gamma}_{w,N} = \frac{\pi R^4}{8\eta_p}$$

Another form of the last equation for $\beta < 0.5$ is

$$\sigma_w = \frac{4}{3}\sigma_y + \eta_p\dot{\gamma}_{w,N}$$

If the real shear rate at a wall, in movement of a visco-plastic liquid, is to be found, it can be done using the following equation

$$\dot{\gamma}_{w,VP} = \dot{\gamma}_{w,N} - \frac{3(1-\beta)}{3 - 4\beta + \beta^4} \qquad [5.55]$$

Values of shear stress and shear rate measured at the same point (at a wall) can be used for constructing flow curves of visco-plastic liquids.

Many other solutions of different hydrodynamic problems are known for visco-plastic liquids. Their main feature is the existence of a non-deformable plug in a zone where stresses are lower than the yield stress in one-dimensional flows or its invariant analogue in multi-dimensional deformation pattern. Analytical solutions of these hydrodynamic problems are used for various applications related to practical use of such materials, for example transportation of greases through tubes or their work in bearings, designing pumping devices for paints, displacement of sealants, and so on.

5.5.4 PENETRATION OF A CYLINDER INTO A VISCOUS MEDIUM

The penetration of a symmetrical hard (solid) body into a viscous medium is a model of numerous real applications, for example, the technology of metal rolling, stamping of plastic materials, moving auger in a soil or oil layer, and so on.

It is possible to separate three main cases:

- flow of a liquid between two coaxial cylinders along their walls - Figure 5.6a
- penetration of a solid body into a vessel with a bottom - Figure 5.6b
- penetration of a solid body into an infinite ”sea" - Figure 5.6c.

The general similarity of all three cases is that they are all drag flows originating from the movement of solid borders. In this sense they are close to the drag flow discussed above. It is especially evident in the first case, because if the gap between cylinders is small we arrive at flow of a liquid between two parallel planes. However, if the gap is not small we meet with a new problem.

The velocity distribution in flow of a Newtonian liquid between two cylinders as in Figure 5.6c is described by the equation

$$v(r) = \frac{(V_i + V_o)\ln r / R_i}{\ln R_o / R_i} - V_i \qquad [5.56]$$

Certainly it is very easy to change this equation for changing directions of movement of both cylinders or to analyze the case when one of the cylinders is not moving (V_o or V_i is zero).

Let us discuss the situation shown in Figure 5.6b. In the general case, the shape of both bodies (a penetrating body and a vessel) can be quite arbitrary, i.e., radii of an inner cylinder, R_i, and an outer cylinder, R_o, are functions of the coordinate z, directed along the axis of cylinders: $R_i(z)$ and $R_o(z)$. Then, two cases are possible: a penetrating body has a sharp top or a flat bottom of the radius R. In

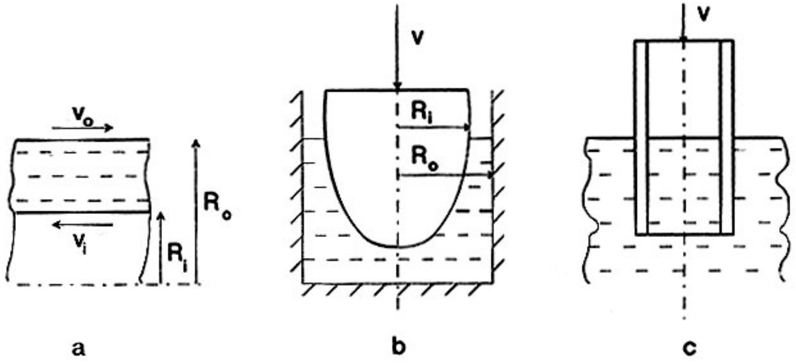

Figure 5.6. Different types of penetration of a cylinder into a liquid: (a) relative movement of two coaxial cylinders; (b) penetration of a cylinder into a vessel (both having arbitrary but symmetric shape); (c) penetration of a cylinder into an unlimited volume.

the latter case $R_i(z = 0) = R$.

The main parameter of interest in this problem is the resistance force F which must be applied in order to push a penetrating body into a viscous liquid. This value consists of two components:

- due to viscous friction along the side surface of a penetrating body, F_f; it can be found if we know shear stresses on the surface;
- due to pressure acting onto the penetrating body F_p; this value is also a sum of two components - pressure on the side surface of a penetrating body, $F_{p,1}$, and pressure acting on the flat bottom, $F_{p,2.}$ The first component is absent if R_i is constant, i.e., if a penetrating body is a straight cylinder of a constant radius, R. The second component is absent if a penetrating body has a sharp top and R = 0.

Let us assume that the gap between a penetrating body and an outer vessel is small, so we can treat the flow as uni-dimensional. The velocity of a movement of a penetrant is V and is assumed to be constant. At the initial moment, a penetrating body touches a surface, then it begins to sink into a liquid forcing a liquid up to a gap. The height of a layer is H, and the distance from the top of a penetrating body to the bottom of a vessel is l, both values are changing in time, proportional to sinking of a body into a liquid.

All conclusions concerning resistance force can be made if we know two characteristics of the flow - velocity and pressure distributions. Certainly both depend on rheological properties of a liquid. Let us analyze the problem for a Newtonian liquid.

The general solution for the velocity distribution in flow between cylinders is known. It looks rather bulky though, in fact, it is not too complicated:

$$V_z(r) = -V\frac{\ln r/R_o}{\ln R_i/R_o} + \frac{1}{4\eta}\frac{\partial p}{\partial z}\left[r^2 - \frac{R_i^2\ln r/R_o - R_o^2\ln r/R_i}{\ln R_i/R_o}\right] \qquad [5.57]$$

where r is a current radius.

The pressure gradient enters Eq 5.57 and it must be found independently. The pressure distribution is

$$p(z) = -4\eta V\int_H^z \frac{dz}{(R_o^2 + R_i^2)\ln R_o/R_i - (R_o^2 - R_i^2)} \qquad [5.58]$$

Now, we can calculate all components of the resistance force.

In order to find F_f, we need to know shear stresses at the solid surface. They are found from

$$\sigma = \eta\left|\frac{dv_z}{dr}\right|, \text{ at } r = R_i(z)$$

Then we can calculate shear friction component of resistance

$$F_f = 2\pi\eta V\int_0^H \frac{(R_o^2 - R_i^2)dz}{(R_o^2 + R_i^2)\ln R_o/R_i - (R_o^2 - R_i^2)} \qquad [5.59]$$

The integral can be easily calculated if both functions $R_i(z)$ and $R_o(z)$ are known, and they are known because in analysis of any real problem, the shape of a penetrating body and a vessel are known.

The component of the resistance, originated from pressure acting onto the side surface of a solid body $F_{p,1}$, is calculated as

$$F_{p,1} = 2\pi\int_0^H p(z)R_i(z)\frac{dR_i}{dz}dz \qquad [5.60]$$

where p(z) is pressure distribution given by Eq 5.58.

Certainly, it is seen that $F_{p,1} = 0$ if $dR_i(z)/dz = 0$, as has been mentioned above.

The component of the resistance, due to pressure acting on the bottom of a penetrating body is calculated as

$$F_{p,2} = \frac{3}{2}\pi\eta V\frac{R^4}{l^3} + 4\pi\eta VR^2\int_0^H \frac{dz}{(R_o^2 + R_i^2)\ln R_o \big/ R_i - (R_o^2 - R_i^2)} \qquad [5.61]$$

where R is a radius of a flat bottom.

If R = 0 (a penetrating body has a sharp top) this component of the resistance force is absent.

An interesting and important case is a narrow gap between two cylinders: $\delta = R_o - R_i << R_i$

In this case all above written formulas can be simplified and the approximate relationships are as follows.

Resistance due to shear friction force:

$$F_f \approx 6\pi\eta V\int_0^H \frac{R_i^2}{\delta^2}dz \qquad [5.62]$$

Resistance due to pressure on the side surface:

$$F_{p,1} \approx 12\pi\eta V\int_0^H\left[\int_0^H \frac{R_i dz}{\delta^3}\right]R_i\frac{dR_i}{dz}dz \qquad [5.63]$$

Resistance due to pressure on the bottom of a penetrating body:

$$F_{p,2} \approx \pi\eta V\left[\frac{3}{2}\frac{R^4}{l^3} + 6R^2\int_0^H \frac{R_i dz}{\delta^3}\right] \qquad [5.64]$$

It is rather evident that the relative impact of all these components on a net resistance force differs, and it depends the depth of penetration of a body into a liquid besides all other factors concerned. It can be analyzed quantitatively based on Eqs 6.62 - 6.64, but it is clear that the role of pressure acting on a bottom of a penetrating body increases when the body approaches the bottom of a vessel.

Let us consider the situation when a round cylinder is penetrating into a cylindrical vessel. In this case we have: $R_i = R = \text{const}$ and $R_o = \text{const}$. Let us assume that $R_o - R << R$, i.e., the gap between cylinders is narrow. In this case $F_{p,1} = 0$. It is also reasonable to think that $F_f < F_{p,2}$. Then, the following equation allows one to calculate the resistance force

$$F \approx \pi\eta V\left(\frac{3}{2}\frac{R^4}{l^3} + \frac{6R^3H}{\delta^3}\right) \qquad [5.65]$$

We can introduce the depth of penetration, ξ, and obtain

$$H \approx \left(1 + \frac{R}{2\delta}\right)\xi$$

The final expression for the resistance force is as follows

$$F \approx \frac{3}{2}\pi\eta V R^3\left[\frac{R}{(l_o - \xi)^3} + \frac{2R\xi}{\delta^4}\right] \qquad [5.66]$$

This solution of the hydrodynamic problem under discussion can be used for designing dampers, calculating forces in hot stamping of metals and plastics when a puncheon is pressing in a liquid medium during a technological process.

If an outer cylinder is absent, it describes penetration of a solid body into infinite liquid medium, as in Figure 5.6c. We may analyze this problem for the case when a penetrating body is a thin flat plane (Figure 5.7). The velocity of penetration is constant and equal to V. In this case, on the contrary to the above discussed, the flow of a liquid is two-dimensional and the component of velocity v_z depends on two coordinates y and z.

The solution of the problem regarding the velocity distribution in a liquid medium is known:

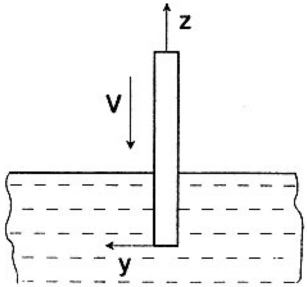

Figure 5.7. Penetration of a thin plane into a liquid medium.

$$v_z(y,z) = -V\left\{1 - \mathrm{Erf}\,\frac{y}{2}\left(\frac{V}{z\eta\rho}\right)^{1/2}\right\} \qquad [5.67]$$

where ρ is density of a liquid and Erf(x) is an error function determined by the equation

$$\mathrm{Erf}(x) = \frac{2}{\pi^{1/2}}\int_0^x e^{-\alpha^2}d\alpha$$

Shear stresses, at the surface of a plane, are

$$\sigma_w = \eta\left|\frac{\partial v_z}{\partial y}\right|_{y=0} = V\left(\frac{\eta V}{\pi z\rho}\right)^{1/2}$$

Now, the final expression for the resistance force, F, for a thin plane penetrating into a viscous Newtonian liquid and the depth of penetration, H, can be found. For a plane of the width B, considering two sides of plane, the following equation is valid:

$$F = 4B\left(\frac{\eta\rho HV^3}{\pi}\right)^{1/2} \qquad [5.68]$$

The situation included in Figure 5.6c - penetration of a cylinder into an infinite medium - can also be analyzed theoretically. The analytical solution of this problem is known and can be found in textbooks on hydrodynamics.

It is worth saying that the last problem is very important for penetration of a tube into different media, for example in oil industry. In this case, the soil can be treated as a Newtonian liquid and the known solutions can be applied to this problem only as the first approximation. In fact, real rheological properties of a medium must be taken into consideration, i.e., those of a soil and an oil layer.

The solution of this problem can be reached if a proper description of the rheological properties of a medium is used, followed by the same formal operations which have been utilized in analyzing the problem for a Newtonian liquid.

5.5.5 RESISTANCE TO ROTATION OF A THIN DISK IN A LIQUID

Let a thin disk rotate in a viscous fluid around its axis. The width of a disc is much smaller than its radius, R, which allows one to neglect the edge effects (the so-called **von Karman problem**).[5] It is necessary to find the resistance to a rotation as a function of its speed and R. This problem is a model for many real technological operations, for example, for mixing a liquid by rotation of an agitator.

The torque, M, is determined for a Newtonian liquid as

$$M = 4\pi\eta\int_0^R r^2 \left|\frac{\partial V_\varphi}{\partial z}\right|_{z=0} dr \qquad [5.69]$$

where z-coordinate axis is oriented normal to the surface of a disc, r-coordinate axis coincides with the radius of a disc, and V_φ is a circular component of the velocity vector.

Detailed calculations of the rate of shear field and then a torque give the following result

$$M = 11.8R^4\left(\eta\rho\Omega^3\right)^{\frac{1}{4}} \qquad [5.70]$$

where Ω is the rate of rotation, and ρ density.

In the theory of mixing (agitation), the dimensionless coefficient of viscous friction, C_{mf}, is usually used. Then, it is easy to demonstrate that the dependence of this coefficient on the dimensionless characteristic Reynolds Number is

$$C_{mf} = \frac{1.8}{Re^{0.5}} \qquad [5.71]$$

where the Reynolds Number for the problem under discussion is expressed as

$$\mathrm{Re} = \frac{R^2\Omega\rho}{\eta}$$

The numerical value of the coefficient in Eq 5.71 is a result of approximate solution of the hydrodynamic problem. In fact, it can be rather different if we take into account the edge effect and some other details. Nevertheless, Eq 5.71 is a good approximation and gives results close to experimental data. Meanwhile, two limitations must be remembered:

- Eq 5.71 is valid for laminar flow only
- Eq 5.71 is found for a Newtonian liquid.

Transition to turbulent flow changes the law of resistance. It can be representative if we consider the dependence of the dimensionless coefficient of viscous friction on the Reynolds Number in logarithmic coordinates (Figure 5.8). At Re < Re* (in laminar flow), Eq 5.71 is obeyed. In transition to the turbulent zone at Re > Re*, where Re* is the critical value of the Reynolds Number corresponding to laminar-to-turbulent transition, the viscous resistance has larger effect than predicted by this equation (dotted line in the range of Re > Re*). Figure 5.8 resembles Figure 4.18, and indeed it represents the same phenomenon of the dependence of hydrodynamic resistance on the rate of flow.

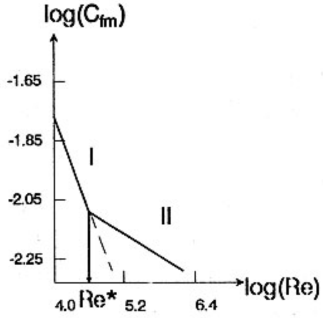

Figure 5.8. Dependence of the coefficient of viscous friction in rotation of a thin disc inside a liquid on the Reynolds Number: transition from a laminar (I) to turbulent (II) zone.

For non-Newtonian flow, Eq 5.71 needs to be modified without changing its structure. The expression for the Reynolds Number reflects non-Newtonian properties of a liquid, as in the case of a power-type liquid discussed above. The value of the numerical coefficient in Eq 5.71 can be different than the 1.8 obtained for a Newtonian liquid. The exact value depends on the rheological properties of a real liquid and can be found theoretically and/or experimentally for a real situation of torque resistance during rotation of a disk in various “rheological” liquids.

5.5.6 CONVERGING (DIVERGING) FLOWS

Converging (or diverging) flows take place when a cross-section of a channel is changing along its axis. Flow in channels with changing cross-section (diffusors - channels with decreasing cross-section, and confusors - channels with increasing cross-sections) is a rather standard situation in different technological apparatuses and transportation pipes. Therefore, this problem was thoroughly studied theoretically, and exact solutions are known for Newtonian liquids only. In all other cases, solutions for "rheological" liquids are found by numerical methods.

The size of a cross-section can be quite arbitrary, but two cases are of main interest to model real situations. That is:

- flow through a cone channel
- flow in a channel formed by two flat inclined planes.

Basic diagram of flow in a flat diffusor[6] is shown in Figure 5.9, where definitions of coordinate axes are given in a cylindrical coordinate system.

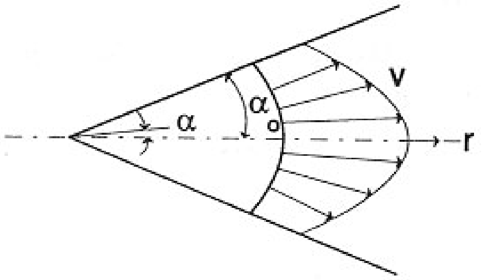

Figure 5.9. Scheme of flow between two flat inclined planes. The cylindrical coordinate system is shown.

We can assume that there is only one non-zero component of velocity, which is radial velocity, as shown in Figure 5.9. Velocity equals zero at the walls, and the velocity profile is symmetrical to the plane $\alpha = 0$.

The solution of a hydrodynamic problem of a Newtonian liquid flow is known, and one can find it in text-books on hydrodynamics. It is expressed in the form of elliptic functions, and velocity profile and pressure gradient can be calculated for any particular case. For non-Newtonian liquids, a solution of the problem of converging (or diverging) flow can be analyzed by computer methods only.

One of the interesting results of the theory of diverging flow of a Newtonian liquid in a diffusor is proof of the fact that a pure converging flow can exist only for sufficiently small angles, α_o, or

$$\alpha_o < \alpha_{max} \qquad [5.72]$$

where $2\alpha_{max}$ is some critical value of the angle between plates and it depends on the Reynolds number, Re.

For the problem under discussion

$$\mathrm{Re} = \frac{Q\rho}{B\eta} = \frac{r\alpha V_o}{B\eta}$$

where Q is volume output, B width of a channel (in the direction perpendicular to the plane of a drawing), V_o average velocity, and r and α are current coordinates.

If the condition 5.72 is not obeyed, zones with back-streams appear. These zones can exist near walls, or zones with direct and back streams can alternate, and the number of such zones depends on Re.

The exact analytical solution for α_{max} is known, though it is rather complex. For Re > 1 (in the limits of laminar flow), a simple approximate relationship takes place:

$$\alpha_{max} \approx \frac{10.2}{\mathrm{Re}}$$

i.e., the value of α_{max} is small.

In the situation when an angle α_o is very small, velocity profile can be calculated as

$$V(r,\alpha) = \frac{3}{2}\frac{Q}{B\alpha_o r}\left[1 - \left(\frac{\alpha}{\alpha_o}\right)^2\right] \qquad [5.73]$$

So, the velocity profile at each cross-section (determined for r = const) is parabolic, and Eq 5.73 is very similar to the well-known Haven-Poisseuille solution for flow of a Newtonian liquid through a flat tube. It is quite an expected result, but it is important to emphasize that it is valid only for very small values of α_o, i.e., for slightly diverging flat tubes. In the opposite case, velocity profiles appear to be non-parabolic.

Let us consider some peculiarities of flow in converging channels (confusors). Again, simple analysis can be done for Re > 1. In this case, we come to the interesting result: velocity profile appears almost flat for the main part of cross-section of a channel, and only near walls is there an abrupt decrease of velocity up to zero at the walls. It means that viscous resistance occurs in a very thin (narrow) layer near the walls. According to the theory, the size of this layer is proportional to $(\text{Re})^{-1/2}$. This fact is the base for the theory of a boundary layer which explores the general ideas: effects of viscous resistance to flow are important only at short distances from the solid surfaces, and then viscous effects are negligible.

The general approach to the theory of flow in conical diverging (converging) channels is very similar to the analysis of flow in a flat channel with changing cross section. It is convenient to analyze the problem in a spherical coordinate system, where the origin is at the apex of a cone (Figure 5.10). The flow is symmetrical in respect to the axis of a cone and two components of velocity V_r and V_α are present, where r is radial, and α angular coordinates.

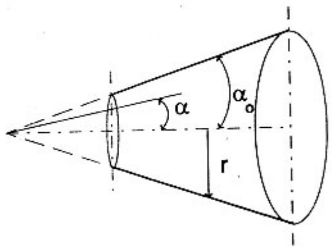

Figure 5.10. Flow in a cone channel. The spherical coordinate system is shown.

Even for a Newtonian liquid, the solutions of hydrodynamic (balance) equations are known in the form of a series only. In the first approximation (when only the older member of the series is preserved), pressure distribution in flow through a round cone channel is represented in the following manner:

$$p - p_o = \frac{\eta Q(1-3\gamma^2)}{\pi(1-\gamma_o)^2(2\gamma_o + 1)}\left(\frac{1}{r_o^3} - \frac{1}{r^3}\right) \qquad [5.74]$$

where $\gamma = \cos\alpha$ and α is a current angle calculated from an axis of a cone, $\gamma_o = \cos\alpha_o$, where α_o is an angle between a solid wall of a cone and its axis, r, is a current radius of a diffusor, r_o is a radius of the edge cross section, p_o is pressure in this section, and Q is a volume output.

The preservation of the first member of a series for p(r) is valid for viscous liquids when their viscosity is sufficiently high. This is true for many liquids, such as polymer melts or crude oils, but for low viscosity liquids, it is necessary to utilize the full solution of a problem, which can be found in standard textbooks on hydrodynamics.

The pressure drop is proportional to the volumetric output and this is a feature typical for Newtonian liquids. In a general case, we can think that the relationship between volumetric output and pressure drop, for a Newtonian liquid, must be linear and can be expressed by an equation

$$Q = K\frac{\Delta P}{\eta}$$

where ΔP is the pressure drop providing volumetric output, Q, for a Newtonian liquid having viscosity, η, and K is the geometrical factor depending on the size of a channel.

The exact expression for K is rather complex, and the first approximation can be found from Eq 5.74. However, one can find a simpler equation for K, based on the following arguments. If we consider a conical channel as a sum of round channels of the length dl, with changing radius, r, it seems reasonable to summarize pressure drops, dp, for all segments of a channel. This values can be calculated from the Hagen-Poisseuille equation, resulting in the expression for ΔP. Along the way we shall find the following result

$$K = \frac{3\pi}{8L}\left(\frac{R_1^3 R_2^3}{R_1^2 + R_1^2 R_2^2 + R_2^2}\right)$$

where R_1 is a radius of a conical channel at the entrance, R_2 is a radius of a conical channel at the exit, and L is the length of a channel (between radii R_1 and R_2). However, this result is not adequate for the rigorous solution expressed by the known series or even its first approximation represented by Eq 5.74.

We can expect that for "rheological" liquids, the relationship between pressure drop and volumetric output will appear non-linear. Indeed, for a power-type liquid, this relationship is expected to be

$$Q = K_{(n)}(\Delta P)^n$$

where the geometrical factor, $K_{(n)}$, can be calculated theoretically from the solution of a balance equation. Again, it seems that calculating $K_{(n)}$ and summarizing pressure drop in cylindrical segments of a channel of the length, dl, can lead to inadequate results.

If a liquid is visco-plastic, the central zone will be motionless, as in flow in cylindrical channels, because shear stress at the axis is absent, and stresses are less than yield stress near the axis. It is clear that the radius of this plug-like zone is changing along its length.

A very interesting, special case is a flow of an elastic liquid (i.e., a liquid able to store large deformation in the course of flow) through a conical channel. Let the radius of a conical channel be changing along its length from R_1 to R_2. Then, bearing in mind that the volume output is constant, we can calculate average velocities at entrance and exit sections $V_{o,1}$ and $V_{o,2}$. They are

$$V_{o,1} = \frac{Q}{\pi R_1^2}; \quad V_{o,2} = \frac{Q}{\pi R_2^2}$$

It means that the flow in a conical channel is accelerating and an extensional gradient of velocities appears. The gradient of velocity equals

$$\dot{\varepsilon} = \frac{V_{o,1} - V_{o,2}}{L}$$

and the extension ratio is

$$\lambda = \left(\frac{R_1}{R_2}\right)^2$$

Flow of an elastic liquid in a conical channel leads to uniaxial extension, and its characteristics can be found using the last two equations.

Extension of an elastic liquid in its flow through a conical channel can be effectively used for creation of an orientation which is fixed beyond the exit section of a channel. This idea is a basis for the technological operation which is utilized in production of high-strength and high-modulus polymeric filaments.

5.5.7 MOVEMENT OF A BALL THROUGH A VISCOUS FLUID

The hydrodynamic problem of calculating the force required for a sphere to move through a viscous liquid was first analyzed by Stokes, and is known as the **Stokes problem**.[7]

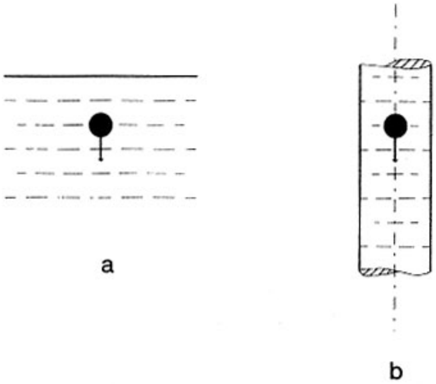

Figure 5.11. Movement of a spherical ball in an infinite volume (a) or inside a vessel (b).

Two cases are possible and are considered in theory. The first is a steady movement of a solid body in unlimited (infinite) volume (see Figure 5.11a). In this case, solid walls are absent or placed so far from a moving ball that their influence is negligible. The second case is a movement of a solid body in a vessel (Figure 5.11b) where the influence of walls on the hydrodynamic situation must be taken into account. The latter case is close to the situation discussed above, when the problem of penetrating a symmetric body into a symmetric vessel was analyzed.

A solid ball moving through a viscous liquid is a very popular model of numerous real situations. The simplest of them is the process of sedimentation of solid particles due to gravitational forces. A moving body does not need to have a spherical shape but a defined geometrical shape instead. It is a model of various bodies moving in a sea (submarines and many others). That is the reason why calculation of a resistance to movement of solid bodies through a viscous liquid is a very important problem met in different applications.

According to a well-known solution by Stokes, the force, F_s, necessary to support the steady movement of a ball in a Newtonian liquid is calculated as

$$F_s = 6\pi\eta RV \qquad [5.75]$$

where R is a radius of a ball (sphere), V velocity of the steady movement.

Further analysis shows that this solution is valid at low Reynolds Numbers calculated as

$$\mathrm{Re} = \frac{2RV\rho}{\eta}$$

where ρ is density of a liquid.

It was shown that influence of inertial forces (i.e., transition to situations when Re is not small) can be analyzed using correction factors. According to Goldstein's calculations, the exact formula for resistance to movement of a ball, when Re is not small, is as follows

$$F = F_s \left[1 + \frac{3}{16}\mathrm{Re} - \frac{19}{1280}\mathrm{Re}^2 + \ldots \right]$$

where F_S is the Stokes force calculated from Eq 5.75.

It is evident that the second member in the brackets (linear correction term) can be neglected in comparison with 1 when the Reynolds Number is of the order of 0.1.

The movement of a ball due to gravitational forces is of special interest. In this situation, the moving force, P, is calculated as a difference between weight of a ball and hydrostatic flotation force:

$$P = \frac{4}{3}\pi R^3 g(\rho_s - \rho_1) \qquad [5.76]$$

where g is the gravitation constant, ρ_s density of a moving solid body, ρ_1 density of a liquid.

In the steady movement, F_s calculated from Eq 5.75 and P calculated from Eq 5.76 are equal, and then we can find the velocity of steady movement

$$V = \frac{2}{9} g R^2 \frac{\rho_s - \rho_1}{\eta} \qquad [5.77]$$

If velocity is measured and densities of a solid ball and liquid are known, Eq 5.77 can be used to determine viscosity of a Newtonian liquid. It is quite evident that

$$\eta = \frac{2}{9}\frac{gR^2}{V}(\rho_s - \rho_1) \qquad [5.78]$$

This formula can be used only with the following limitations:

- it is valid for steady movement of a ball
- it is possible to neglect the influence of walls of a vessel
- rheological properties of a liquid are described by the Newton-Stokes Law
- movement of a ball is rather slow and $Re < 0.1$.

If movement of a ball is not very slow, and inertial effects must be taken into consideration, the equation for viscosity calculation must be modified:

$$\eta = \eta_s \left[1 - \frac{27}{16}\frac{V^2}{gR}\frac{\rho_1}{\rho_s - \rho_1}\right]$$

where η_s is viscosity, calculated according to the Stokes formula, Eq. 5.77. The second member in the brackets is a correction factor for inertial effects.

A very special modification of the Stokes problem is related to the situation when a moving ball is not a solid but liquid and its viscosity is η^o. Theoretical calculations show that in this case the velocity of steady movement can be calculated as[9]

$$V = \frac{2}{3}\frac{g(\rho^o - \rho_1)R^2}{\eta}\frac{\eta + \eta^o}{2\eta + 3\eta^o} \qquad [5.79]$$

where ρ^o is density of a liquid ball, and η^o its viscosity.

It is evident that if $\eta^o \to \infty$, we may apply Eq 5.77 for a solid ball moving in a viscous liquid. Another limiting case is connected with the assumption that $\eta^o << \eta$, for example, the case of a gas bubble in a viscous liquid. Then

$$V = -\frac{1}{3}\frac{g\rho R^2}{\eta} \qquad [5.80]$$

The “minus" sign, in the last equation, shows that a gas bubble moves in a direction opposite to the positive coordinate axis, i.e., up rather than down as in former cases.

Both Eqs 5.79 and 5.80 can be used for practical applications in different technological problems related to liquid-liquid separation, degassing, and so on.

Eq 5.77 is a linear relationship between velocity and reciprocal viscosity. Then, for a Newtonian liquid, the resistance to movement of a ball can be written as

$$F = K\eta V \qquad [5.81]$$

where K is a geometrical factor. For a spherical body

$$K = 6\pi R$$

For solid bodies of various shapes, Eq 5.81 seems to stay valid but the problem of calculation of the geometrical factor is quite independent and requires separate theoretical or experimental determination. Sometimes, the same equation, as for a sphere, is used, and in such case, R means some geometrical parameter. For example, if a moving body is a thin disk of a radius, R, and a disc is moving in the direction perpendicular to its plane, then

$$R = \frac{8a}{3\pi}$$

If this disk is moving along its plane, then

$$R = \frac{16a}{9\pi}$$

Other situations (for example, ellipsoids, cylinders, and so on, moving in a Newtonian liquid) also can be investigated by methods of theoretical hydrodynamics which allow us to establish values of the geometrical factor. Nevertheless, in practice, especially for bodies of complicated geometrical shape (for example, submarines), it is preferable and more reliable to find values of K experimentally or on the basis of some empirical formulas.

It is also useful to have a formula for calculation of stress field around a moving ball. The complete stress distribution can be calculated but the solution is rather complex. The most important value is the maximum shear stress. It acts at the surface of a ball and can be found as

$$\sigma_{max} = \frac{R}{3}(\rho_s - \rho_1)g \qquad [5.82]$$

Now, let us consider what happens if a ball moves, not in infinite liquid space, but in a vessel where the influence of its walls cannot be neglected; for example, if a ball is falling in a cylindrical tube.

Theoretical analysis shows that in this case, Eq 5.77 for viscosity must be modified by adding a correction factor. According to the well-known calculations by Faxen-Ladenburg, viscosity of a Newtonian liquid is expressed as[8]

$$\eta = \eta_s \left[1 - 2.104\left(\frac{R}{R_o}\right) + 2.09\left(\frac{R}{R_o}\right)^2 - 0.95\left(\frac{R}{R_o}\right)^4 \right]$$

where R_o is a radius of an outer cylinder (tube) along which a ball is moving and η_s is viscosity calculated from the Stokes equation (5.77).

It is easily seen that corrections become comparable with 1 at $(R/R_o) > 0.01$. Then, in many practical cases, the introduction of corrections is necessary, and only in some special cases, is it reasonable to neglect the influence of the walls of a vessel.

If a liquid is non-Newtonian, the resistance force can be found by numerical solution of hydrodynamic equations with an appropriate constitutive equation. Simple final expressions are absent, but we can think that, for a "power law" liquid, the dependence of the resistance to movement, F, at velocity, V, can be expressed by the power equation

$$F = K_{(n)} V^n$$

where $K_{(n)}$ is a geometrical factor, as before, and n an exponent in a power law (of the rheological equation of state).

In application to shear-rate dependent viscosity, results of determination of apparent viscosity depend on a driving force, or shear stress. In this case the following procedure is useful: it is necessary to make measurements and calculate apparent viscosity at different shear stresses and then extrapolate experimental data to "zero" conditions (zero shear stress or zero shear rate). This limiting "zero" apparent viscosity can be treated as a quite reliable value of maximum Newtonian viscosity.

The method of extrapolation can be rather arbitrary. For example, we can assume that in the range of relatively low shear stress, the dependence of apparent viscosity on shear stress is expressed as

$$\eta = \frac{\eta_o}{1 + A\sigma^2}$$

where η_o is maximum ("zero-shear") Newtonian viscosity and A is constant.

Then, Newtonian viscosity is found by extrapolation of $\eta(\sigma)$ dependence to $\sigma = 0$ in coordinates $\eta^{-1} - \sigma^2$. Shear stress is calculated from Eq 5.82.

Other methods of extrapolation, to $\sigma = 0$ in various coordinate systems used to determine "zero-shear" Newtonian viscosity, can also be found in the literature.

If a liquid is visco-plastic, then it can flow (i.e, a ball can move through such a medium) only if maximal shear stress calculated from Eq 5.82 exceeds yield stress. In the opposite case, a medium behaves as a solid and it is irrelevant to consider resistance to the movement of a ball.

5.5.8 COMPRESSION OF A LIQUID BETWEEN TWO PARALLEL DISKS

Let a Newtonian liquid be placed between two parallel round plates (discs). The liquid layer is compressed because of bringing the plates together (Figure 5.12). This problem was first analyzed by Reynolds.[10]

There are peculiarities of flow under discussion, as follows:

- It is reasonable to assume that the radial component of velocity dominates, i.e.,

$$v_z << v_r$$

and besides

$$\frac{\partial v_r}{\partial r} << \frac{\partial v_z}{\partial z}$$

(orientation of the axes is shown in Figure 5.12).

- Inertial forces are neglected, i.e., we analyze the case of relatively low values of the Reynolds Number.
- The flow is symmetrical in respect to the axis passing through the center of the disks.

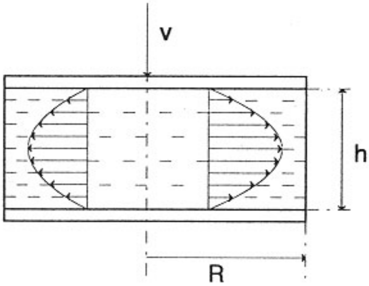

Figure 5.12. Compression of a liquid layer between two parallel plates (discs) squeezing out a liquid from the gap.

Two different basic cases are of primary interest:

- flow induced by the preset constant velocity of the upper plate moving down:

  at $z = h$, $v_z = -V = \text{const}$, and $v_r = 0$

  where h is the distance between parallel plates.
- flow generated by a constant force applied to the upper plate.

Let the velocity of the upper plate, -V, be known. Then, we would like to know

- time dependence of the force which resists approaching the disks and must be applied in order to support movement
- velocity and pressure profiles.

First, let us consider the situation when a liquid completely fills the space between disks and when they are approaching each other the surplus of a liquid squeezes out the gap and does not take part in further consideration, so the volume of a liquid in the gap decreases with time.

It is evident that, at V = const, the distance between disks, h, is linearly decreasing with time because

$$v = \frac{dh}{dt}$$

The solution of the problem under discussion for velocity distribution is

$$v_r = \frac{1}{2\eta}\frac{\partial p}{\partial r}(z^2 - hz) \qquad [5.83]$$

and we need to know pressure distribution

$$\frac{\partial p}{\partial r} = -\frac{6\eta v_r}{h^3} \qquad [5.84]$$

finally we have

$$\frac{v_r}{V} = 3\alpha(\gamma - \gamma^2) \qquad [5.85]$$

where dimensionless sizes are used:

$$\alpha = \frac{r}{h;} \quad \gamma = \frac{z}{h}$$

Pressure distribution along the radius is

$$p = p_o + \frac{3\eta V}{h^3 R^2}(1 - \zeta^2) \qquad [5.86]$$

where $\zeta = r/R$ is a dimensionless radius, and p_o is pressure at the outer free surface, at $r = R$.

The integral of p(r) along the radius gives the full force, F, required to create movement with constant velocity

$$F = \frac{3\pi\eta V R^4}{3h^3} \qquad [5.87]$$

The resistance to approaching plates increases with h^{-3}, and h grows (at V = const) linear to time. These results show why it is so difficult to squeeze out a liquid from narrow gaps pressing solid boundary surfaces: when the distance between surfaces, h, becomes very small, the force grows rapidly up to unlimitedly high values, and a very thin film of a liquid always stays in a gap.

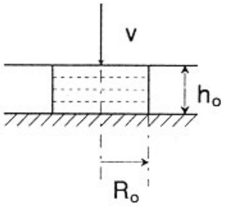

Figure 5.13. Compressing of a liquid between two parallel plates when a liquid stays in the gap.

Let us now discuss the situation when the size of discs is large and a liquid stays in the gap between discs (Figure 5.13), i.e., we wish to compress a small liquid drop. In this case the condition of constant liquid volume is valid

$$\pi R_o^2 h_o = \pi R^2 h$$

where R_o and h_o are initial radius and height of a liquid droplet, respectively, and R and h are current (time-dependent) values of the droplet sizes.

In this situation the resistance force is calculated as

$$F = \frac{3\pi\eta V R_o^4 h_o^2}{h^5}$$

and, in the case of constant volume of a liquid droplet, the resistance force increases with h^{-5}, i.e., even faster than in the former case, when a liquid is squeezed out the gap.

If a liquid placed between plates is non-Newtonian, it is not very difficult to make all necessary calculations and find all analogous formulas for velocity and pressure distribution, resistance force, and so on. The form of these formulas depends on the accepted rheological equation of state of a liquid.

However, if a liquid is not only viscous but viscoelastic (see Chapter 7), the general solution does not exist.

When a compressing force, but not a velocity, is preset, the movement of an upper plate becomes slower and slower when discs are approaching each other because of increasing resistance to flow in a narrow gap, which again demonstrates how difficult it is to squeeze out a liquid from a narrow gap.

The results of theoretical calculations discussed above are widely used in the rubber industry. There are some standard methods to characterize raw materials by their behavior in compression between parallel plates (in so-called compression plastometers). These methods are particularly convenient for such highly viscous liquids as raw rubbers.

Perhaps the main application of the flow of a liquid between compressing plates is related to understanding the performance characteristics of greases in sliding bearings, and this problem successfully models the main peculiarities of grease performance. However, industrial greases are very often visco-plastic and/or viscoelastic liquids, and when quantitative characteristics of their performance are of interest, it requires rigorous analysis of the complete hydrodynamic problem with an appropriate rheological equation of state. In this case, taking into account plasticity of a liquid is especially important, because it is easy to imagine that a thin layer of a solid-like material will stay in the gap between solid surfaces, and this circumstance prevents the contact of sliding bodies.

5.5.9 HYDRODYNAMICS OF ROLLING

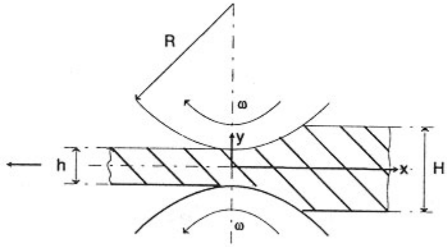

Figure 5.14. Model of rolling.

The situation shown in Figure 5.14 is a model of many industrial applications including rolling of metal slabs, stretching wires, processing of plastics and rubber compounds, and so on. That is why this model was investigated for different rheological liquids. In order to give an idea about main peculiarities of the model, we shall cite some results primarily related to flow of a Newtonian liquid.[11]

Let a flat slab (strip) of a viscous or visco-plastic liquid pass through the gap between two rolls, with the driving force for this movement being the rotation of the rolls. The initial width of a strip is 2H and the width of a gap is 2h, H and h being much less than the radius of the rolls, R. The main characteristic parameter of the stream is the **outstripping factor**, δ, determined as

$$\delta = \frac{Q - Q_o}{Q_o}$$

where Q_o is an apparent quantity of a material which would pass through the gap if a material is solid-like and moves with the circumferential velocity of the rolls:

$$Q_o = 2\omega RBh$$

where B is the length of the rolls, ω is angular velocity (frequency of rotation), and Q is a real quantity of a material passing through a gap between the rolls:

$$Q = 2\int_0^h v_x dy \qquad [5.88]$$

v_x is a velocity component directed along the x-axis.

Theoretical calculations give the following approximate expression for the δ-factor in rolling of a Newtonian liquid:

$$\delta = \frac{\alpha - 1}{\alpha + 1}\left[1 + 2\alpha\beta\left(1 - \frac{5}{6}\alpha + \frac{1}{3}\alpha^2\right)\right] \qquad [5.89]$$

where $\alpha = H/h$ and $\beta = h/R$ are dimensionless geometrical parameters and $\beta << 1$.

It appears that the δ-factor is completely determined by geometrical sizes of the apparatus used. This is true for a Newtonian liquid. But in fact (and experiments confirm it) the δ-factor depends on rheological properties of liquid and can be distinguished from the values calculated using Eq 5.89.

Theory also gives formulas for pressure distribution along the surface of rolls, net force, F, which moves rolls apart, and power consumption in roll rotation. For a Newtonian liquid, F can be expressed by a linear relationship:

$$F = K\eta\omega$$

where K is a geometrical factor, calculated via α, β, and R.

There are a lot of publications devoted to calculations of the dependencies of the force, F, on geometrical sizes of an apparatus and rheological properties of a material for non-Newtonian and visco-plastic liquids. The results were obtained by either analytical or finite element analysis methods and can be used to design industrial equipment and determine its technological characteristics. The final formulas and applied guidelines for calculations can be found elsewhere.[12] One important fact worth mentioning: for "rheological" liquids, the dependence of F on angular velocity is not linear as for a Newtonian liquid; this result is quite analogous to other above-discussed conclusions for flows of different types when we transit from Newtonian to non-Newtonian liquids.

5.5.10 FLOW IN A LUBRICANT LAYER

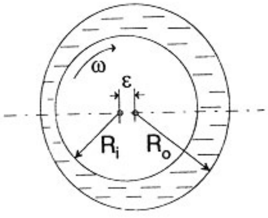

Figure 5.15. Flow in a lubricating layer between two eccentric cylinders.

This is a rather special but very important case of flow, modelling deformations of a grease in a gap, not in compression (as discussed in previous section), but in a tangential movement. In fact, it is a development of a theory of flow between two round cylinders when eccentricity (shift in position of axes of cylinders) exists, as shown in Figure 5.15. It is a model of a radial bearing with a lubricant and shift of a bob (rotating shaft) from the common axis can be initiated by a radial force.

Theoretical calculations[10,13] give the angular distribution of pressure. If we integrate this distribution through an angle, we arrive at the main result of the theory of lubrication. This result is a proof that an additional radial supporting force appears, and this force prevents shift of a bob from the common axis and favors its stabilization in rotation. This force, F, is calculated as

$$F = \frac{6\eta S R_i V_i \alpha^2}{\delta^2 (1 + 2\alpha^2)(\alpha^2 - 1)^{\frac{1}{2}}} \qquad [5.90]$$

where R_i is a radius of a bob (inner cylinder or a rotating shaft), V_i is a speed at the surface of a bob ($V_i = \omega R_i$), $\omega$is frequency of rotation, S is the surface of a bearing ($S = 2\pi R_i L$), L is the length of a bob, δ is the average gap between cylinders ($\delta = R_o - R_i$), R_o is a radius of an outer cylinder, α is dimensionless eccentricity: $\alpha = \delta / \varepsilon$ and ε is eccentricity, i.e., the distance between axes of inner and outer cylinders.

It is also possible to find the torque, M, for a rotating bob. The resulting equation is

$$M = \frac{\eta S V_i R_i}{\delta} \frac{2\alpha(2+\alpha^2)}{(1+2\alpha^2)(\alpha^2-1)^{\frac{1}{2}}} \qquad [5.91]$$

There is a correspondence between eccentricity and two main parameters: supporting force, F, and torque, M. Eq 5.90 can be rewritten as

$$\frac{F\delta^2}{6\eta S V_i R_i} = \gamma$$

where

$$\gamma = \frac{\alpha^2}{(1+2\alpha^2)(\alpha^2-1)^{\frac{1}{2}}}$$

is a function of eccentricity.

Then, it can be easily demonstrated that at low values of γ (i.e., at low radial forces or - what is more important - at high velocities of rotation) α grows unlimitedly (i.e., eccentricity, ε, becomes very small). It means that an increase in rate of rotation really results in stabilization of the position of a bob close to the axis of an outer cylinder.

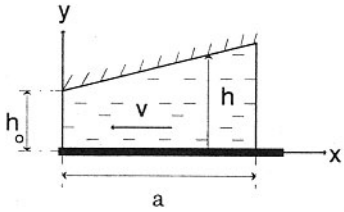

Figure 5.16. Flow between a flat surface and a sliding inclined plate.

The limiting situation corresponds to the case of $\alpha \to \infty$. This case can be modeled as shown in Figure 5.16: an inclined plate is moving relative to a flat surface. Change of the distance between plates is characterized by the linear relationship

$$h = h_o\left(1 + k\frac{x}{a}\right)$$

where the meaning of notations a, x, h, and h_o is given in Figure 5.16 and k characterizes the inclination of the upper plate. Coordinate axes are also shown in this Figure.

Sliding of a flat plate is a limiting case of the full theory, which corresponds to a slightly forced or very quickly rotating shaft when the eccentricity is small. In this situation, a supporting force, F, also appears, and it is calculated as

$$F = \frac{6\eta VBa^2}{k^2h_o^2}\left[\ln(1+k) - \frac{2k}{2+k}\right] \qquad [5.92]$$

where B is the size of plates in the direction perpendicular to the plane of the drawing.

It is easy to prove that P passes through a maximum at $k \approx 1.2$, and at this value of k, maximal value of the supporting force is

$$F_{max} \approx 0.16\eta V \frac{a^2B}{h_o^2}$$

It is also possible to find the resistance force, P, which acts against the direction of movement (sliding) of an upper plate

$$P = \frac{\eta VBa^2}{kh_o}\left[4\ln(1+k) - \frac{6k}{2+k}\right] \qquad [5.93]$$

Thus, due to the appearance of a supporting force, F, a lubricating layer can resist pressure and this is the physical reason why a lubricant works.

Though the classical theory of lubrication was developed for a Newtonian liquid, in fact, the majority of lubricants used in industry are “rheological” liquids and the whole theoretical structure built for a Newtonian liquid must be repeated for any other liquid if quantitative results are expected. It is relatively simple for a pure viscous liquid, but introduction of elasticity leads to many new effects which depend on real properties of a medium (or, in other words, on the rheological model used). Therefore no general solution exists, but the main idea concerning the existence of a supporting force in a lubricant layer is valid for any liquid.

5.6 CONCLUDING REMARKS

In real life we meet with **liquids** very often. In some cases we cannot be quite sure whether a material is a liquid or not. This is true, for example, for such substances as resins (especially at low temperatures), bitumen, semi-liquid glasses, glues, and so on. Therefore, we need a rigorous definition of a liquid. Such definition can be based on the idea that liquid is a material which **flows**, i.e., its **deformations are irreversible**, and for a pure liquid, **no elastic deformation** can exist. Moreover, liquid is a substance which can flow at infinitesimally small stresses. However, this definition requires estimation of a **time factor**, because development of deformation proceeds in time and always there is a danger that an experimenter did not have enough time to observe any deformations at all. That is why it is correct to consider *liquid-like behavior* of matter "**from an experimental point of view**". If relaxation takes place much quicker than deformation (or stress) is measured, it is reasonable to treat this substance as a liquid.

Another approach to an idea of flow of a liquid is related to the concept of **dissipation of energy** supplied to create flow: work done for deformation of a liquid is completely converted to heat (dissipates), which is opposite to deformation of solids, where work is completely stored, or to viscoelastic media, where work is partly stored.

The position intermediate between solids and liquids is occupied by **visco-plastic bodies**: they cannot flow up to some limit of stress (**yield stress**) and at low stress they behave as solid-like bodies. But at stress higher than the yield stress, such media flow, i.e., they behave as typical liquids. The level of the yield stress can be very low (infinitesimally small), and that is why, in practice, it is not always possible to distinguish between pure viscous and visco-plastic media.

Rheological equation of state (constitutive equation) for any liquid can be formulated either in terms of relationship between invariants of stress and rate of deformation tensors or as energy dissipated as a function of invariants of these tensors. In this case, the criterion of yielding for a visco-plastic liquid must be also established in terms of invariants of the stress tensor.

One of the fundamental concepts in rheology is an idea of a **Newtonian (or Newton - Stokes) liquid**. This is the simplest **linear liquid**, i.e., liquid for which linear relationships between components of stress and rate of deformation tensors exist. The coefficient for this linear relationship is **viscosity** (or Newtonian viscosity), and according to the definition, viscosity of Newtonian liquids is a material characteristic of a liquid which does not depend on conditions of flow (i.e., on stresses or rates of deformation).

Viscosity of a Newtonian liquid can be measured at different geometrical schemes of deformations. As a general rule, the term viscosity is related to shear flow, and this coefficient is a constant of proportionality between shear stress and rate of shear. All other coefficients of viscosity are related to this value. For example, a coefficient between normal stress and rate of extension measured in uni-dimensional stretching, called **Trouton viscosity**, is equal to the three-fold value of the shear viscosity of this liquid. It means that shear viscosity is a unique material parameter of a Newtonian liquid.

However, if a liquid is **anisotropic** (as liquid crystals), some independent viscosities exist even in a linear model of a liquid, and viscosity appears to be a tensor value by itself.

Many real liquids are **non-Newtonian**. It means that their apparent coefficient of viscosity, determined as a ratio of shear stress to shear rate of deformations, depends on conditions of flow. Various mathematical models of non-Newtonian flow have been proposed, discussed in literature, and used for solving applied problems. Among them, one of the most popular is the so-called **“power” liquid**. This liquid is characterized by power dependence of shear stress on shear rate.

Different mathematical equations are proposed for visco-plastic liquids, too. The simplest of them is the **Bingham model**. In this model, shear rate is proportional to the difference between current shear stress and the yield stress. But apparent viscosity of the Bingham model is not constant, but rather, is a decreasing function of shear stress.

Rheological models of liquids are used by for comparison of different liquids. This comparison can be done for two levels:

- different liquids can be distinguished by the constitutive equation which describes their flow properties in the best way
- liquids of the same rheological type can be distinguished by the values of material constants which enter these equations as numerical coefficients.

The main field of application for rheological equations of state (constitutive equations) is in **solving hydrodynamic problems**, which are described by balance equations with appropriate boundary conditions.

To solve a hydrodynamic problem means:

- to find space distribution of stresses, velocities, and pressures for a certain volume determined by solid boundaries
- to establish relationship between integral force and kinematic parameters of flow, such as pressure drop and output in flow through channels (**inner problems**) or resistance force and velocity for movement of a solid body through a liquid (**outer problems**).

There is a great variety of hydrodynamic problems because the number of possible configurations of channels through which liquids flow and solid bodies moving inside a liquid is unlimited. But some situations are very typical and are widely-used for modelling real technological and engineering situations. These are: plane uni-dimensional flow, flow through tubes with different constants and changing cross-section, movement of solid bodies in a liquid, compression of a liquid layer between planes, rotating rolls, and so on.

These are only a few examples, and certainly many other hydrodynamic situations exist. For any of them, the hydrodynamic problem can be solved by analytical and/or computer methods.

If any of these hydrodynamic situations is analyzed for a Newtonian liquid, we can expect that a linear relationship between integral force (or torque) and kinematic parameters (velocities) takes place. For non-Newtonian liquids, analogous relationships are nonlinear. In the case of visco-plastic media, motionless zones appear in areas where stresses do not exceed yield stress of a material.

Some hydrodynamic problems for a Newtonian liquid can be solved analytically; others require applying approximate or computer methods to find solutions. For non-Newtonian liquids, mathematics becomes (as a general rule) too complex to find solution in an analytical form and the methods of computational analysis are used.

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6

ELASTIC SOLIDS

6.1 DEFINITIONS

The concept of an elastic solid is an idealization of the real behavior of numerous materials. Some of them are close to this model – for example, steel and stone. Others are rather far from this ideal model, but in some applications they can also be treated as elastic solids – for example, wood, rubber, and concrete. These examples show that *the elastic solid is in fact a concept of behavior rather than a particular material*. On the other hand, the same material can behave as a *solid-like* or *liquid-like* material, depending on the time-scale of observation. Consequently, the type of rheological behavior is determined by the Deborah Number, i.e., the ratio of inner and outer time-scales.

The basic idea of an **elastic solid** has already been formulated in Chapter 4. The elastic solids are materials which completely store work of their deformation and return energy after removal of the outer forces.

Another approach to the idea of elastic solids can also be advanced. If elastic solids are treated as materials with an unambiguous relationship between stresses and deformations, i.e., if we know the stress field, we know the space distribution of deformations, and *vice versa*.

The main point in both concepts is *absence of time or time-effects*. If deformation is time-dependent (in a permanent stress field), it is always a characteristic feature of viscous (or dissipative) behavior of matter, though it can be combined with elasticity.

The next step in formulating the rheological model of an elastic solid, i.e., in writing its rheological equation of state (or constitutive equation), is a transition from components of stress and deformation tensors observed in any experiment dealing with invariant formulation. It can be an expression for elastic potential (stored energy) as a function of invariants of stress or deformation tensor or both. It can also be a relationship between invariants of stress and deformation tensors. Both approaches work in formulating rheological equation of state, and the result can be reformulated from the energy concept to the components of stress-vs-deformation tensors.

This transition is based on a fundamental expression for elastic potential (stored energy):

$$dW = \sum_{i} \sum_{j} \sigma_{ij} d\varepsilon_{ij} \qquad [6.1]$$

Continuing, we arrive at the following evident formula for the stress components calculated from an elastic potential

$$\sigma_{ij} = \frac{\partial W}{\partial \varepsilon_{ij}} \qquad [6.2]$$

and if we know W as a function of deformations, then components of the stress tensor can be easily calculated from Eq 6.2.

It is also important to have a method of conversion from the stress-vs-deformation relationship, written in invariants, to the elastic potential function. W can be written as a function of three invariants:

$$W = W(E_1, E_2, E_3)$$

where E_1, E_2, and E_3 are invariants of the tensor of large deformations.

Then using the ordinary rule of differentiating complex functions, we have

$$\sigma_{ij} = \frac{\partial W}{\partial \varepsilon_{ij}} = \sum_{k=1}^{3} \frac{\partial W}{\partial E_k} \frac{\partial E_k}{\partial \varepsilon_{ij}} \qquad [6.3]$$

The last equation gives an answer to the problem formulated above: indeed, if a function $W(E_1, E_2, E_3)$ is known, we can calculate components of the stress tensor from Eq 6.3.

6.2 HOOKEAN ELASTIC MATERIAL

The initial formulation of the concept of the Hookean elastic material has been given for uniaxial extension by Eq 1.2.

$$\sigma_E = E\varepsilon$$

where E is the elastic (Young) modulus.

Sometimes a constant reciprocal to the elastic modulus is also used. This constant is called **compliance**, I:

$$I = \frac{1}{E}$$

or

$$\varepsilon = I\sigma_E$$

Analogous relationships can be written for other geometrical schemes of deformation. For bulk (volume) compression, we have

$$\varepsilon_v = \frac{1}{B}|p|$$

where ε_v is a relative change of volume:

$$\varepsilon_v = \frac{\Delta V}{V}$$

p is hydrostatic pressure and B is **bulk modulus of compressibility.**

Linear elastic behavior in shear is expressed by the equation

$$\varepsilon = \frac{1}{G}\sigma \qquad [6.4]$$

Here ε is shear, G is the **shear modulus**, and σ is tangential (shear) stress.

In Chapter 3, discussing uniaxial extension, we introduced the values of the **Young modulus**, E, and the **Poisson coefficient (ratio)**, μ. Evidently, there are many characteristics of linear rheological behavior of a material - bulk, shear, Young moduli, Poisson coefficient. It is also possible to think about other types of deformations (e.g., biaxial extension), and it would be necessary to introduce "moduli" characterizing linear behavior of a material. Then the main questions are:

- how to write the general rheological equation of state for such material, reflecting its linear elastic properties in different modes of deformations which would include all these relationships?
- what is a minimal number of independent characteristic constants ("moduli") describing all types of deformation of a material?

The first, most straightforward attempt to construct the general rheological equation of state for a linear elastic material appears to consist of an assumption of linear relationship between corresponding components of the stress and deformation tensors, such as

$$\sigma_{ij} = k\varepsilon_{ij} \qquad [6.5]$$

where k should be an universal constant characterizing properties of a material.

But this approach is evidently wrong. Indeed:

- experiments show that the constant k is not universal because coefficients of linear equations for bulk compression, extension, and shear are different and this is not reflected in the concept of the linear relationship between corresponding components of stress and deformation tensors
- in uniaxial extension, ε_{22} and ε_{33} (in directions perpendicular to the line of extension) are not zero because an extended body compresses in perpendicular directions, but the components of the stress tensor σ_{22} and σ_{33} are absent, and this means that there is no simple correlation between σ_{ij} and σ_{ij}.

Therefore, one needs to find a different form of invariant description of rheological properties of a linear (Hookean) elastic material.

The basic idea of constructing such a description is related to the fact that in uniaxial extension, not only the form but a volume of a body changes, and these are different and independent effects. In a more general sense, we assume that shape (form) and bulk (volume) changes in deformation are independent phenomena and must be considered separately. That is why we need to introduce at least two independent constants for complete characterization of resistance of a material to volume changes, on one hand, and the resistance to shape changes, on the other. This recalls the idea of splitting stress and deformation tensors into spherical (isotropic) and deviatoric parts.

Assuming that linear relationships between spherical and deviatoric parts of both tensors exist separately

$$I_1 = kE_1 \qquad [6.6]$$

and

$$\sigma'_{ij} = 2G\varepsilon'_{ij} \qquad [6.7]$$

where I_1 is the first invariant of the stress tensor (measure of hydrostatic pressure); E_1 is the first invariant of the deformation tensor (measure of relative volume changes); σ'_{ij} are deviatoric components of the stress tensor, ε'_{ij} are deviatoric components of the deformation tensor; and k and G are material constants, the first of them characterizing resistance to volume and the second one, shape changes of a material.

If we recall that hydrostatic pressure

$$p = -\frac{I_1}{3} \qquad [6.8]$$

then Eq 6.6 can be rewritten as

$$p = -BE_1$$

where B = -k/3 is the bulk modulus of elasticity. The two fundamental coefficients, B and G, are sometimes called **Lamé factors**.

The value of G in Eq 6.7 is the shear modulus, and the coefficient 2 in Eq 6.7 relates the formal definition of components of the deformation tensor.

We can assume that Eqs 6.6 and 6.7 are valid for any type of deformation and that they are the invariant definition of a Hookean elastic material (body). It is important to connect the constants in Eqs 6.6 and 6.7 with those which are directly measured in a standard experiment - uniaxial extension.

Let σ_E to be the extensional (normal) stress, and discuss the situation in the limits of instantaneous deformations. Then, as shown in Chapter 3,

$$\varepsilon_{11} = \frac{\sigma_E}{E}; \quad \varepsilon_{22} = \varepsilon_{33} = -\mu\varepsilon_{11}$$

and

$$E_1 = (1-2\mu)\frac{\sigma_E}{E}$$

where E is the Young modulus and μ the Poisson ratio.

Hydrostatic pressure, p, in uniaxial extension is

$$p = -\sum_i \sigma_{ii} = -\frac{\sigma_E}{3}$$

Then, according to Eq 6.6, we come to the equality

$$\frac{\sigma_E}{3} = B(1-2\mu)\frac{\sigma_E}{E}$$

and then we have

$$E = 3(1-2\mu)B$$

This equation also gives us useful information because

$$\sigma_E = 2G(1+\mu)\frac{\sigma_o}{E}$$

and as a final result

$$E = 2G(1+\mu)$$

We can now calculate any pair of constants for any pair of variables, as summarized below.

- for known constants E and μ

$$B = \frac{E}{3(1-2\mu)}; \qquad G = \frac{E}{2(1+\mu)}$$

- for known constants B and G

$$E = \frac{9BG}{3B+G}; \qquad \mu = \frac{3B-2G}{6B+2G}$$

- for known G and μ

$$E = 2G(1+\mu); \qquad B = \frac{2G(1+\mu)}{3(1-2\mu)}$$

- and for known E and G

$$B = \frac{EG}{3(3G-E)}; \qquad \mu = \frac{E-2G}{2G}$$

This set of relationships allows one to find any value of a material constant from two other values measured experimentally. It is important to note that in a general case there are **only two independent constants** which need to be measured. It is interesting to consider the expression for the bulk modulus via constants E and μ.

It is quite evident that when we compress a body, its volume cannot increase; it can only decrease or may not change at all, if a body is incompressible. It means that there is a principle limitation:

$$B \geq 0$$

Then, it is also evident that $E > 0$, and this inequality can be fulfilled only if

$$\mu \leq 0.5$$

The particular case of *incompressible material* is of special interest. The fact is that for many solids

$$B >> G$$

i.e., it is much easier to change the shape of a body than its relative volume (density).

In some cases, it is reasonable to accept that $B \to \infty$, i.e., to think that some materials are completely incompressible. It is a good model (or it is almost true) for all liquids and rubbers. Then we have two simple relations

$$\mu = 0.5$$

and

$$E = 3G$$

It means that *for incompressible media there is only one independent or "free" material constant.*

Now, we can reformulate the rheological equation of state for a linear Hookean elastic material in terms of the elastic potential function. Let us consider (for the sake of simplicity) an incompressible body. Then, $E_1 = 0$, and W can be a function of E_2 and E_3 only.

The simplest idea is an assumption of linear relationship between W and E_2, i.e.,

$$W = -BE_2 \qquad [6.9]$$

where B is a material constant.

Then we can use Eq 6.9 to calculate all items entering this equation. It is easily seen that

$$\frac{\partial E_2}{\partial \varepsilon_{ii}} = -\varepsilon_{ii} \qquad \text{(both indices are the same)}$$

and

$$\frac{\partial E_2}{\partial \varepsilon_{ij}} = \frac{-1}{2}\varepsilon_{ij} \qquad \text{(indices are different)}$$

As a result we come to the linear relationship between deviatoric components of the stress and deformation tensors as indicated by Eq 6.7, i.e., the conclusion is equivalent to the above-formulated concept of a Hookean elastic material. It means that Eq 6.9 can be treated as an invariant definition of an incompressible linear elastic body in the limits of small deformations.

Though both definitions are equivalent, it seems that Eq 6.9 does not offer any additional advantages in comparison with the standard definition describing the relation between components of stress and deformation tensors. However, it is not completely true, and when we come to the discussion of finite (large) deformations of an elastic body, we may see that formulation of the rheological equation of state through an elastic potential function is preferable because it is more evident and elegant.

It should be useful to illustrate the real range of changes in modulus for some typical materials:

Material	**Young modulus**
High modulus, oriented fibers	> 300 GPa
Steels	200 GPa
Copper, aluminum, and alloys	100 GPa
Stones	40 - 60 GPa
Engineering plastics	10 GPa
Ice	10 GPa
Wood	1 - 10 GPa
Leathers	1 - 100 MPa
Rubbers	0.1 - 1 MPa
Polymer and some colloid solutions	1 - 100 Pa

Certainly, all values, listed for illustrative purposes, give only an impression of the ranges of possible values of elasticity modulus. The Young modulus can change in the range of more than 11 decimal orders. On the contrary, the Poisson ratio is a much more conservative value. The ordinary range of its values is 0.3-0.4, and only for rubbers is it very close to 0.5.

6.3 LINEAR ANISOTROPIC MATERIALS

One of the main ideas used in all the above formulations is the concept of isotropic properties of a material, i.e., the elastic modulus is the same, regardless of the direction of deformation. Meanwhile, there are many elastic bodies which are characterized by the existence of dependence of their properties on the direction of deformation. Such bodies are called **anisotropic**. Typical and important representatives of anisotropic elastic bodies are monocrystals, liquid crystals, wood, reinforced plastics; all these materials and many others possess an inherent regular structure which leads to anisotropy of their properties.

Rheological equation of state of such "structured" materials must reflect the anisotropy of their properties. Then, in a general case, we can write the following expression for the components of the stress tensor:

$$\sigma_{ij} = \sum_{l=1}^{3} \sum_{m=1}^{3} k_{ijlm} \varepsilon_{lm} \qquad [6.10]$$

i.e., it is assumed that σ_{ij} depends on all components of the deformation tensor. The set of constants k_{ijlm} are in fact components of the **tensor of moduli**. So rheological properties of an elastic anisotropic material are represented by a tensor, i.e., by the set of its components, not by two independent factors (Young modulus and Poisson ratio) as was the case of an ideal Hookean solid.

Elastic potential for an anisotropic elastic material is

$$W = \sum_{i,j} \sum_{l,m} k_{ijlm} \varepsilon_{il} \varepsilon_{jm} \qquad [6.11]$$

The tensor k_{ijlm} is symmetrical, and this fact diminishes the number of independent constants characterizing elastic properties of a material. This number in fact depends on the class of symmetry of a solid.

It can be proven that for the highest class of symmetry, the number of independent constants is 21. This is true for crystals of triclinic symmetry. For monoclinic crystals we have only 13 independent constants. For orthorhombic crystals there are 9 independent constants, and for cubic crystal, only 3 independent constants ("moduli") still remain valid. For isotropic bodies with infinite axes of symmetry (amorphous or polycrystal where differences of properties are averaged because of coexistence of large number of individual anisotropic crystals oriented statistically in space), the number of constants is only two, and we come back to an ideal Hookean material.

6.4 LARGE ELASTIC DEFORMATIONS IN SOLIDS

Discussion of large elastic deformations in solids is the most important for rubbers and rubber compounds because their main characteristic is their ability to undergo large recoverable deformations. Articles made of rubbery materials (**elastomers**) work in various applications in which they are subjected to a three-dimensional stress state. Meanwhile, as a general rule, the mechanical testing of these (and other) materials is carried out in uni-dimensional extension.

Some equations describing dependence of normal (extensional) stress on the ratio of extension has been already brought to attention in Chapter 4. Now, our main goal is to find ways for generalizing these equations in order to have a possibility to transit from the results obtained in experiment to predictions of mechanical behavior in arbitrary geometrical schemes of deformation (or loading). It means that the task is to formulate a rheological equation of state (constitutive equation) for rubbery materials in an invariant form.

An invariant form of the Hooke Law, i.e., of the linear relationship between stresses and deformations, has been formulated above: Eq 6.9, as a linear dependence of an elastic potential on the second invariant of the deformation tensor. In the limits of the Hooke Law, it is the tensor of infinitesimal deformations. As discussed in Chapter 3, in the case of large deformations, it is necessary to utilize the theory of finite deformations and use some measures of large deformations. It is a quite natural way for the generalization of the Hooke Law, though we must not forget the ambiguity of measures of large deformations, which may lead to different possibilities of representation of the relationship under discussion.

Rubbery materials can be treated as incompressible because their Poisson ratio is very close to 0.5. The first invariant of the deformation tensor, in the limit of small deformations, has the sense of volume changes (see Chapter 3), and that is why in this limit $E_1 = 0$. In the range of large deformations, E_1 does not have such a simple sense, but the condition of constant volume at deformations of any type permits us to diminish the number of independent invariants to two, because the equality

$$(1 + E_1)(1 + E_2)(1 + E_3) = 1 \qquad [6.12]$$

is always valid for incompressible materials.

Then, we can exclude any invariant representing it as a function of two others. For example, it can be the third invariant which is expressed by means of Eq 6.12 as

$$E_3 = \frac{1}{(1+ E_1)(1+ E_2)} - 1 \qquad [6.13]$$

Then, we can consider a dependence of W on two independent variables only:

$$W = W(E_1, E_2)$$

As the first approximation (or as the first reasonable simple idea), let us assume that an elastic potential is a linear function of the first invariant of the tensor of large deformations:

$$W = AE_1 \qquad [6.14]$$

Let us analyze the consequences of this supposition, i.e., Eq 6.14, for different geometries of deformation.

Eq 6.14, in an expanded form, can be written as

$$W = A(\gamma_1 + \gamma_2 + \gamma_3) = A\left[\frac{\lambda_1^2 - 1}{2} + \frac{\lambda_2^2 - 1}{2} + \frac{\lambda_3^2 - 1}{2}\right]$$

or

$$W = \frac{A}{2}\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2\right) \qquad [6.15]$$

where λ_i are principle ratios of extension.

This formula is equivalent to the linear relationship between an elastic potential, W, and the first invariant, C_I, of the Cauchy - Green tensor of large deformations

$$W = \frac{A}{2}(C_I - 3) \qquad [6.16]$$

Let us consider now the problem of three-dimensional elongation of a body "at a point" by calculating elastic potential of deformations in the principle axes. From the definition of W, it is easy to show that elastic potential is expressed via principle ratios of extension as

$$dW = \sigma_1 \frac{d\lambda_1}{\lambda_1} + \sigma_2 \frac{d\lambda_2}{\lambda_2} + \sigma_3 \frac{d\lambda_3}{\lambda_3}$$

We know that for incompressible materials

$$\lambda_1\lambda_2\lambda_3 = 1$$

and

$$d(\lambda_1\lambda_2\lambda_3) = 0$$

Then, after some simple rearrangements, we come to the following formula for dW:

$$dW = (\sigma_1 - \sigma_2)\frac{d\lambda_1}{\lambda_1} + (\sigma_1 - \sigma_2)\frac{d\lambda_2}{\lambda_2}$$

Based on Eq 6.15, we can come to the following expression for dW:

$$dW = A\left[(\lambda_1^2 - \lambda_3^2)\frac{d\lambda_1}{\lambda_1} + (\lambda_2^2 - \lambda_3^2)\frac{d\lambda_2}{\lambda_2}\right]$$

Direct comparison of two latter formulas for dW gives the following system of equations

$$\begin{aligned} \sigma_1 - \sigma_3 &= A(\lambda_1^2 - \lambda_3^2) \\ \sigma_2 - \sigma_3 &= A(\lambda_2^2 - \lambda_3^2) \end{aligned} \qquad [6.17]$$

The last system of equations is a solution to the problem of calculation of normal stresses at known principal elongations.

Certainly, this solution is not complete because we have only two separate equations for three independent variables, σ_1, σ_2, and σ_3. This result is not unexpected because we consider deformations in an incompressible medium. The last limitation means that, in principle, stresses can be determined as $\sigma_{ij} + C$, where C is a constant which cannot be determined unambiguously. Superposition of arbitrary hydrostatic pressure changing stress state of a medium does not influence its deformations. As a result, the system of Eq 6.17 determines components of the stress tensor in relation to constant C, depending on hydrostatic pressure.

Therefore, the general solution in determining principle stresses in a three-dimensional deformation state (i.e., when deformations are known or preset) can be written, in accordance to Eqs 6.17, in the following form:

$$\begin{aligned} \sigma_1 &= A\lambda_1^2 + C \\ \sigma_2 &= A\lambda_2^2 + C \\ \sigma_3 &= A\lambda_3^2 + C \end{aligned} \qquad [6.18]$$

where the constant C might be found if hydrostatic pressure is known beforehand.

Now, it is possible to analyze the main cases of deformations of an elastic solid body with rheological properties obeying Eq 6.14. It is quite evident that in uniaxial extension along the axis x_1, we have $\sigma_2 = 0$ and $\sigma_3 = 0$. If the elongation ratio λ_1 along the axis x_1 is equal to λ, the condition of the constant volume of a body under deformation results in the following relationship:

$$\lambda_2 = \lambda_3 = \lambda^{-1/2}$$

Then, any of the last two equations of the system [6.18] gives

$$C = -A\lambda^{-1}$$

Finally, we come to the formula for normal stress in uniaxial extension for a material with rheological properties described by Eq 6.14:

$$\sigma_1 = A\left(\lambda^2 - \frac{1}{\lambda}\right) \qquad [6.19]$$

It is a well-known equation, which was included in Chapter 4 as one of the possible methods of representation of experimental data for large deformations of elastic materials. This equation is a consequence of Eq 6.14 or a generalization of experimental data obtained in uniaxial extension, described by Eq 6.19.

There is not much new information in these statements. They only show that there is a possibility to apply Eq 6.14 to other modes of deformation than uniaxial extension. Simple shear is one of the most interesting and relatively easy to study by experimental methods. This mode of deformation can be realized by twisting a thin-walled cylinder. In simple shear, the principal elongations are calculated as

$$\lambda_1 = \mathrm{cotan}\beta; \qquad \lambda_2 = \tan\beta; \qquad \lambda_3 = 1$$

and the meaning of the angle β was explained in Chapter 3.

Now, we can calculate an elastic potential

$$W = \frac{1}{2}A\gamma^2$$

where γ is a magnitude of shift.

The following equation for shear stresses is obtained

$$\sigma = \frac{dW}{d\gamma} = A\gamma \qquad [6.20]$$

In accordance with Eq 6.14, the dependence of shear stress on deformation in shear must be linear and thus the value of the constant A in this equation has the meaning of shear modulus. However, if a material really behaves in shear, as predicted by Eq 6.20, its modulus of elasticity in uniaxial extension is not expected to be equal to 3A as for a Hookean solid, and in extension the dependence of stress on deformation is non-linear, as described by Eq 6.19.

Therefore, the following points can be made:

- shear behavior of two different kinds of material (Hookean and described by the rheological equation of state, 6.14) can be the same, even though they are quite different rheological materials, as proven by the difference in their behavior in extension. It is the proof of the thesis that investigation of stress-deformation behavior in one mode of loading does not yet give enough basis for estimating the type of rheological model of a material
- elastic potential (Eq 6.14) predicts non-linear behavior of a material in extension and this non-linearity is a direct consequence of large deformations by itself. This rheological equation of state contains only one material constant, which has the meaning of the shear modulus, and can be used for prediction of deformation behavior of a material at any mode of loading.

Elastic potential (Eq 6.9) is an invariant rheological equation of state describing properties of a Hookean material and that is why it can be called the **Hooke potential.**

Elastic potential in the form of Eq 6.14 was formulated in publications by Kuhn, Guth, James, Mark, and others as a result of the molecular (kinetic) statistical theory of rubbery elasticity. That is why it can be called the **Kuhn-Guth-James-Mark potential.**

The potential function (Eq 6.14) was proposed for rubbers and indeed it can be considered as a first approximation describing deformations of rubbers in equilibrium conditions. The last limitation implies that we do not consider time effects, though effects of such kind are quite typical for rubbers and stress-vs-deformation relationships.

The idea of representation of rheological properties of solid materials via an elastic potential function $W(C_1, C_2)$ is quite equivalent, after some formal mathematical transformations, to representing it as a function $W(C_1, C_1^{-1})$, i.e., it is possible to use first invariants of the Cauchy-Green and Finger tensors of large deformations. There is great freedom in varying any conceivable form of this function in an attempt to fit various experimental data. Formally, no limitations in approximating a function $W(C_1, C_1^{-1})$ exist because any of them obey the general principle of invariance. Certainly, in real practice it is desirable to search for these approximations in the simplest possible form.

The most simple form is linear, and one of the examples of linear elastic potential is given by Eq 6.14, but it contains only one argument C_1. Then the next possible approximation is a combination of linear functions in the form

$$W = AC_1 + BC_2 \qquad [6.21]$$

where A and B are material constants.

This elastic potential can be rewritten via principle of extension ratios. After quite evident mathematical transformation, we come to the following formula:

$$W = G_1(\lambda_1^2 + \lambda_2^2 + \lambda_3^2) + G_2\left(\frac{1}{\lambda_1^2} + \frac{1}{\lambda_2^2} + \frac{1}{\lambda_3^2}\right) \qquad [6.22]$$

where “new” constants, G_1 and G_2, are expressed by “old” ones, A and B, as

$$G_1 = \frac{A - B}{2}; \qquad G_2 = \frac{B}{4}$$

and the final result is

$$W = G_1(C_1 - 3) + G_2(C_1^{-1} - 3) \qquad [6.23]$$

This result confirms the above-mentioned general idea about equivalence of functions $W(C_1, C_2)$ and $W(C_1, C_1^{-1})$. An elastic potential in the form of Eq 6.23 was proposed independently and based on different concepts by Mooney and Rivlin and is called the **Mooney-Rivlin potential**.

Let us illustrate the role of the second term in Eq 6.23 by discussing predictions of stress-deformation dependencies for uniaxial extension and shear.

In uniaxial extension

$$\lambda_1 = \lambda; \quad \lambda_2 = \lambda_3 = \lambda^{-1/2}$$

where λ is an extension ratio.

Using formulas for components of stresses discussed above, we can show that normal stress in the direction of stretching is

$$\sigma_E = 2\left[G_1\left(\lambda^2 - \frac{1}{\lambda}\right) + G_2\left(\lambda - \frac{1}{\lambda^2}\right)\right] \quad [6.24]$$

with two other stress components absent.

Sometimes, it is more traditional to relate acting force, not to the current but to the initial crosssection of a stretched sample. This section is λ times larger than a current section and that is why an "engineering" (or conventional) stress, σ_e, is

$$\sigma_e = 2\left(G_1 + \frac{G_2}{\lambda}\right)\left(\lambda - \frac{1}{\lambda^2}\right) \quad [6.25]$$

The structure of Eq 6.25 demonstrates that addition of the second item in Eq 6.23 leads to the "correction" term in Eq 6.25, and if $G_2 = 0$, we come back to the well-known formula for the stress related to a one-member elastic potential function. The difference is connected with the item $2G_2/\lambda$ in Eq 6.25. The influence of this correction can be estimated if we remember that according to the experimental data, $G_2 \approx 0.1G_1$, but addition of the second item is of principle value, especially considering that other relationships between both constants are not excluded.

Let us discuss shear deformations calculated in accordance with predictions of Eq 6.25. It is easy to show that Eq 6.25 leads to the following dependence of shear stress, σ, on deformation, γ,

$$\sigma = 2(G_1 + G_2)\gamma \qquad [6.26]$$

where the sum ($G_1 + G_1$) is shear modulus, and the potential (Eq 6.25), similar to the rheological equation of state (Eq 6.23), predicts linear behavior in shear, though it is non-linear in extension.

Repeatedly, this is a proof that the same rheological behavior in deformations of one type (in this case, in linear stress-vs-deformation in shear) does not mean that the type of deformation under other conditions (in the case under discussion - stress-vs-deformation in uniaxial extension) must be the same. The result demonstrates again that data obtained in experiments of one type cannot be a criterion for the choice of rheological equation of state (constitutive equation) and cannot be used for unambiguous predictions of stress-vs-deformation dependencies in different modes of deformations.

Eqs 6.21 or 6.23 can be formally treated as first approximations (first members of a series) for some non-linear functions $W(C_1, C_2)$ or $W(C_1, C_1^{-1})$. If we add some other members, with their own material constants, we may expect to improve correspondence between the theoretical predictions and the experimental data. In particular, it is important for shear studies because the linear relationship in Eq 6.26 is not a realistic result.

If linear functions (Eq 6.21 or Eq 6.23) are not sufficient, we can try to add the quadratic member and write an expression for an elastic potential as

$$W = AE_1 + BE_2 + ME_1^2 = G_1(C_1 - 3) + G_2(C_1^{-1} - 3) + G_3(C_1 - 3)^2 \qquad [6.27]$$

where A, B, M, G_1, G_2, and G_3 are material constants and the latter three are expressed via A, B, and M.

Based on Eq 6.27, the following formula for normal engineering stress in uniaxial extension can be derived:

$$\sigma_e = 2\left(G_1 + \frac{G_2}{\lambda} + G_3\lambda^2\right)\left(\lambda - \frac{1}{\lambda^2}\right) \qquad [6.28]$$

It is evident that Eq 6.28 contains a new quadratic term with its own material constant in a "correction" member, compared to Eq 6.25. Certainly, three empirical constants allow us to fit experimental points much better than one or even two "free" constants in Eq 6.25, and that is why Eq 6.28 approximates different experimental data quite satisfactorily. Moreover, Eq 6.28 predicts non-linear stress-vs-deformation dependence in a simple shear.

The most general form of an elastic potential function is

$$W = \sum_{\alpha,\beta,\gamma=0}^{\infty} K_{\alpha,\beta,\gamma}(C_1 - 3)^{\alpha}(C_2 - 3)^{\beta}(C_3 - 3)^{\gamma}$$

where $K_{\alpha,\beta,\gamma}$ are empirical constants and $K_{000} = 0$ because elastic energy of an undeformed body is assumed to be zero.

For an incompressible material, $C_3 = 0$, and we can obtain a simpler general form of elastic potential:

$$W = \sum_{\alpha,\beta=0}^{\infty} K_{\alpha,\beta}(C_1 - 3)^{\alpha}(C_2 - 3)^{\beta}$$

A very interesting and principle problem arises concerning the practical possibility of finding W as a function of invariants. The general answer to this problem is that it is necessary to compare results of experiments carried out at different geometrical schemes of loading. For example, a normal stress in uniaxial extension for an arbitrary function $W(C_1, C_2)$ can be expressed as

$$\sigma_E = 2\left(\lambda^2 - \frac{1}{\lambda}\right)\left(\frac{\partial W}{\partial C_1} + \frac{1}{\lambda}\frac{\partial W}{\partial C_2}\right)$$

The dependence of shear stress on deformation (its measure will be written as γ) for simple shear can be formulated as

$$\sigma = \left(\frac{\partial W}{\partial C_1} + \frac{\partial W}{\partial C_2}\right)$$

The normal and shear stresses depend on an elastic potential function in a different manner. Comparing dependencies of σ_E normalized by $2(\lambda^2 - \lambda^{-1})$ and σ normalized by 2γ, the difference is evident from comparison of the right sides of both expressions, and it is possible to calculate an elastic potential function.

Certainly, other types of fundamental experiments can also be used to find an elastic potential function $W(C_1, C_2)$ but it is essential that at least two different geometrical schemes of loading should be used and compared.

The idea that a function $W(E_1, E_2)$ can be expanded into a power series, and that it is possible to use any desirable member of series, allows one to reach a reasonable degree of correspondence between a theoretical curve and experimental data, achieved by adding new arbitrary ("free") empirical constants.

The same idea can be realized in a somewhat different way. From the very beginning, we can think that an elastic potential has the form of Eq 6.14, but in reality a material "constant" is not constant but depends on deformations. It must be expressed as a dependence of A on invariants of the deformation tensor. It means that non-linearity appears not only as a consequence of large deformations by itself but also as a function of some physical phenomenon (for example, structure transformations happening in the course, and as a consequence, of large deformations), i.e., if the simplest quasi-linear potential (Eq 6.14) is not sufficient for fitting experimental data, then a physical non-linear effect is encountered.

Both approaches - expanding the dependence $W(E_1, E_2)$ into a power series or treating the material parameter A in Eq 6.14 as a function of invariants of the deformation tensor - are a rather formal generalization of Eq 6.14. Meanwhile, Eq 6.14 can be based on some reasonable physical arguments ("*statistical theory of rubber elasticity*") but its generalization has no such physical ground and must be treated as an empirical relationship invented for fitting experimental data.

The last remark in this Section relates to the time effects. Generally speaking, *time must not be mentioned in this Chapter at all*, because this concept is not consistent with the idea of elastic (instantaneous) reaction of a material to applied force. This fundamental idea already has been emphasized when we said that all stress-vs-deformation relationships discussed in this Chapter are valid for equilibrium conditions. However, there is a great difference between instantaneous and equilibrium reactions and the gap between both is the field of time effects. Moreover, large deformations and rubbery elasticity on the whole are relevant primarily to polymeric materials and various time effects (relaxation and all others). That is why it is very important (and in some cases very difficult) to separate time effects and distinguish "pure" (equilibrium) stress-vs-deformation dependence. Nevertheless, all the above is true for equilibrium deformations. Constructing elastic potential and comparing theoretical results with experimental data, we must be very careful in order not to go outside the boundaries of this principle limitation.

6.5 LIMITS OF ELASTICITY

The idea of elastic behavior of a material has its natural limits. It is evident that when stress or deformation exceeds a certain value, the material breaks. It is opposite to the behavior of liquid, in which case the deformations (or flow) seems to continue unlimitedly, if transition to instability of any kind does not occur. The rupture of a solid body can also be treated as a limit of a steady regime of deformations.

The stress increase eventually can lead to a macro-rupture of a body and also to a phenomenon which can be called an **elastic-to-plastic** transition. Indeed, numerous experiments show that many materials behave, up to some critical stress (or deformation), as elastic. After this critical state has been reached, the deformations may grow unlimitedly as if a material became a liquid: this phenomenon is called **plasticity**. The situation reminds us visco-plastic behavior discussed in Chapter 5. As in the case of visco-plastic liquids, a solid material capable of elastic-to-plastic transition is not linear because the relationship between stresses and deformations in a plastic range is not linear.

The difference between the two phenomena is rather formal but essential. We are not monitoring what happened to a visco-plastic medium *before* the yield point; in fact, the deformations are neglected up to this point and the rheological behavior of material is only considered at stresses exceeding the yield stress. It is quite opposite to the evaluation of behavior of plastic solids at stresses lower than the limits of plasticity (a limiting stress analogous to the yield stress), and deformations in this range are treated as purely elastic. Also, as a general rule, there is not much attention given to behavior after this limit has been exceeded. Particularly, the point of behavior change is of principle interest for evaluation of solid-like behavior.

The critical stress (*limit of plasticity or yield stress*) is a characteristic point dividing two ranges with different rheological behavior. For liquid, it is the lowest point and measurement begins at stresses higher than this point; for solids, it is the value of highest strain up to which a material is still elastic and thus can be treated as a solid. Nevertheless, in both cases the method of calculation of this state for multi-axial stress state is of primary importance and interest.

We have already discussed the practical implications of such behavior in liquids. In the case of solids, the limit of plasticity determines:

- the maximal permissible load in engineering designs (because it is a measure of the material strength)
- force which must be applied in different technological operations affecting plastic deformations such as shaping of materials which proceeds by plastic (irreversible) deformations.

It is easy to find these limiting stresses in the regime of uniaxial extension or at any other simple (uni-dimensional) scheme of deformation. In many real situations, the superposition of different components of the stress tensor occurs at any point. It is thus necessary to estimate some "**equivalent**" stress which would lead to the critical state.

For this discussion, it is not important to distinguish which critical state is considered, because from a formal point of view, the rupture, yielding, or plasticity are phenomena treated by the same terms in the language of invariants of stress and/or deformation tensors.

Then, the main question is: which method of calculation must be followed to estimate the equivalent stress? The answer to this question depends on the concept of strength discussed below. Certainly, the independent key question is: what are the reasons for the material rupture? The discussion of physical causes and possible mechanisms of this phenomenon is out of the scope of rheology (or the mechanics of continuum). That is why the answer to this key question is given in terms of stresses and deformations only, i.e., in scientific terms.

There are different possible answers to this question and they can be formulated as the **hypothesis of strength.** Among others, the four following concepts are of primary importance. Below, we shall formulate them for the rather simple case when only two components of the stress tensor (normal, σ_E, and shear, σ, stresses) act, though it is not difficult to extend our reasoning to the complete tensor of stresses.

α: According to a concept of **maximal normal stresses**, a criterion of rupture is the exceeding of maximal principal stress. Then the criterion of strength is

$$\frac{1}{2}[\sigma_E + (\sigma_E^2 + 4\sigma^2)^{1/2}] < [\sigma]$$

where [σ] is the maximal permissible stress, or strength.

β**: According to the concept of maximal deformations**, the criterion of strength for Hookean bodies is

$$\left[\frac{1}{2}(\sigma_E + (\sigma_E^2 + 4\sigma^2)^{1/2} - \frac{1}{2}\mu(\sigma_E - (\sigma_E^2 + 4\sigma^2)^{1/2}\right] < [\sigma]$$

where μ is the Poisson ratio (coefficient).

For other rheological models, this criterion certainly looks different.

γ: According to the concept of **maximal shear stresses**, the criterion of strength is

$$\sigma_{\max} = (\sigma_E^2 + 4\sigma^2)^{1/2} < [\sigma]$$

δ: According to the concept of **maximal potential energy** of deformation of a Hookean solid, we have

$$(\sigma_E^2 + 3\sigma^2)^{1/2} < [\sigma]$$

This condition is also known as the **von Mises criterion**, and for simple shear, when $\sigma_E = 0$, it is simplified to the condition

$$\sigma = \frac{[\sigma]}{\sqrt{3}}$$

This rather simple form of the criterion is directly related to a Hookean model of rheological behavior of a material, and for other materials the same criterion can be written in a different way, adopting the idea of a critical level of stored energy (at some point), but the reason for rupture remains valid.

One may see that all four concepts of strength give close, but not equivalent, predictions concerning conditions of rupture, to some extent differing in estimation of relative input of normal and shear stresses into critical value of an equivalent limiting stress.

6.6 SOME BASIC PROBLEMS

6.6.1 GENERAL FORMULATION

Let us discuss some fundamental problems of deformations of elastic bodies. It is important that in some situations, stress distribution in a body can be found, regardless of the rheological properties of a material (see Chapter 2); in other cases, the same is true for deformations (see Chapter 3). But in the general case, it is impossible to find (to calculate) stresses and deformations in a body if we do not know the rheological properties of a material (i.e., the relationship between stress and deformation "at a point"). Indeed, stress and deformation distributions must be found by solving balance (equilibrium) equations with appropriate boundary conditions and stresses entering these equations via rheological equations of state (constitutive equations). Therefore, the system of equations is not closed or incomplete, i.e., the number of variables is less than the number of equations, if not including rheological equations of state.

One of the most important and general problems for an elastic body is formulated as a task of calculating stress and displacement (or deformations) distributions of a bar (beam) loaded at its ends by an arbitrary combination of stresses and torques. It is called the **Saint-Venant problem.**

The general approach to solving this and many other problems is based on the physical idea (or supposition) known as the **Saint-Venant principle.** According to this concept: any statically equivalent set of forces and torques produces the same stress distribution at distances *far enough* from the site of force application. This assumption excludes from consideration some areas near the ends of a bar (beam) and states that details of force distribution (where they act) are immaterial for solutions of balance equations almost throughout the whole volume of a bar.

Certainly, the principle contains some ambiguous terms, such as "enough"and "almost". This uncertainty must not astonish, because the Saint-Venant problem and all other problems of such kind are not pure mathematical but physical tasks, and it is necessary to find some *physical arguments* for their solution. One such physical concept is a rheological equation of state which is not an inherent part of a mathematical formulation but must be taken "from an outside". Another is the Saint-Venant principle, which governs transition from outer forces to the inner situation inside a material and cannot be rigorously proven. However, the latter is not a very serious limitation because, as a general rule, it is

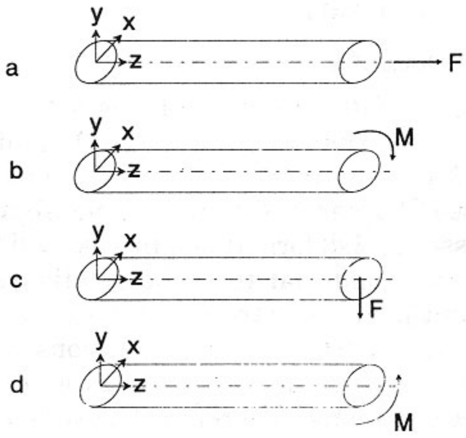

Figure 6.1. Model cases of loading a beam (bar). a: uniaxial extension; b: bending by a torque; c: bending by a transverse force; d: torsion by a twisting torque.

reasonable to think that an uncertain distance from an end must be of the order of a linear size of a bar end. The longitudinal size of a bar is much larger than its transverse size, which means that all solutions of the Saint-Venant problem are valid throughout the major part of a bar, but not close to its ends. In further discussion, the solutions will be given “excluding ends”.

The value of the Saint-Venant principle for solving the balance equations is related to the possibility to change a complex, not very definite set of outer forces to some simple model combinations of a force and a torque, which must only satisfy one condition: be statically equivalent to the initial set.

The Saint-Venant principle allows us to bring the general problem to four independent model situations (Figure 6.1):

- uniaxial extension
- bending by a pair of forces (by a torque)
- bending by a transverse force
- torsion by a torque.

The Saint-Venant problem does not envelope all possible cases of loading and deformations but contains many important situations.

6.6.2 UNIAXIAL EXTENSION (FIGURE 6.1a)

The primary analysis of the problem was given in Chapter 3. A bar (beam) loaded by a constant force F has a uniform stress field:

$$\sigma_x = \sigma_E = \frac{F}{S} = \text{const}; \quad \sigma_y = \sigma_z = 0$$

where x is a longitudinal direction (along an axis of a bar), y and z are transverse directions, and S is an area of a crosssection of a bar.

If we are interested to know deformations, it is necessary to apply a rheological equation of state. For example, if the Hooke Law is valid, deformations are also uniform and are calculated as:

- in direction of stretching

$$\varepsilon_x = \frac{\sigma_E}{E}$$

where E is the Young modulus

- and in transverse directions for a symmetrical cross section

$$\varepsilon_y = \varepsilon_z = -\mu\varepsilon_x = -\mu\frac{\sigma_E}{E}$$

where μ is the Poisson coefficient.

These relationships are a complete solution of the Saint-Venant problem for stretching of a bar made of a Hookean elastic material.

Hooke himself considered the possibility of non-linear relationship between stresses and deformations, for example, expressed by a power-type equation

$$\sigma_E = K\varepsilon^n$$

where K and n are material constants.

In this case, at σ_E = const, we have an evident solution

$$\varepsilon = \left(\frac{\sigma_E}{K}\right)^{1/n}$$

If rheological properties of material are described by the exponential function (6.15), and σ_E = const, then for large deformations (elongation ratio $\lambda >> 1$), we have

$$\sigma_E = A\lambda^2$$

and

$$\varepsilon = \lambda - 1 = \left(\frac{\sigma_E}{A}\right)^{1/2} \qquad [6.29]$$

where ε is an "engineering" measure of deformations.

Now we must distinguish between two conditions: σ_E = const and F = const. The difference between the two cases is immaterial for infinitesimal deformations because we can neglect changes of a crosssectional area in the course of stretching, but it would not be true for large deformations. Eq 6.29 relates to the condition σ_E = const, but in the case F = const, we must use Eq 6.19, which gives

$$\varepsilon = \lambda - 1 = \frac{1}{A}\sigma_E = \frac{1}{A}\frac{F}{S}$$

The last equation looks linear, as an analogue of the Hooke equation, but in fact it is not, because the value σ_E entering this equation is not a real stress but some conventional measure of stress only.

Any other rheological equation of state also can be used to calculate deformations. Perhaps it is worth repeating that all of them give unambiguous correspondence between stresses and deformations, and that time does not enter any of these equations. It is a special case of purely elastic bodies, opposite to viscous fluids (Chapter 5) and viscoelastic materials (Chapter 7).

Measurements of forces (and stresses) and deformations are very simple and practical for uniaxial extension. That is why it is a basic experiment in numerous applications.

Two measurements are of primary importance:

- standardized testing of a material
- determining the characteristic rheological parameters of a material.

The first is of absolute importance, regardless of any particular rheological properties of a solid. The only requirement which must be imposed is to follow very rigorously the standard conditions of an experiment. In such a case, unambiguous results of comparison of different materials will be obtained, useful for quality testing of industrial products and other purposes.

The second experimental approach is based on assumption of a type of rheological behavior of a material under testing. Comparing experimental and calculated stress-vs-deformation curves, a conclusion as to the correctness of the assumption and numerical values of material parameters entering the constitutive equation can be derived. It is necessary to emphasize that a negative answer to the question of correspondence between the experimental and calculated results is sufficient to reject the theoretical model, but a positive answer is not sufficient to accept it. Various rheological models can give the same relationships in an experiment of one type; thus experiments of different types must be carried out to confirm or to reject a proposed rheological equation of state.

6.6.3 BENDING BY A TORQUE (FIGURE 6.1b)

If static forces acting at the ends of a bar are equivalent to a torque, M, bending the bar, it is possible to prove that the stress distribution is the same along the length of a bar at all crosssections.

This balance equation for each crosssection is given by

$$\int_s \sigma_E z\,ds = M$$

where ds is an infinitesimal area (part of crosssection), z is a distance from point ds to a so-called neutral axis. Integration is done for a whole crosssection of an area s.

Stresses are absent at a neutral axis which passes through a center of gravity of a crosssection and is perpendicular to the plane where normal stresses act. Only normal stresses act at this point and they counteract the bending moment, M. No shear stresses are present, at least within the limits of small deformations.

Stress distribution across a section of a bar depends on the type of rheological behavior of a material. It is possible to show that for a Hookean material, this distribution can be represented by an equation:

$$\sigma_E = \frac{Mz}{I} \qquad [6.30]$$

The value I is given by the equation:

$$I = \int_s z^2 ds$$

Integration is carried out for the whole crosssection of a bar. I is an *axial (or equatorial) moment of inertia*. It is the main geometrical characteristic of the shape of crosssection on bending.

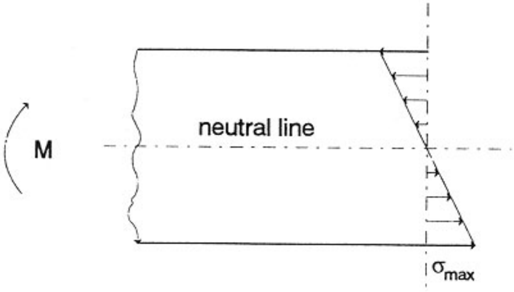

Figure 6.2. Linear distribution of stresses along a crosssection of a bar.

Eq 6.30 shows that there is a linear distribution of stresses along the height of a crosssection (see Figure 6.2). This is true if a bar is made of a material with rheological properties described by the Hooke Law.

The value I characterizes the **bending rigidity** of a bar. For a Hookean body the following relationship can be proven:

$$\frac{1}{\rho} = \frac{M}{EI}$$

where ρ is a radius of curvature of a bar (more exactly, a neutral axis of a bar). It is evident that with I increasing, bar bending diminishes (ρ higher).

If the bar cross-section is circular (R - radius), then

$$I = \frac{\pi R^4}{4}$$

For a rectangular cross-section (h - height, b - width):

$$I = \frac{bh^3}{12}$$

Eq 6.30 indicates that maximum stresses appear at a surface of a bar (at the highest value of z), and that they are positive (stretching) on one side and negative (compressive) on the other. This again shows that the surface is the most vulnerable part. It may then be understood why surface reinforcement (hardening, chemical treatment, etc.) is frequently used in engineering practice. Also, special profiles with increased surface (e.g., T-beams) are used for bars subjected to bending forces.

If material is non-Hookean, stress distribution throughout the crosssection differs. The geometrical analysis of bending leads to a linear distribution of deformation along a distance from a neutral axis:

$$\varepsilon = \frac{z}{\rho}$$

Only for a Hookean solid, linear stress distribution is observed:

$$\sigma_E = E\varepsilon = E\frac{z}{\rho}$$

After some rearrangements, the last formula gives Eq 6.30.

In all other cases, stress distribution is more complex. Bending of elastic solid with transition to plastic deformation is one interesting example. A plastic zone appears at a surface. When normal stress reaches a yield threshold, this zone moves inside the material, with an increase in torque. Stress distribution at $|z| \geq z^*$

$$\sigma_E = \sigma_y \frac{z}{z^*}$$

and at $|z| \geq z^*$ (closer to bar surface):

$$\sigma = \sigma_y \mathrm{sign} z$$

where z* is a distance from a neutral axis to a boarder of a plastic zone, and the symbol *sign* means that the sign of a stress is determined by the sign of z-coordinate, i.e., stresses can be positive or negative, depending on direction from the neutral axis.

When a plastic zone appears, a torque, M, is calculated from the equation

$$M = \frac{\sigma_y}{z*} I_e + \sigma_y S_p$$

where I_e is a moment of inertia of an elastic core (material remains elastic), and S_p is a static moment of one of the plastic zones:

$$S_p = 2\int_{z*}^{h} b(z)zdz$$

Here h is height of a cross-section and b is width of a section (inside a plastic zone). In the general case, b varies along z.

6.6.4 BENDING BY A TRANSVERSE FORCE (FIGURE 6.1c)

There are various modes possible by which a transverse force can be applied to a bar. However, the principle concept can be understood from analysis of a simple model situation when a force is applied at the end of a bar along the x-axis and perpendicular to the axis of a bar (z-axis), as shown in Figure 6.3.

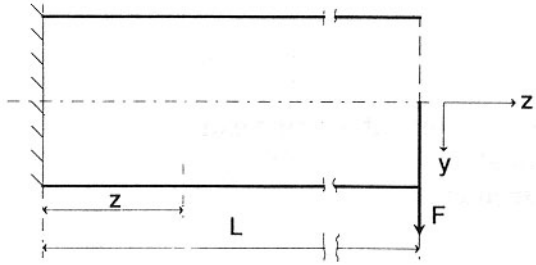

Figure 6.3. A bar loaded by a transverse force at the end. Coordinate system shown.

Let us consider the equilibrium state of any section of a bar at the distance, z, from an opposite end of this bar (taken as a 0 point). Evidently, a static equilibrium is reached when a bending moment in this section equals to

$$M(z) = F(L - z)$$

and a transverse force is constant and equal to F.

Longitudinal distributions of bending moments and transverse forces are shown in Figure 6.4. At the cross-section of a bar on the surface of a wall, a force, F, and a bending moment, M, have the following relationship

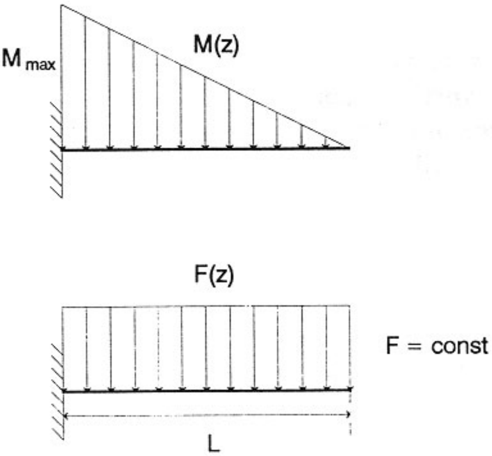

Figure 6.4. Longitudinal distributions of a bending torque, M, and a transverse force, F, for a bar loaded at its end.

$$M = FL$$

Any section is subjected to the bending torque, and a force exerted produces stress. The resultant superimposed action of a moment, M(z), and a force, F, at an arbitrary section of a bar is further discussed.

In the previous Section, it was concluded that applying torque results in the appearance of normal stresses across a cross-section of a bar. Certainly, normal stresses cannot balance action of a transverse force, F, because they are perpendicular to each other. It means that application of a transverse force, F, results in shear stresses.

Two problems thus exist which must be solved consecutively:

- it is necessary to find torque and force distribution along a bar acting at each cross-section; this distribution is a result of action of outer forces in static equilibrium preserved at any section of a bar;
- torques and forces at any section result in normal and shear stresses and their calculation is based on balance equations which must be satisfied at any local "point" of a cross-section of a bar.

The problem of calculating normal stresses as a result of torque action has been discussed already. Now, we shall discuss the results of action of transverse force leading to shear stress.

Distribution of shear stress in a cross-section depends on its configuration. If a cross-section is symmetrical and the line of application of a force, F, passes through the axis of this symmetry, then the shear stress distribution is a function of the y-coordinate only and in a general case can be written as

$$\sigma(y) = \frac{F}{I_x} f(y)$$

where I_x is a moment of inertia relative to a vertical transverse axis x (as in Figure 6.3) and f(y) is a function of a vertical coordinate y only.

For example, if a cross-section is rectangular, and its vertical size is H, the horizontal size is b, then $\sigma(y)$ is expressed as follows:

$$\sigma(y) = \frac{3F}{2bh}\left[1 - \left(\frac{2y}{H}\right)^2\right]$$

where $y = 0$ is a horizontal axis of a rectangle.

Then maximal shear stress σ_{max} acts at an axis and it is

$$\sigma_{max} = \frac{3F}{2bH}$$

If a cross-section is a circle with a radius, R, the maximal shear stress acts at the horizontal axis and it is

$$\sigma_{max} = \frac{4F}{3\pi R^2}$$

The theory of bending by a transverse force gives three main results:

- stress distribution at any cross-section of a bar, offering concept of strength and rupture of a material;
- deformation of a material at any point;
- deflection (macrodeformation or macrodisplacement) of a bar.

There are two distributions at any cross-section of a bar (beam) bent by a transverse force:

- distribution of normal stresses $\sigma_E(y)$
- distribution of shear stresses $\sigma(y)$.

One can find σ_E and σ for any point of a cross-section. Therefore, it is important to calculate principle stresses as a function of σ_E and σ. According to the theoretical results included in Chapter 2, it is easy to show that

$$\sigma_{1,2} = \frac{1}{2}[\sigma_E \pm (\sigma_E^2 + 4\sigma^2)^{1/2}]; \quad \sigma_3 = 0 \qquad [6.31]$$

In order to calculate deformations at any point, it is necessary to use a rheological equation of state. In the simplest case, it is the Hooke Law, and the resulting formulas can be easily found in numerous textbooks on strength of materials.

Deflection of a bar depends on its rigidity. The latter term is evident, on a qualitative level, and as a quantitative term rigidity of a Hookean body is determined by a product EI_x, where I_x is the moment of inertia of a cross-section of a bar.

Deflection of a bar loaded by a transverse force varies along the length of a bar. It is quite evident that maximal deflection, f_{max}, for a force applied at the end of a bar (as shown in Figure 6.3) takes place at this end. Its absolute value is

$$f_{max} = \frac{FL^3}{3EI_x}$$

where L is a length of a bar.

The mode of loading shown in Figure 6.3 is only one of possible cases of the application of a transverse forces. Certainly, the number of possible schemes of loading is unlimited, and each of them models real situations met in engineering practice. Theory of strength of materials gives methods used for calculation of bending torques and transverse forces at any cross-section of a bar. These methods are based on general balance equations of a bar, which were illustrated by the above-discussed example of transverse force applied at the end of a bar.

Another interesting example is given below to demonstrate the differences in results for two cases. This is a loading of a bar by a transverse force applied at the central plane with a position of both ends of a bar fixed in space, allowing bar to turn, as shown in Figure 6.5. This mode of loading is typical in many applications, and in particular, this scheme is used for testing materials according to standards.

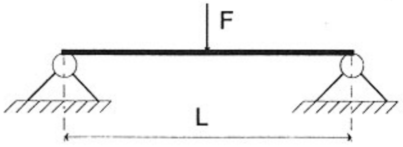

Figure 6.5. A bar loaded by a transverse force applied at the center.

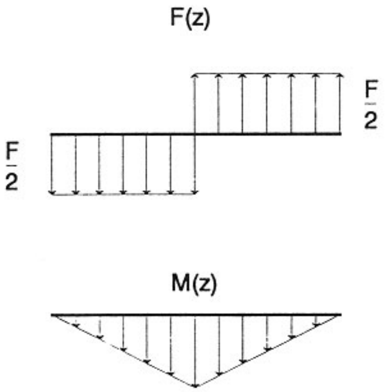

Figure 6.6. Distributions of a transverse force and a bending torque along a bar loaded at the central plane.

A bending torque (moment) and a transverse force distribution for this mode of loading are drawn in Figure 6.6.

Let us discuss characteristic parameters for a bar of the length, L. Some of them are quite evident from the balance equations. That is:

- forces acting at the ends of a bar F_o and F_L (resistance of supports) are equal to

$$F_o = F_L = \frac{F}{2}$$

- torque (bending moment) at the central plane of a bar which is the maximal torque M_{max} is

$$M_{max} = \frac{FL}{4}$$

The central plane is the most “vulnerable” crosssection because a bending torque and a transverse force are maximal here. Based on these values of a moment and a force, one can find stresses for any shape of a crosssection (as was done above) and estimate the strength of a bar according to the accepted concept of rupture.

The other useful parameter needed in engineering practice is the maximal deflection, f_{max}. Certainly, it occurs in a central plane and is equal to

$$f_{max} = \frac{FL^3}{48EI_x}$$

More examples can be found in other textbooks and/or reference books. It should be remembered from this discussion that the majority of formulas available in these books are valid for Hookean materials.

Our next discussion is devoted to the cases of some of the simplest deviations from Hookean behavior. The first illustration is the situation when properties of a material are different in compression and extension. In bending, the different layers of a bar are either compressed or stretched.

For example, in application of a force as in Figure 6.5, lower layers of a bar are stretched and upper ones are compressed. It does not influence the result of applied calculations if a material is Hookean. But even in the case when behavior of a material is still Hookean but moduli in extension, E_T, and compression, E_C, are different, the results of calculations differ as well. In fact, it can be proven that all formulas obtained for a Hookean material can be used but the Hooke modulus of elasticity must be substituted by an apparent modulus, E_a, which is calculated via moduli in extension, E_T, and compression, E_C, as

$$E_a = E_T\left(\frac{2(E_T / E_C)^{1/2}}{(1+(E_T / E_C)^{1/2}}\right)^2 \qquad [6.32]$$

The Eq 6.32 can be used to determine the modulus of elasticity in compression. For this purpose, the modulus in extension, in a standard experiment of specimen stretching, must be determined and then an apparent modulus in bending must be measured according to the schemes in Figures 6.3 or 6.5. As a result, the modulus of compression can be calculated from Eq 6.32.

The next illustration of non-Hookean behavior in bending by transverse force is related to the case when rheological properties of a solid (elastic) material are described by a power law:

$$\sigma_E = A\varepsilon^n$$

where A and n are material parameters of a non-Hookean body.

Let a crosssection of a bar be a rectangle of the height, H, and width, B. We shall discuss the mode of loading shown in Figure 6.5. The moment of inertia of a crosssection, I_x, is $BH^3/12$. If rheological properties of a material are Hookean, then according to the above formulas, its flexure in a central plane is

$$f_{\max} = \frac{FL^3}{4EBH^3}$$

If rheological properties are described by a power law, the expression for a maximal flexure becomes

$$f_{\max} = \frac{n}{n+1}\frac{L^3}{2H}\left[\frac{n+2}{2}\frac{FL}{ABH^2}\right]^{1/n}$$

It is evident that for n = 1, the latter equation transforms to the equation for flexure of a Hookean body. It is essential to note that the moment of inertia of a crosssection does not appear in the latter equation in a clear form, meaning that the theory of stresses and deformations for any non-Hookean material must be redesigned when a rheological equation of state (constitutive equation) is chosen.

Let us now discuss such a rheological effect as plasticity in relation to bending. In Section 6.5, it was emphasized that there are some natural limits of elastic behavior of solids. One of them is determined by plasticity of materials. According to this rheological model, a material can be treated as an elastic (Hookean) up to the yield stress σ_y, and at $\sigma_E = \sigma_y$, yielding takes place.

Plastic behavior of solids results from spreading of a plastic zone from the point at which the stress state attains a critical point corresponding to the yield stress.

According to the theory of bending of a Hookean body, the most vulnerable point is positioned at the surface of a bar. If a crosssection is a rectangle, yielding occurs when a torque is

$$M_y = \frac{BH^2}{6}\sigma_y$$

It is possible to increase the bending moment, but such action does not result in increase of stress because it cannot exceed the yield stress. It means that by increasing the torque, a plastic zone is widened. Then, if $M > M_y$, transverse stress distribution is as shown in Figure 6.7. In this case, the plastic zone corresponds to a part of a crosssection in which $\sigma_E = \sigma_y = \text{const}$.

Plastic behavior in bending leads to the effect of **plastic collapse** in flexure, which is evident from the dependence of deflection, d, at the central plane of a bar on the applied load, F, as in Figure 6.5. When a plastic zone appears and then begins to spread throughout a cross-section, the deflection increases with a higher rate than a transverse force because the resistance (rigidity) of a material also decreases. This effect is illustrated in Figure 6.8. The initial slope of a straight line is equal to ($L^3/4EBH^2$) since it is within a Hookean limit. Then, at the point A, a plastic zone appears and an acceleration of the deflection growth is observed. Finally, at some critical force, F_y, calculated as

$$F_y = \frac{BH^2}{L}\sigma_y$$

the deflection increases limitlessly without a further increase in force because at this point a plastic zone occupies the whole cross-section. This unlimited growth of the deflection can be called plastic collapse.

It is also interesting to mention that in the range of forces between F_A and F_y, a plastic zone is spreading not only into the center of a bar throughout the cross-section but also from the central plane to the end supports.

In the previous discussion, it was assumed that a line of application of a transverse force passes through the center of a cross-section. In reality, it is not always the case, as shown in Figure 6.9. A line of force

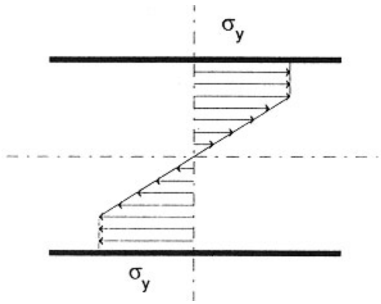

Figure 6.7. Stress distribution through a crosssection of a plastic material when yielding begins.

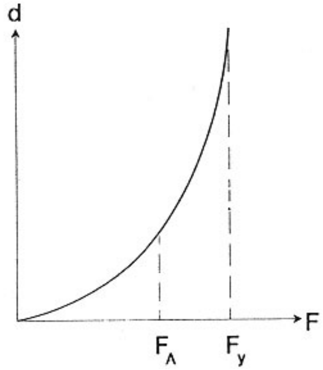

Figure 6.8. Dependence of deflection, in a centrally loaded beam, on a load if stresses pass through the yield point.

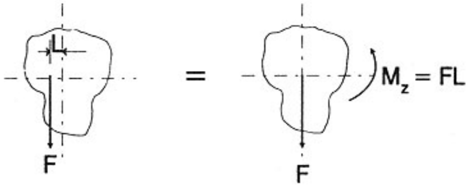

Figure 6.9. Bending by a transverse force passing the center of a cross-section.

action can pass through the center of a cross-section. According to the fundamental Saint-Venent principle, this situation can be substituted by a statically equivalent sum of a transverse forces passing through the center and a twisting moment (torque) as drawn in Figure 6.9. It shows that by-force can be represented as a combination of bending (discussed above) and torsion (discussed in the next Section).

6.6.5 TORSION OF A BAR (FIGURE 6.1d)

Torsion or twisting of bars (beams) is a very popular model of numerous cases of applied engineering practice. Indeed, shafts, power transmissions, twisting springs, screws, and many other devices are subjected to twisting torques, frequently causing deformation and even breakdown of these components. It is thus important to have a method for calculating stresses acting in a bar and its deformations.

The formulation of the problem consists of the application of a twisting torque (moment), M_z, (around the z-axis) at an end of a bar. Then, it is possible to show that only shear stresses σ_{xz} and σ_{yz} are non-zero and that they do not depend on the z-coordinate, i.e., the distribution of stresses is constant along the axis of a bar, though stresses depend on transverse coordinates. It is necessary to find stresses and deformations in a bar. Besides stresses and deformations “at a point”, it is also important to estimate the relative angle of turn, ϕ_{sp}, of a cross-sections along the length of a bar. This value is defined as an angle of a relative turn of two cross-sections, separated from each other by distance, L.

A general solution to the problem under discussion is rather complex, but simple and quite evident results for ordinary shapes of a cross-section can also be obtained. For a circular cross-section, the distribution of shear stresses along the radius $\sigma(r)$ is

$$\sigma = \frac{M_z}{I_p} r \qquad [6.33]$$

where I_p is a polar moment of inertia of a cross-section, defined for an arbitrary geometrical form of a cross-section as

$$I_p = \int_s r^2 ds$$

Then for a round cross-section, I_p is

$$I_p = \frac{\pi R^4}{2}$$

and for a cylindrical cross-section

$$I_p = \frac{\pi R^4}{2}(1-\beta^4)$$

where R is an outer radius of a cylinder, and β is the ratio of inner to outer radii of a cylinder.

The maximal shear stress σ_{max} is

$$\sigma_{max} = \frac{2M_z}{\pi R^3}(1-\beta^4) \qquad [6.34]$$

For a thin-walled cylinder when $\beta << 1$, shear stress can be considered as constant through the wall, and calculated as

$$\sigma = \frac{2M_z}{\pi(2R+\delta)^2\delta}$$

where R is a radius of a cylinder and δ is the width of a wall ($\delta << R$).

For a round cross-section $\beta = 0$ and σ_{max} can be found as

$$\sigma_{\max} = \frac{2M_z}{\pi R^3}$$

Torsion of a straight bar causes a turn of neighboring cross-sections along the length of a bar relative to each other. The angle of a turn, ϕ, depends on rheological properties of a material. For a Hookean body

$$\phi(z) = \frac{M_z}{GI_p} z \qquad [6.35]$$

i.e., ϕ is a linear function of a longitudinal coordinate z.

If a net length of a bar is L, the angle of a turn between ends of a bar $\phi_{\max}$ is

$$\phi_{\max} = \frac{M_z L}{GI_p}$$

where G is shear modulus of a Hookean body.

The relative angle of turn can be found as

$$\phi_{sp} = \frac{M_z}{GI_p}$$

and the maximal stress can be correlated with the relative angle of turn

$$\sigma_{\max} = GR\phi_{sp} \qquad [6.36]$$

The value of the product GI_p can be called **rigidity in torsion**, and the higher this product is, the lower the value of turn along the length of a bar.

In the engineering practice of design of shafts, transmitting power, etc., the acceptable limit for the twisting torque can be chosen, either based on maximal stress (if strength is a limiting factor) or a number of permissible turns calculated as an angle of twisting per an unit of length (if rigidity is a limiting factor).

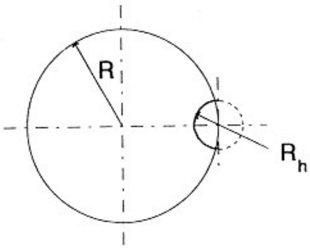

Figure 6.10. Cross-section of a round shaft with surface defect.

In twisting of round bars, when deformations are small, all cross-sections remain parallel to each other. In other shapes of cross-sections, even for such simple ones as square or elliptic, the deplanation effect takes place, even in the limit of infinitesimal deformations, i.e., distortion of plane sections is necessary to maintain a continuity of deformations.

In engineering practice, it is common to observe defects on the surface of a shaft. Such local defects are especially important for torsion effects because shear stresses are maximal at the surface. A typical example is shown in Figure 6.10, where a small semi-round hole of a radius, R_h, is made on the surface of a bar (shaft). In this case, the maximal shear stress is

$$\tau_{max} = \frac{2MR}{I_p}\left(1 - \frac{R_h}{2R}\right) = 2GR\phi_{sp}\left(1 - \frac{R_h}{2R}\right)$$

and comparing this formula with Eq 6.36, one can see that a small surface defect results in doubling shear stresses.

Crosssections other than circular can also be met in engineering practice. In many cases, the analytical solutions to boundary problems are also known, though they can be formulated to series or approximate formulas. For example, for a shaft of a rectangular crosssection (H is its height, and B is its width), maximal shear stress can be calculated as

$$\sigma_{max} \approx GB\phi_{sp}\left[1 - \frac{8}{\pi^2}\frac{1}{\cos\left(\frac{\pi H}{2B}\right)}\right] \qquad [6.37]$$

However, discussing deformations in twisting of non-round bars, we must not forget about the effect of deplanation, which always appears in all these cases.

In the case of torsion of thin-walled cylindrical shafts, it is easy to follow the effect of plasticity in relation to the yield stress in shear, σ_y, because stresses are almost uniform throughout the crosssection. If we accept that yielding in shear deformations takes place according to the von Mises condition, then

$$\sigma = \sqrt{3}\sigma_y$$

we can find that the torque value, M_y, causing yielding is

$$M_y = \frac{\pi}{2\sqrt{3}}\sigma_y(2R + \delta)^2\delta$$

In the case of a non-uniform stress field, the critical condition is reached at a certain point but not throughout the whole crosssection simultaneously.

6.6.6 TEMPERATURE STRESSES

Change in temperature results in expansion (or compression) of a material. If deformations of such kind are prevented by outer boundaries, internal stresses appear in a body. This effect is well known and must be taken into account in numerous applications. For example, it is important to maintain gaps between neighboring rail sections because the temperature change would otherwise distort them.

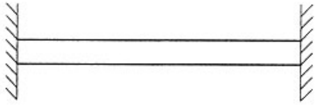

Figure 6.11. A bar placed between two rigid walls: stresses appearing due to temperature increase.

In the simplest model of temperature stresses, we can consider a bar between two rigid (non-deformed) walls (Figure 6.11). In fact, it is model of an above-mentioned situation of a rail section placed between two others. Let temperature of a bar increase by T, assuming that walls prevent free movement of the bar. It means that the normal stresses appear in a material and their value can be calculated as

$$\sigma_E = \alpha E \Delta T \qquad [6.38]$$

where α is a coefficient of linear thermal expansion, and E is the Young modulus, as usual.

Temperature stresses exist not only in bodies restricted by outer boundaries but in materials which may have unrestricted movement but the temperature field inside them is not homogeneous. In this situation, stresses at boundaries are absent but they exist inside a body and their value depends on temperature distribution.

6.6.7 CYLINDER UNDER INTERNAL PRESSURE

We shall consider stresses and deformations in walls of a thin-walled cylinder with an internal pressure, P. This scheme is a quite evident model of many real situations, for example, tanks working under pressure.

A definition of a thin-walled cylinder is

$$\delta << R$$

where δ is the width of a wall, and R is an inner radius of a cylinder.

The primary discussion concerning components of the stress tensor in a thin-walled cylinder has been already included in Chapter 2. Here, some additional "rheological" arguments are introduced to this discussion.

α For a Hookean body (in the limits of small deformations), it is easy to find deformations. According to the definition of the Hookean body, it is evident that

$$\varepsilon_\theta = \frac{1}{E}(\sigma_\theta - \mu\sigma_z)$$

where ε_θ is a circumferential component of the deformation tensor, and σ_θ and σ_z are components of the stress tensor.

Components of the stress tensor for different modes of loading of a cylinder (open or closed ends) were calculated in Chapter 2. Now, we can find deformations.

β Let an elastic material become plastic at some value of yield stress, σ_y. There are two components of the stress tensor σ_θ and σ_z acting in a wall. According to the von Mises criterion, the relationship between the yield stress and components of the stress tensor is as follows,

$$\sigma_y = (\sigma_\theta^2 + \sigma_z^2 - \sigma_\theta \sigma_z)^{1/2}$$

If ends of a cylinder are open, $\sigma_z = 0$, and

$$\sigma_\theta = \sigma_z$$

If a cylinder is sealed (ends are closed)

$$\sigma_\theta = \frac{2}{\sqrt{3}} \sigma_y$$

From the above equations, one can find critical (limiting) pressure corresponding to a transition of a material into a "plastic state".

γ Let us discuss the situation when rheological properties of a solid body are described by the Mooney-Rivlin potential function which is formulated via the first and second invariants of the tensor of large deformations

$$W = \frac{A}{2}(I_1 - 3) + \frac{B}{2}(I_2 - 3)$$

where A and B are material constants.

If one assumes that a material is incompressible, then it is possible to show that the stress components are

$$\sigma_\theta = (A + B\lambda_z^2)\left(\lambda_\theta^2 - \frac{1}{\lambda_\theta^2 \lambda_z^2}\right)$$

and

$$\sigma_z = (A + B\lambda_\theta^2)\left(\lambda_z^2 - \frac{1}{\lambda_\theta^2 \lambda_z^2}\right)$$

where λ_θ and λ_z are principle ratios of extension in two directions.

The general solution for λ_θ and λ_z can be found from these equations without problems. It is simpler to illustrate the solution for the case when B = 0, the more so when B << A, and it is reasonable to neglect B in comparison with A. For this case

$$\lambda_z^2 = \frac{\lambda_\theta^2}{4}\left[1+\left(1+\frac{8}{\lambda_\theta^6}\right)^{1/2}\right]$$

Now, we can exclude λ_z in equations for stress components, and find σ_θ and σ_z in an analytical form. Perhaps the final expression looks cumbersome, but it is quite possible to use it to calculate deformations of, for example, an elastic cylinder made of a rubbery material under an internal pressure.

6.6.8 PRESSURE INSIDE A SPHERE

Let us attempt to calculate stresses and deformations in the wall of a sphere loaded by internal pressure, p. It is evident that due to the central symmetry of the body, all shear components of the stress tensor are equal zero, and normal stresses (which are the principle stresses) must be found in a polar (spherical) coordinate system. Two of them are equal ($\sigma_\theta = \sigma_\phi$), and we need to calculate radial normal stress σ_r, where θ, ϕ, and r are spherical coordinates.

If an inner radius of a sphere is R_i and outer radius is R_o we have the following boundary conditions

at $r = R_i$ $\sigma_r = -p$;

at $r = R_o$ $\sigma_r = 0$.

where r is a current radius ($R_i \le r \le R_o$).

The solution for a Hookean medium is well known and is expressed as

$$\sigma_r = \sigma_{av} = \left[1-\left(\frac{R_o}{r}\right)^3\right]$$

$$\sigma_\theta = \sigma_\phi = \sigma_{av}\left[1+\frac{1}{2}\left(\frac{R_o}{r}\right)^3\right]$$

where an “average” stress σ_{av} is

$$\sigma_{av} = p\frac{\left(\frac{R_i}{R_o}\right)^3}{1-\left(\frac{R_i}{R_o}\right)^3}$$

Deformations and displacements can be easily calculated according to the definition of a Hookean body.

Now, it is interesting to investigate the critical conditions for elastic-to-plastic transition. If we assume that this transition occurs due to the action of shear stresses and is described by von Mises criterion, then maximal shear stress σ_{max} acts at the inner surface of a sphere and can be calculated as

$$\sigma_{max} = \sigma_{av}\frac{\sqrt{3}}{2}\left(\frac{R_o}{R_i}\right)^3$$

The critical value of pressure p* inside a sphere, which corresponds to elastic-to-plastic transition, can be found from equation

$$p^* = \frac{2}{3}\left(\frac{R_o}{R_i}\right)^3\left[\left(\frac{R_o}{R_i}\right)^3 - 1\right]\sigma_y$$

where σ_y is the normal stress at which elastic-to plastic transition (or yielding) takes place in uniaxial extension.

The last equation allows one to calculate the limiting pressure in thin balloons made of plastic materials or to find permissible pressure in high-pressure chemical reactors.

6.6.9 STRESSES AND DEFORMATIONS IN MEMBRANES

Membranes loaded by forces normal to their surfaces are a standard element of many engineering designs. In all these cases, a membrane can be regarded as a thin sheet which does not resist shearing, and therefore, bending moments at all points of a membrane are absent. A loaded membrane is a good approximation of shells, thin sheets, films, and so on.

In the limit of infinitesimal (or small enough) deformations, the shape of a membrane does not change under loading. Static equilibrium and forces and then stresses can be calculated from appropriate balance equations.

A typical example of a loaded membrane is a hemispheric cup under its own weight. The stress analysis of this problem was conducted in Chapter 2. If deformations are small, they can be easily calculated from the stress distribution according to the Hooke Law. In this case, rheological arguments practically do not add anything new to the stress analysis, except for deformations and relative displacement points of a membrane, and since they are small, they do not result in distortion of a shape of a membrane.

The situation becomes more complex if large (final) deformations occur, and one must consider large displacements and distortions of the shape of a membrane. As an example, let us follow deformations in a flat membrane which budges due to the action of external forces (Figure 6.12). This is a typical case of large deformations and it is rather instructive to follow complications which appear in the analysis of this problem due to large deformations and distortion of a shape of a membrane.

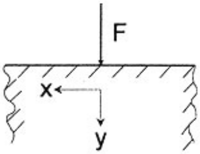

Figure 6.12. Budging of a flat membrane due to

First of all, we do not know the final shape of a membrane which is definitely different than its initial shape. In the case under discussion, it is reasonable to think that an initially flat sheet becomes closer to a sphere. Then, its shape can be approximated by a formula

$$r = R\sin\alpha$$

where R is a radius of a membrane and α is an angle calculated from an axis of symmetry.

Balance equations show that specific (i.e., calculated per unit of the length of a membrane) circumferential force, F, and meridional force, F_θ, are the same and both can be found as

$$F_\theta = F_l = \frac{Pr}{2\sin\alpha} = \frac{PR}{2}$$

where P is pressure required to bulge a membrane.

As a result of this equality, both components of principle extension ratios must also be equal:

$$\lambda_\theta = \lambda_1$$

Both extension ratios can be easily found from purely geometrical arguments and they are

$$\lambda_\theta = \lambda_1 = \frac{R + (R^2 - r^2)^{1/2}}{R + (R^2 - a^2)^{1/2}}$$

where 2a is the initial size of a membrane.

Extension ratios can also be expressed via central (maximal) deflection, f, which is related to R by an equation

$$R = \frac{a^2 + f^2}{2f}$$

Substituting, we obtain

$$\lambda_\theta = \lambda_1 = 1 + \frac{fh}{a^2}$$

It is interesting to calculate the third principle extension ratio, λ_r. From the assumption of the constant volume of a material in deformations, the value of λ_r is calculated from equation

$$\lambda_r = \frac{1}{\lambda_\theta \lambda_1} = \frac{1}{\left(1 + \frac{fh}{a^2}\right)^2}$$

The last equation shows that the reduction of membrane thickness is not uniform. It does not occur near the ends of a membrane (where $h = 0$ and $\lambda = 1$) and it the largest at the top, where h = f and

$$\lambda_{r,\max} = [1 + (f \diagup a)^2]^{-2}$$

In further analysis, it is confirmed that the assumption about spherical form of a deformed sheet is rather artificial, and as a result, one may come to the conclusion that deformations are absent at the ends of a membrane, meaning that stresses must be zero at the edge. Certainly, this is not the actual case and such a solution is invalid near the edge. That is why it is reasonable to use an averaged value of λ_r, determined as

$$\lambda_{r,av} = \frac{1}{f}\int_0^f \left(1 + \frac{fh}{a^2}\right)^{-2} dh$$

and

$$\lambda_{r,av} = \left[1 + \left(\frac{f}{a}\right)^2\right]^{\backslash 1}$$

Two other averaged values of extension ratios are

$$\lambda_{\theta,av} = \lambda_{i,av} = \left[1 + \left(\frac{f}{a}\right)^2\right]^{1/2}$$

We can use any stress-vs-deformation relationship to calculate $\lambda_{i,\,av}$ for known stresses in a membrane. They are

$$\sigma_1 = \left(\frac{PR}{2\delta_o}\right)\left[1 + \left(\frac{f}{a}\right)^2\right]^{1/2}$$

where δ_o is the initial thickness of a membrane and its final thickness δ is expressed as

$$\delta = \frac{\delta_o}{1 + \left(\frac{f}{a}\right)^2}$$

For example, let a non-linear relationship between stresses, σ, and deformation, ε, be expressed by an elastic potential (6.14). Then

$$\sigma_1 = \sigma_\theta = A\left(\lambda_2 - \frac{1}{\lambda^4}\right)$$

where

$$\lambda \equiv \lambda_{1N} = \lambda_\theta$$

For the purpose of further simplification, we can assume that $\lambda >> 1$, and then

$$\sigma_E = A\lambda^2$$

Now, it is possible to show that the resulting formula has the following form:

$$\frac{Pa}{2\delta_o} = A\frac{2\left(\frac{f}{a}\right)}{1 + \left(\frac{f}{a}\right)^2}$$

The last equation allows us to calculate the deflection, f, as a solution of the quadratic equation and to find dimensions of a deformed membrane.

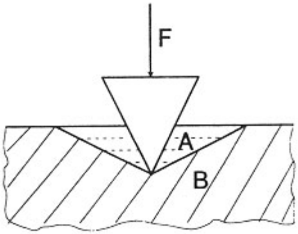

Figure 6.13. A local force acting at a solid elastic surface. Plastic (A) and elastic (B) zones around the top of a wedge penetrating into a solid material.

6.6.10 CONTACT (LOCAL) STRESSES

Let us assume that a force, F, is acting normal to the surface of an elastic body at "a point". Formally, it means that the intensity (specific force, or force divided by an area on which it acts) of the local force at this point is infinite. In reality, any force, even very localized, acts on some finite area and stresses cannot be infinite. Moreover, any force results in deformations of a material and reorganizes an area where it is applied. The stresses created are called **contact stresses**, and they are discussed below. Now, we shall consider the case of "point" application of a force (Figure 6.13).

Though a force cannot be applied to "a point", this scheme is a good model of numerous real situations; for example, nails driven into a solid wall, a heavy wheel on a road, a ball in a ball bearing, etc.

Solution of the problem under discussion can be easily formulated in polar coordinates, which are introduced as

$$x = r\cos\theta; \quad y = r\sin\theta$$

where r is the distance from the point of force application and θ is a polar angle.

Then, it is possible to find that for a Hookean elastic material, absolute values of the components of the stress tensor are

$$\sigma_{xx} = \frac{2F}{\pi}\frac{\sin\theta}{r}\cos^2\theta$$

$$\sigma_{yy} = \frac{2F}{\pi}\frac{\sin\theta}{r}\sin^2\theta$$

$$\sigma_{xy} = \frac{F}{\pi}\frac{\sin\theta}{r}\sin^2\theta$$

It is also possible to find principal stresses

$$\sigma_1 = 0; \quad \sigma_2 = \frac{2F}{\pi}\frac{\sin\theta}{r}$$

Certainly, all these equations are invalid in the close vicinity of the point of force application because the true force distribution around this point is not properly modeled. Nevertheless, the results of calculations are rather interesting because they show that stresses are decreasing rather slowly from the point of force application, proportional to the distance from this point.

If a material becomes plastic, which happens with stresses exceeding the yield stress (when $\sigma > \sigma_y$), we arrive at a rather interesting picture drawn in a qualitative form in Figure 6.13. Near the top of a wedge penetrating into a solid body, a plastic zone appears, surrounded by an elastically deformed material. This scheme of deformation reflects a situation common to many technological processes of the shaping of solid (elastic) materials which become capable to plastic deformations at $\sigma > \sigma_y$ (i.e., they conserve a new form created by an action of external forces if they exceed the yield stress). Certainly, the form of material deformation can vary, but a zone of plastic deformation appears near the sharp edges of material breakdown; for example, near the corners of a rectangular punch. If the rheological equation of state (constitutive equation) of such elastic material, transiting into a plastic state at $\sigma > \sigma_y$, is known, then it is possible to calculate stress and deformation distributions through the volume of a body.

Calculation of contact stresses in solid bodies under force, F, deserves some explanation. It is so-called **Hertz problem**, and its solution depends on the shape of the body which exerts this force. If both materials are Hookean and their rheological properties are characterized by the same value of the Young modulus, E, the equations, for the main cases, are well known. For example, if two contacting bodies are spherical, the maximal stress, σ_{max}, is calculated as

$$\sigma_{max} = 0.388\left[FE^2 \frac{(R_1 + R_2)^2}{(R_1 R_2)^2}\right]^{1/3}$$

where R_1 and R_2 are radii of contacting spheres.

If one of the spheres is replaced by a flat plane (i.e. if $R_1 = 0$ and $R \to \infty$), we have

$$\sigma_{max} = 0.388\left(\frac{FE^2}{R^2}\right)^{1/3}$$

It is interesting to mention that in all cases when two Hookean bodies are in contact, and one of them is a sphere, the maximal stress is proportional to the complex $(FE^2)^{1/3}$. As a general rule, an elastic material can sustain great contact stresses. It is explained that a contact force leads to a three-dimensional compressive stress state, which is not as dangerous to a material as tensile stresses.

It is possible to prove that the most dangerous point is positioned not on the surface at the place of a contact but at some distance under the point of contact, and the principle stresses in this point are lower than the maximal stress, σ_{max}. That is why plastic deformations with the yield stress exceeded occur inside the volume of contacting bodies before they can spread to the surface.

6.7 CONCLUDING REMARKS

A great number of materials used in engineering practice and in numerous applications can be treated as **solids** or **elastic solids**. It means that the *energy of deformation is stored in a material*, and after the action of external forces ceases, this stored energy is used for restoration of the initial form of a body. In this sense, we may say that an elastic material remembers the history of its deformation. An ideal elastic material stores and returns the energy of deformation completely and instantaneously. It is interesting to mention that the work of deformation of an ideal elastic material does not depend on the route from the initial to the final configuration. That is why **stored energy** is a *potential function* (i.e., a function which does not depend on the manner of movement in space of variables but depends on positions of starting and final points in this space only).

Certainly the concept of ideal elasticity is only a model of behavior of real solid materials in which elastic (recoverable) deformations dominate. In reality, neither is storage of energy of deformation complete (part of it dissipates even though it can be only a slight part of the full energy involved) nor is the reaction of a material after removal of external loading instantaneous (though it can be very rapid). Moreover, the same material can behave differently, depending on the time-scale of deformations. An idea of elasticity is primarily related to the behavior of a material, rather than to the material itself, though this difference does not appear obligatory and in some cases can be evaluated in specially-designed experiments (in a very prolonged observation only).

Moreover, even if a material is elastic (or close to the ideal elastic behavior), this type of rheological property can exist up to a definite limit of stresses. This limit is restricted by one of the two reasons:

- rupture of a material when stresses exceed its strength
- transition to a plastic state if stresses exceed the *yield stress* of a material.

Both critical situations are predicted on the basis of a concept of an "equivalent" state calculated as a function of invariants of stress and/or deformation tensors. This formal approach does not answer the question regarding the reasons for rupture or elastic-to-plastic transition, and generally the answer is out of sphere of rheology, belonging rather to the physics of solid state. This is not surprising because the reason for material to obey the Hooke Law is not discussed in mechanics (or rheology of continuum) since it belongs to the physics of solids. According to the classification of the rheological effects (Chapter 3), we only can state that both phenomena can be treated as manifestations of *phase non-linearity* in the rheological behavior of a solid material. It is rather evident from transition to plastic state, for example, in neck formation on uniaxial stretching, but the same can be valid in relation to rupture.

The existence of the limiting point for elastic materials is outside of the concept of elasticity and must be introduced from some independent arguments. This point is very important for all applications, because a model of an elastic material is very widely used for countless engineering problems and it is necessary to know the limits of its applicability.

The central position in rheology of solids is occupied by the search for a valid rheological equation of state (constitutive equation) used for description of mechanical behavior of real material. There are two rational ways to build a rheological equation of state for an elastic material. *The first* is based on the fundamental concept of elasticity and representation of an elastic energy of deformations (or elastic potential function) in the form of a combination of stresses and deformations. *The second* approach utilizes possible versions of reasonable relationships between stresses and deformations. Both methods formulate rheological equations of state in invariant form, i.e., they are based on rational functions and may relate invariants (or principal values) of the stress and deformation tensors. It is always possible to switch from one method of formulating to the other.

The simplest rheological equation of state of an isotropic elastic body is the Hooke Law, which postulates the linear relationship between normal stresses and deformations in uniaxial extension and introduces two rheological (material) parameters

- the **Young modulus**, which is determined as a coefficient of proportionality between stresses and deformations in uniaxial extension. The value reciprocal to the Young modulus is called elastic **compliance** (in extension)
- **Poisson ratio**, which is an absolute value of the ratio of transverse to longitudinal deformations measured in uniaxial extension.

Generalization of the Hooke equation to three-dimensional deformations cannot be done in a straightforward way, because the simplest possible assumption that all components of stress and deformation tensors are proportional to each other is evidently wrong. Such generalization requires splitting of both tensors into spherical and deviatoric parts, and only for these components of tensors separately does the idea of linear proportionality work well and allow one to build a reasonable rheological equation of state of the simplest elastic body which is correct for the range of small (or infinitesimal) deformations. This is the simplest possible model which includes two independent material parameters (coefficients of proportionality) of a medium called the **Lamé factors**. Their physical meanings are:

- **modulus of volume compressibility**, characterizing the resistance of a material to homogeneous volume changes, under hydrostatic pressure, without changes in shape of a body;
- **shear modulus**, characterizes resistance to changes in the form of a body at its constant volume.

Any pair of constants can be recalculated to each other so there are only two independent constants which represent rheological properties of an isotropic elastic material. Moreover, a medium is incompressible when Poisson ratio is 0.5 and only one independent constant describes mechanical behavior of an isotropic elastic material. It can be the Young modulus or shear modulus.

If an elastic material is *anisotropic*, i.e., its properties depend on directions of force application and deformation measurements, the number of independent constants (moduli or compliances) is more than 2 and their exact quantity depends on the class of symmetry of an anisotropic material. For example, it is true for monocrystals, liquid crystals, reinforced plastics. The maximal number of independent constants for bodies of the highest class of symmetry is 21 and this number diminishes with a decrease in the class of symmetry.

Elastic deformations can be large (in comparison with 1), and in this case, it is necessary to refer to the theory of finite deformations in order to construct a rheological equation of state.

A general approach to solving this problem consists of an application of various hypotheses concerning functional dependencies of an elastic potential on invariant of the tensor of large deformations. The simplest case is an assumption of linear dependence of an elastic potential on the first invariant of this tensor or on the combination of the first and the second invariants, and so on. If it is not sufficient, it appears necessary to introduce higher members of the series with own coefficients (material constants). The same results are achieved if we use linear combinations of the Cauchy-Green and Finger tensors of large deformations.

In all these cases (even if we use linear members of the series only), the stress-vs-deformation relationships in extension become non-linear, though they may stay linear for shear deformations. It demonstrates that the same results obtained in an experiment of one type can be compatible with qualitatively different results of an experiment in another geometrical scheme of sample loading. It is thus necessary to combine different geometrical modes of loading if a solid conclusion about the type of the rheological equation of state of a material is expected.

Rheological equations of state of an elastic solids are used to solve *boundary problems*, i.e., they are used to find stresses and deformations inside a body loaded on its surface, and sometimes macro-deformations (for example, deflections and twisting of bars) are also a subject of investigation. There are different classes of boundary problems. Among them, the **Saint-Venant problem** is one of the most popular and important. This problem is formulated as a task of calculating stresses and deformations in bars (beams) loaded at their ends in an arbitrary manner, primarily by a stretching force, by a transverse force, by a bending torque (moment), or by a twisting torque.

The general approach to solving this problem is based on the **Saint-Venant principle.** According to this concept, the resulting distribution of stresses inside a material does not depend on detailed manner of force and torque application at the ends of a beam, if direct vicinity of the ends is not of special interest. This approach allows one to find normal and shear stresses (and then principle stresses at any point) at any crosssection of a bar of an arbitrary form. These solutions are very widely used in engineering practice for calculating strength of materials. When stresses exceed the yield stress, plastic deformations appear in the the center of action of maximal stresses, and plastic zones are spreading throughout a sample.

Besides the Saint-Venant problem, other situations also can be investigated, if the rheological equation of state of a material is known. *The contact stresses* in case a highly localized force applied to the surface of a body can be other example of application. As a result, the stress distribution through the volume of a body can be found and the transition to plastic deformation at yield stress estimated.

7

VISCOELASTICITY

7.1 INTRODUCTION

Rheological behavior related to **viscoelasticity** is the most relevant for the description of a majority of real materials. Viscoelastic effects exist in Newtonian liquids (e.g., water) under special conditions of measurement, such as very high frequencies. The other extreme of viscoelastic effects is offered by the example of vibration damping in bells, due to “viscous” losses in metal.

In general, viscoelasticity is a combination (or superposition) of properties characteristic for liquids (viscous dissipative losses) and solids (storage of elastic energy). Therefore, a general definition of viscoelastic materials includes two components — elastic potential and intensity of dissipative losses. However, these two values are factors of a different dimension. The main characteristic material constants (i.e., viscosity and modulus of elasticity) are also values of a different dimension. The approach taken to combine elastic and viscous characteristics of a material for description of its viscoelastic properties is worth a special discussion because it leads to various models of a viscoelastic body.

Viscoelastic behavior can be considered as a *slow (or delayed)* development of stresses and deformations in time, and this delay must not be confused with inertial effects also characterized by a specific lag time. A very important, although not explicit, word in the last sentence is “slow”. In order to discover viscoelastic effects in regular liquids, we need to use ultra-high frequencies (characteristic time of an experiment in this case is about 10^{-7} s), whereas time delay effects, in deformations of concrete rods and plastic tubes under pressure, require years of observation (characteristic time is about 10^8 s). Moreover, one can treat deformations of stones as a very slow process, realizing that it requires geological periods of time (characteristic time is of the order of 10^{17} s; as we know only the Lord has enough time to observe it).

The dimensionless criterion called the Deborah Number, De, was introduced to be a measure of a ratio between characteristic time of observation, t_{obs}, and the time scale of inherent processes in a material, t_{inh}. Then

$$De = t_{obs}/t_{inh}$$

The physical meaning of the value t_{inh} is not identified here, and in fact, it can differ. In a general sense, t_{inh} characterizes the rate of inherent rearrangement of the material structure. Since the level of structure organization, its rupture and restoration can vary, we can find very different values of characteristic times for the same material. Therefore, in principle, different values of the Deborah Number are expected to exist.

The Deborah Number is especially important for viscoelastic phenomena because they always proceed in time. Since the time interval is very wide, we must encounter a situation when the Deborah Number is of the order of 1, i.e., an observer can "feel" that something happens with (or inside) a material. All this means that complete description of viscoelastic phenomena includes experiments which must occupy no less than 15 decimal orders along the time scale. Certainly, in the majority of cases, this is not very realistic. Therefore, two general approaches are usually taken to investigate viscoelastic phenomena:

- The measurement is done in a limited *window* along the time scale (for example, from 10^{-1} to 10^3s) and the experimental data extrapolated beyond the borders of the window
- Special methods are used to accelerate (or decelerate) viscoelastic processes and then empirical (or semi-theoretical) approaches applied to modify the time-scale. For example, one may increase temperature to accelerate the process. Then, it is assumed that the change in temperature is equivalent to some change in the time-scale (for example, what occurs at 100°C in 10 s requires 10^4 s at 20°C).

Both general approaches are empirical, and even in the best case, if they are based on some theoretical ideas, they may or may not be correct. Besides, any experimental data includes a scatter of points due to unavoidable errors of measurement. The scatter of predictions (extrapolations) from this not-ideally-clear window, with dispersed field points, is increasingly wider the farther we depart from the borders of the window. It is thus rather dangerous to make far extrapolations, even though it is very attractive to observe deformations during 10 h and predict further development of deformations for 10 years.

Viscoelastic phenomena belong to the fundamental rheological effects describing the relationship between stresses and deformations. A general theory of viscoelasticity is thus based on three-dimensional analysis and consideration of concepts as tensor values. Quite adequate understanding of basic ideas of viscoelasticity is available for uni-dimensional deformations. Especially, it is true, for small deformations when non-linear effects of any kind do not appear. In this case, it is not the mode of deformations which is important. That is why, in the following Sections of this Chapter, discussion of simple deformations and stresses *does not identify the geometrical mode of deformation.*

In specialized books, one can find a very rigorous and complete account of the theory of (linear) viscoelasticity. The first comprehensive account of the *linear theory of viscoelasticity* was published by B. Gross,[1] followed by several books containing mathematical foundations and main results.[2-4] There are also some textbooks containing not only main results of phenomenological theory but also numerous ideas concerning its physical meaning and illustrating applications.[5-7] It is now a homogeneous theory, based on solid mathematical background, containing all necessary theorems and answers to pertinent questions. However, following the line of this book, we do not attempt to prove statements of the theory and conclusions discussed below. The major points – physical ideas used in the theory, definitions, main results and relationships, not requiring high mathematical analysis – are included for the practical purpose of their application in observation of material behavior.

In order to complete this introduction, it is worth mentioning that those professionals who know the theory of electrical networks may notice that ideas, conclusions, and relationships of the theory of viscoelasticity can be restructured into terms of electrical networks by simple substitution of symbols. The same is true for the theory of dielectric properties of materials. The same mathematical structure of the theory is used, even though the physical objects differ.

7.2 DEFINITIONS

This Section is devoted to the quantitative theory of effects briefly described in Chapter 4.

Three fundamental experiments form the basis for the discussion:

- creep
- relaxation
- periodic deformations.

It is possible to discuss any other time-dependent stress or/and deformation modes, but these three are the simplest, and they allow us to define the main concepts used for description of viscoelastic effects.

7.2.1 CREEP

At constant stress, σ_o, applied at initial time (t = 0), slow (or delayed) development of deformations, $\varepsilon(t)$, is observed, and this phenomenon is called **creep**. The function $\varepsilon(t)$ can be considered as consisting of three components:

$$\varepsilon(t) = \varepsilon_o(t,\sigma_o) + \Psi(t,\sigma_o) + \frac{t}{\eta(\sigma_o)}\sigma_o \qquad [7.1]$$

where ε_o is an instantaneous deformation, $\Psi(t,\sigma_o)$ a function describing delayed development of deformations, $\eta(\sigma_o)$ viscosity, which (in a general case) can depend on stress, t current time.

Another form of Eq 7.1 is

$$\frac{\eta(t)}{\sigma} = I(t) = I_o(\sigma) + \psi(t,\sigma) + \frac{t}{\eta(\sigma)} \qquad [7.2]$$

where the value I(t) is called **compliance**, I_o an instantaneous compliance, and $\psi(t)$ a creep function. Subscript zero at σ is omitted in this equation.

As pointed out above, in formulating Eqs 7.1 and 7.2, the type of deformation (extension, shear, and so on) is not specific but it must be accepted that deformation is unidimensional.

A material is called **linear viscoelastic** if material parameters I_o, $\psi(t)$, and η do not depend on stress; in the opposite case, material has *non-linear viscoelastic behavior.*

It is necessary to separate two main cases shown in Figure 4.20:

- if η is unlimitedly high, the last member in Eq 4.2 is absent and we deal with *a solid viscoelastic body*. For linear viscoelastic solids, the value $\psi_\infty = \psi(t \to \infty)$ is limited and the sum

$$I_\infty = I_o + \psi_\infty \qquad [7.3]$$

  is called **equilibrium compliance**.
- For *viscoelastic liquids* (curve 2 in Figure 4.20), deformation increases unlimitedly due to the linear (in time) increase of input of the last item in Eq 7.2. For viscoelastic liquids, equilibrium compliance equals zero.

Accelerated growth of deformation in creep (as shown by the curve 3 in Figure 4.20) is characteristic for non-linear viscoelastic behavior and acceleration starts at lower deformations.

Measurements of creep in long-term loading of materials are widely used for many fabricated goods and parts of machinery, continuously exploited under stress; for example, pipes for transporting gases under pressure. In all these situations, creep has a detrimental effect on applied properties of materials. However, in technological practice, creep is used as a method to produce orientation in drawing of fibers, films, and so on, with posterior fixation of the oriented state.

7.2.2 RELAXATION

At constant deformation, ε_o, set at some initial moment of time, t = 0, we can observe slow decay of stresses in time $\sigma(t)$. This phenomenon is called **relaxation**. The function $\sigma(t)$ can be presented as consisting of two components

$$\sigma(t) = \Phi(t,\varepsilon_o) + E_\infty(\varepsilon_o)\varepsilon_o \qquad [7.4]$$

where $\Phi(t,\varepsilon_o)$ is a function describing decay of stresses and E_∞ represents a residual (non-relaxing) or equilibrium component of stress.

Another form of Eq 7.4 is

$$\frac{\sigma(t)}{\varepsilon_o} = \phi(t,\varepsilon) + E_\infty(\varepsilon) \qquad [7.5]$$

where $\phi(t,\varepsilon)$ is a function of stresses, called **relaxation function** (sometimes this function is called relaxation modulus) and E_∞ is called an **equilibrium modulus**.

A material is called linear viscoelastic if $\phi(t)$ and E_∞ do not depend on initial deformation, ε; in the opposite case, material exhibits non-linear relaxation. As a rule, even with non-linear behavior, E_∞ does not depend on ε, but the rate of relaxation represented by the function $\phi(t)$ does.

Similar to creep, it is reasonable to separate two main cases:

- if $E_\infty = 0$ material is a *viscoelastic liquid*
- if $E_\infty > 0$, it means that a material can support stresses and therefore it is considered a *viscoelastic solid*. In the latter case, the value

$$E_o = \phi(0) + E_\infty \qquad [7.6]$$

is called **initial** (or instantaneous) **modulus**.

Stress relaxation is a very important phenomenon in technological practice. If it occurs with too slow a rate, the material is capable of storing residual (frozen) stress, and this effect strongly influences its quality. A rapid relaxation can also have adverse effect in use of some materials. For example, seals should exclude gas or liquid leakages in equipments working under pressure. This can only be achieved if a seal is continuously stressed during exploitation; relaxation leads to loss of close contact between a seal and a solid wall of an apparatus.

7.2.3 PERIODIC OSCILLATIONS

It is the third well defined regime of deformations. The form of time-dependent periodic deformation can be arbitrary but the theory deals with harmonic oscillations. It is quite natural because a signal of any arbitrary form can be expanded into Fourier series to form a harmonic function.

For mathematical convenience, periodic signals can be written in complex exponential functions $\exp(i\omega t)$ using Euler's rule:

$$e^{i\omega t} = \cos\omega t + i\sin\omega t$$

It can be assumed that stress, $\sigma(t)$, changes as

$$\sigma(t) = \sigma_o e^{i\omega t} \qquad [7.7]$$

where σ_o is an amplitude of stress, and ω its frequency of oscillations.

One may expect that deformations will change periodically, and in the first approximation, $\varepsilon(t)$ is described by a harmonic function with some delay with respect to $\sigma(t)$. Then

$$\varepsilon(t) = \varepsilon_o e^{i(\omega t - \delta)} \qquad [7.8]$$

where ε_o is an amplitude value of deformations and δ the phase angle (i.e., a value characterizing the phase difference in oscillations of stresses and deformations); this value is also called **loss angle** and the physical meaning of this term is discussed below.

If deformation, not stress, is a preset function, i.e.

$$\varepsilon(t) = \varepsilon_o e^{i\omega t} \qquad [7.9]$$

then stress is changing according to the equation

$$\sigma(t) = \sigma_o e^{i(\omega t + \delta)} \qquad [7.10]$$

Certainly, Eqs 7.9 - 7.10 are equivalent to Eqs 7.7 - 7.8.

Now, let us introduce the main parameter used to characterize viscoelastic properties of a material measured by periodic oscillations. It is a **dynamic modulus** of elasticity, E*, determined as

$$E^* = \frac{\sigma_o}{\varepsilon_o} = \frac{\sigma_o}{\varepsilon_o}\left(\cos\delta + i\sin\delta\right) \qquad [7.11]$$

It is evident that E* is characterized by two parameters: its absolute value

$$E_o = \frac{\sigma_o}{\varepsilon_o} \qquad [7.12]$$

and phase angle, δ.

Both factors can depend on frequency and (in principle) on amplitude of deformation. For a linear viscoelastic body, the amplitude dependencies of E_o and

δ are absent, which is an additional definition of linear viscoelastic behavior.

Dynamic modulus can be represented by two elements

$$E^* = E' + iE'' \qquad [7.13]$$

where

$$E' = \frac{\sigma_o}{\varepsilon_o}\cos\delta; \quad E'' = \frac{\sigma_o}{\varepsilon_o}\sin\delta \qquad [7.14]$$

These parameters are called **real and imaginary components** of dynamic modulus, respectively, or E′ is called **storage modulus** and E′′ **loss modulus**.

Absolute value of dynamic modulus is expressed through E′ and E′′ as

$$|E^*| = [(E')^2 + (E'')^2]^{1/2} \qquad [7.15]$$

Instead of E^* and its components E′ and E′′, their reciprocal values can also be used. They are called **dynamic compliance**

$$I^* = I' - iI'' \qquad [7.16]$$

determined as

$$I' = \frac{\varepsilon_o}{\sigma_o}\cos\delta; \quad I'' = \frac{\varepsilon_o}{\sigma_o}\sin\delta \qquad [7.17]$$

The relationship between complex modulus and complex compliance is simple and evident

$$E^* I^* = 1 \qquad [7.18]$$

and relationships between components of E* and I* are established from Eq 7.18 according to the rules of operation with complex numbers. They can be written as

δ

$$E' = \frac{I'}{[(I')^2 + (I'')^2]^{1/2}}; \quad E'' = \frac{I''}{[(I')^2 + (I'')^2]^{1/2}} \qquad [7.19]$$

and *vice versa*:

$$I' = \frac{E'}{[(E')^2 + (E'')^2]^{1/2}}; \quad I'' = \frac{E''}{[(E')^2 + (E'')^2]^{1/2}} \qquad [7.20]$$

The last useful final expression in the theory of periodic oscillations is derived from Eqs 7.14 and 7.17. It connects loss angle with components of dynamic modulus and compliance:

$$\tan\delta = \frac{E''}{E'} = \frac{I''}{I'} \qquad [7.21]$$

When liquids are studied by a method of periodic oscillations, sometimes it is more convenient to use rates of deformation rather than deformations themselves. If $\varepsilon(t)$ is changing in accordance with Eq 7.8 then

$$\dot{\varepsilon} = \frac{d\varepsilon}{dt} = \varepsilon_o i\omega e^{i(\omega t-\delta)} = i\omega\varepsilon$$

A new parameter, characterizing viscoelastic properties and defined as regular viscosity by the ratio of stress to rate of deformation, can be introduced. This parameter is called **dynamic viscosity** and is expressed as

$$\eta^* = \frac{\sigma}{\dot{\varepsilon}} = \frac{\sigma_o}{\varepsilon_o\omega}(\sin\delta - i\cos\delta) = \eta' - \eta'' \qquad [7.22]$$

where

$$\eta' = \frac{\sigma_o}{\varepsilon_o\omega}\sin\delta = \frac{E''}{\omega}; \quad \eta'' = \frac{\sigma_o}{\varepsilon_o\omega}\cos\delta = \frac{E'}{\omega} \qquad [7.23]$$

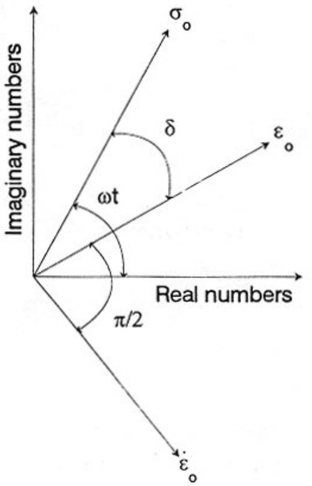

Figure 7.1. Graphic interpretation of oscillatory measurements: scheme illustrating interrelations of all main parameters of viscoelastic behavior and their definitions.

Any pair of the above-introduced parameters is a complete measure of viscoelastic properties of a material. It can be E′ and E′′ (or E′ and tanδ), or I′ and I′′ or η′ and η′′. All other parameters can be calculated from any pair by means of simple algebraic operations written above.

Concepts and definitions discussed above can be visually interpreted by the graph (Figure 7.1). Let deformations and stresses be depicted by vectors with their length equal to their amplitude values, $|\varepsilon_o|$ and $|\sigma_o|$, respectively. Vector of deformation rate is also given. Coordinate axes are formed by real and imaginary numbers. The angle between vectors of deformation and stress equals the loss angle δ. Let all vectors in Figure 7.1 rotate counter-clockwise with angular velocity ω. It means that the angle between the vector σ_o and abscissa equals ωt, and between the vector ε_o and abscissa is (ωt – δ).

This figure allows for the following interpretation of the main parameters considered in the theory of viscoelasticity. If we project the vector of stress onto the vector of deformation, the value of $\sigma_o \cos\delta$ and the ratio of this projection to the length of the vector of deformation gives the real component of dynamic modulus, E′. If we take the projection of σ_o onto the direction perpendicular to the vector of deformation and calculate the ratio of this projection (equal to $\sigma_o \sin\delta$) to the length of the vector of deformation, the imaginary part of dynamic modulus, E′′, is received.

If we project the vector of deformation onto the vector of stress and onto the perpendicular direction to find the ratios of lengths, the definition of I′ and I′′ is obtained. Then the analogous procedure with the vector of rate of deformation leads to the components of dynamic viscosity.

The graphic interpretation of oscillatory measurements allows one to treat linearity of viscoelastic behavior for a linear viscoelastic material:

- by changing the length of one of the vectors in Figure 7.1, all other vectors change proportionally to the first

- the angle between stress and deformation vectors does not depend on their lengths and does not change during rotation of all vectors at any angular velocity.

One more geometrical interpretation of viscoelastic behavior, very useful and utilized in practice, can be obtained from rearrangement of Eqs 7.7 and 7.8 and by excluding time as a parameter of these equations. The direct relationship between stress and deformation then has the following form:

$$\left(\frac{\sigma}{\sigma_o}\right)^2 + \left(\frac{\varepsilon}{\varepsilon_o}\right)^2 = \sin^2\delta + 2\left(\frac{\sigma}{\sigma_o}\right)\left(\frac{\varepsilon}{\varepsilon_o}\right)\cos\delta \qquad [7.24]$$

This equation is that of an *ellipsis*.

The following designations can be introduced in order to simplify the interpretation of experimental results:

$$x = \frac{\sigma}{\sigma_o}; \quad y = \frac{\varepsilon}{\varepsilon_o}$$

Then Eq 7.24 can be written as

$$x^2 + y^2 = \sin^2\delta + 2xy\cos\delta \qquad [7.25]$$

The characteristics (ellipsis) described by Eq 7.25 is drawn in Figure 7.2. Calculations show that the area of the ellipsis A is

$$A = \pi\varepsilon_o\sigma_o\sin\delta \qquad [7.26]$$

i.e., the area of the ellipsis is proportional to the amplitude values of stress and deformation and depends on loss angle, δ.

There are two limiting cases important for further interpretation:

- if $\delta = \pi/2$, then Eq 7.25 has the form:

  $$x^2 + y^2 = \sin^2\delta$$

  it means that an ellipsis degenerates into a circle;

- if $\delta = 0$, then Eq 7.25 degenerates into

$$x = y$$

which is an equation of a straight line.

Graphic interpretation of stress-vs-deformation dependence in the form of ellipsis allows one to make some comments concerning inputs of elastic and dissipative components in deformation of viscoelastic material. For this purpose, let us calculate the work, W, produced during a cycle of deformation of a viscoelastic body. This work is found as

$$W = \int_0^T \sigma(t)d\varepsilon \qquad [7.27]$$

where $T = 2\pi/\omega$ is a duration of an oscillation cycle.

Direct calculations show that the work, W, is

$$W = \pi\varepsilon_o\sigma_o\sin\delta \qquad [7.28]$$

The identity of expressions in Eqs 7.26 and 7.28 is obvious and gives the interpretation of the area of ellipsis in Figure 7.2 as the work produced during an oscillation cycle. Certainly, there is no elastic (stored) energy when a cycle is completed, because otherwise an unlimited increase in stored energy from cycle to cycle would be observed, which is physically impossible. That is why the energy calculated from Eq 7.28 reflects the work dissipated during a cycle of oscillation. The ellipsis, as in Figure 7.2, is called a **hysteresis loop** because it represents a delayed part of deformation.

Eq 7.28 allows one to propose the interpretation of a physical meaning of components of dynamic modulus and compliance. If we substitute expressions for E'' by I'', the following equation is obtained:

$$W = \pi\varepsilon_o^2E'' = \pi\sigma_o^2I'' \qquad [7.29]$$

Both values, E'' and I'', are measures of energy dissipation during periodical oscillations.

It is also possible to show that real components of dynamic modulus and compliance, E' and I', are measures of elasticity because energy stored (and then returned) during the cycle of oscillation is proportional to them.

The loss angle can be found from Figure 7.2 by the following simple method. The area of a rectangle circumscribed around an ellipsis is equal to $4\sigma_o\varepsilon_o$. The ratio of areas of an ellipsis to a circumscribed rectangle equals $\sin\delta/4$. Then it is possible to find the loss angle from this ratio without the measurement of amplitudes of stress and deformation. This approach is used in some standards, and instrumental measurements were introduced in studies of damping characteristics of rubbers and rubber compounds. Hysteresis loop surface area (see Figure 7.2) is a measure of mechanical losses on deformation.

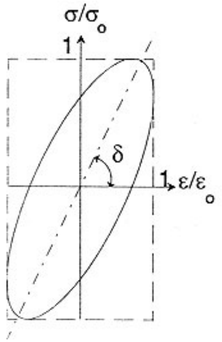

Figure 7.2. Ellipsis in stress - deformation coordinates as a representation of viscoelastic properties of material.

Now, we can come back to two limiting cases of the values of δ mentioned above. If $\delta = \pi/2$ and $\sin\delta = 1$, the energy dissipation is at its maximum, typical for liquid without any elastic properties. If $\delta = 0$ and $\sin\delta = 0$, there is no energy dissipation, corresponding to the other limiting case of an elastic material without viscous losses. In all other situations, intermediate cases are met in which the value of the loss angle characterizes the ratio of viscous-to-elastic properties in viscoelastic materials. By decreasing δ, and consequently decreasing viscous losses, material transits from pure viscous to pure elastic.

In real practice, viscoelastic materials are in the form of springs, rings, and so on. Engineering constructions must be as highly elastic as possible (losses must be low). Shock-absorbers, sound isolators, and materials for many other similar applications must possess a high dissipative function, meaning that the loss angle of such materials must be as close to $\pi/2$ as possible.

The above-formulated functions are used to describe viscoelastic effects and characterize properties of real materials. However, it is necessary to emphasize that the definition of all these functions implies that they must be defined (measured) in the range of their arguments (time or frequency as a value reciprocal to time) from zero and to infinity. It already has been mentioned that this is unreal, and such a requirement is the main problem in practical applications of the viscoelasticity theory. It is not a formal point but a serious physical limitation of the theory. It is easy to write equations including these limits, and below, many equations of this kind are presented, including the above-introduced parameters, because they are frequently used in the theory of viscoelasticity. At the same, it is very difficult to use equations in practice because input of some viscoelastic functions (creep, relaxation, dynamic modulus) beyond the limits of their direct measurement (beyond an experimental "window") can lead to uncertain errors in predicting deformation behavior of a real material. We shall revisit this problem in the following sections of this chapter.

7.3 PRINCIPLE OF SUPERPOSITION

The general theory of viscoelasticity is designed to answer two related questions:

- either functions, introduced for formal description of deformations or stresses in the fundamental experiments (creep, relaxation, periodic oscillation), are independent characteristics of material or they are inherently connected to each other
- if one or some basic functions of viscoelastic material are known (have been measured), can one describe its deformation-vs-stress behavior in any arbitrary mode of deformation (for example, find evolution of deformation for arbitrary history of loading)?

The answer to these questions is the main content of the theory of viscoelasticity. And this answer is: "yes", all fundamental functions are inherently related to each other, and "yes" to the second question means that we can describe deformational behavior of material if at least one basic viscoelastic function has been measured beforehand.

Both positive answers are founded based on the **principle of linear superposition** of stresses and/or deformations. This principle was formulated by Boltzmann.[8-11] The concept may have different forms, but the basic idea is related to the mutual independence of all consequent events happening to the material. In fact, it means that all materials are sufficiently weak, therefore they cannot change the mode of reaction to an external action. The material reacts to the next action as if no former action took place. In other words, the structure and properties of material are not changed, regardless of its deformation, and the last statement is a real physical meaning of the Boltzmann Principle.

Now, let us write the above-stated concept in the form of mathematical symbols. Let the initial stress, acting from the moment $t = 0$, be equal to σ_o. Then, deformations change according to Eq 7.2. At some point of time, t', let stress change by $\Delta\sigma$. The principle of linear superposition assumes that in this case, deformation changes accordingly:

$$\varepsilon(t) = \sigma_o \left[I_o + \varphi(t) + \frac{t}{\eta} \right] + \Delta\sigma \left[I_o + \varphi(T - t') + \frac{t - t'}{\eta} \right]$$

Stress can change at any given time which follows. For any such moment of time and any corresponding change of stress, one can add an independent item in the last equation for $\varepsilon(t)$.

Certainly, stress can change continuously, and bearing this in mind, we come to the final integral (instead of sum) formulation of the Boltzmann principle of linear superposition:

$$\varepsilon(t) = \int_0^t \left[I_o + \psi(t - t') + \frac{t - t'}{\eta} \right] d\sigma \qquad [7.30]$$

or

$$\varepsilon(t) = \int_0^t \frac{d\sigma}{dt'} \left[I_0 + \psi(t - t') + \frac{t - t'}{\eta} \right] dt' \qquad [7.31]$$

The analogous line of arguments can be used to describe changes in deformation, and in this case, Eq 7.5 is a starting-point. The final result is quite similar to Eq 7.31, and can be written as

$$\sigma(t) = \int_0^t \frac{d\varepsilon}{dt'} [\varphi(t - t') + E_\infty] dt' \qquad [7.32]$$

The pair of symmetrical Eqs 7.31 - 7.32 is called the **Boltzmann-Volterra equations**.[12,13] They are the mathematical formulation of the **principle of linear superposition**.

It is possible to illustrate the behavior of viscoelastic material according to the principle of superposition by the following example for elastic recoil (retardation) after forced deformation of a body.

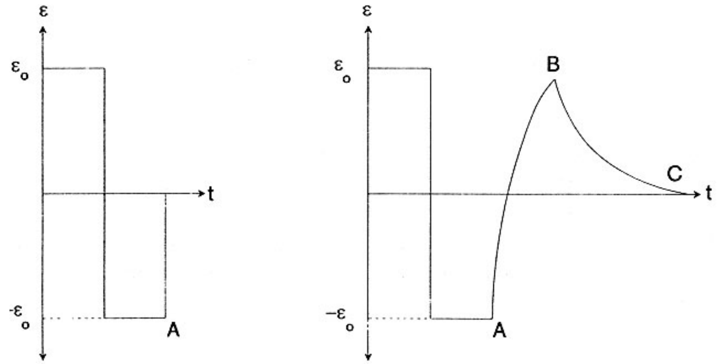

Figure 7.3. Deformation history (a) and the reaction (from the point A when outside force is removed) of ideal elastic (b) and viscoelastic (c) materials.

Let the history of deformations be as shown in Figure 7.3a: the external force created deformation, ε_o, and then (very rapidly) the same deformation but with the opposite sign, $-\varepsilon_o$. When the force was acting during two short periods of time, one could neglect partial relaxation at deformations ε_o and $-\varepsilon_o$. The question is: what happens if, at the moment A, the external force is removed? Ideal elastic body immediately returns to its initial state, as shown by the vertical line from the point A in Figure 7.3b. The behavior of viscoelastic body is quite different, as illustrated by the line ABC in Figure 7.3c. The first part of this line, AB, is retardation from the second deformation, $-\varepsilon_o$, not to zero but to a state determined by the first deformation, ε_o. Only after that slow (delayed) action, a return to the zero state occurs.

Another very interesting (and important for technological applications) example of influence of deformational prehistory on the behavior of a material is related to the processing of polymers (thermoplastics and rubber compounds). During extrusion of continuous profiles, a molten material moves between a screw and a barrel of an extruder, then it passes transient channels. Finally, it is shaped in an outlet section of a die. It would be desirable that the shape of a final profile is equivalent to the shape an outlet section of a die. On the contrary, the material continues to react to all deformations which took place before the outlet section of a die. As a result, distortion of its shape occurs; therefore, the final section of a part can be very different than expected. The distortions can be so severe that "melt fracture" (shown in Figures 4.14 and 4.15) is observed.

These and many other examples are characteristic for technological practice. Viscoelastic materials have *fading memory of the history of previous deforma-*

tions. In this sense, the integrals 7.31 and 7.32 are called **hereditary integrals** because they summarize events which took place before the current moment of time and are responsible for the stress (or deformation) state of a material at the current moment.

The relaxation function $\phi(t)$ is a decreasing function. Therefore, its values are higher when the argument is smaller. It means that the changes of deformation, which happened earlier, influence stress in lesser degree than later changes. In the first case, the value of the argument (t-t′) in Eq 7.32, for the fixed moment of time, t, is smaller than for events which happened later because values of t′ are smaller. In other words, a material continuously "forgets" what happened before and therefore integrals in Eqs 7.31 and 7.32 form a model of material with "fading memory".

It is interesting to outline the limiting cases. They are:

- liquid which "forgets" everything immediately (energy of deformation completely dissipates); in this case, the integral 7.32 transforms to the Newton-Stokes Law
- solid which "remembers" everything (energy of deformation is completely stored), and in this case, the integrals 7.31 and 7.32 transform to the Hooke Law.

Both Eqs 7.31 and 7.32 contain deformation and stress, and each of them can be treated as an equation either of stress or deformation. Eq 7.31 determines the development of deformations for known evolution of stresses. It can be considered as an integral equation for $\sigma(t)$ if the function $\varepsilon(t)$ is known. The same is true for Eq 7.32. Therefore, it is possible to exclude these functions by substituting, for example, the function $\varepsilon(t)$ from Eq 7.31 to the right side of Eq 7.32. After some formal mathematical rearrangements, the relationship between rheological parameters does not contain either $\sigma(t)$ nor $\varepsilon(t)$. The resulting equation includes creep and relaxation functions in the following form:

$$E_\infty I_o + I_o \varphi(t) + E_\infty \left[\frac{t}{\eta} + \psi(t) \right] + \int_0^t \varphi(t') \left[\frac{1}{\eta} + \frac{d\psi(t-t')}{d(t-t')} \right] dt' = 1 \qquad [7.33]$$

where E_∞ is an equilibrium modulus, I_0 an instantaneous compliance, η viscosity, $\phi(t)$ a relaxation function, and $\psi(t)$ creep function.

Eq 7.33 shows that the relaxation and creep functions are not independent but related to each other by the integral equation. If one of these functions is known (measured, calculated, assumed), the other can be found from Eq 7.33. This equation formally, and quite rigorously, confirms the above-formulated statement that the behavior of material, in different modes of deformations, is governed by the same inherent properties.

Eqs 7.31 and 7.32 give mathematical ground for calculation of stress-vs-deformation relationship at any arbitrary path of material loading. The only essential limitation in application of these equations is the requirement of linearity of rheological behavior of a medium, i.e., independence of all material constants and functions entered to these equations (instantaneous compliance, equilibrium modulus, viscosity, relaxation and creep functions) on stresses and deformations.

Certainly, Eqs 7.31 and 7.32 are rheological equations of state for viscoelastic materials. It is necessary to remember that everything discussed above is related to "a point" in the sense as adapted for a Newtonian liquid and a Hookean solid and in general for any rheological equation of state. In order to find stress-deformation distribution throughout a body, one must combine these equations with equilibrium conditions (equations of conservation, introduced in Chapter 2) and appropriate boundary conditions as suggested in Chapters 5 and 6 for any liquid and solid.

7.4 RELAXATION AND RETARDATION SPECTRA

Relaxation, $\varphi(t)$, is a decreasing (at least not increasing) function of time. As a first approximation, it is reasonable to estimate it by an exponential function:

$$\varphi(t) = E_o e^{-t/\theta} \qquad [7.34]$$

where E_o is a instantaneous modulus and θ is a value called a **relaxation time**.

Relaxation process is described by a single exponential function called Maxwell (or Maxwellian) relaxation. However, it is a rather rough approximation and it can be improved by increasing the number of exponents, i.e., by expansion of $\varphi(t)$ into a sum of N exponents:

$$\varphi(t) = \sum_{i=1}^{N} E_i e^{-t/\theta_i} \qquad [7.35]$$

$$E_o = \sum_{i=1}^{N} E_i$$

where E_i are called partial moduli, and θ_i are the set (or a spectrum) of relaxation times.

Such spectrum can be called *discrete* and can be drawn by a set of lines as in Figure 7.4, where each value of E_i (length of a line) is put in correspondence to its argument equal to θ_i. In the limiting case, the lines in Figure 7.4 can fill all the graph if they are situated very close and their tops form a continuous curve. In this limiting case, we have the transition from the sum in Eq 7.35 to the integral

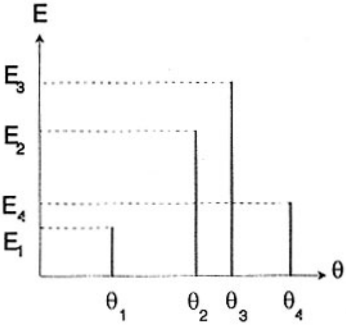

Figure 7.4. Discrete relaxation spectrum.

$$\varphi(t) = \int_0^{\infty} F(\theta) e^{-t/\theta} d\theta \qquad [7.36]$$

where the value $F(\theta)d\theta$ plays a role of a partial modulus as in Eq 7.35 and the function $F(\theta)$ is called a **relaxation spectrum** or a *distribution of relaxation times*.

There is a mathematical theorem stating that any decreasing function (in our case, the relaxation function, $\varphi(t)$), of any kind can be represented by its exponential image, i.e., by the integral (Eq 7.36). This statement leads to the conclusion that there is an unambiguous correspondence between any relaxation function, $\varphi(t)$, and the relaxation spectrum, $F(\theta)$.

In principle, a relaxation spectrum can be found as a solution of the integral in Eq 7.36. Certainly, it is always possible to know the analytical form of the function $\varphi(t)$ in its full interval from 0 to ∞. It appears simple in a theoretical approach, but not so easy in treatment of experimental data.

There are two reasons complicating a problem of the transition from experimental points to solution of the integral Eq 7.36. Both reasons already have been mentioned above: the first is an uncertainty in behavior of an experimental function beyond the borders of measurements (close to zero and at high values of the argument, at $t \to \infty$), and the second concerns the natural scatter of experimental points, which makes the analytical approximation of these points, and extrapolation beyond the experimental window, an ambiguous procedure.

It is very important to know the relaxation spectrum because in many theoretical investigations a relaxation spectrum, is directly related to molecular movements and thus to molecular structure of matter. Therefore, many different methods were proposed which give a solution of this problem. Below, comments are included concerning their validity.

7.4.1 CALCULATING CONTINUOUS SPECTRUM

The method is based on direct solving of Eq 7.36. There are two possible ways to do so. The first consists of analytical approximation of experimental points by appropriate formula and direct solving of Eq 7.36 using numerous published tables of conversion of exponential images. The error of approximation must be lower than an experimental error, and many such analytical approximations are possible. Each of them gives a different spectrum.[1-6] If the error of approximation is sufficiently low, it does not yet imply that the error of a calculated spectrum is acceptable.

It is also possible to use the second, rather old, method[6] of finding a rough solution of Eq 7.36. For this purpose, one can substitute an exponential function in Eq 7.36 by its approximate expression:

$$\exp(-t/\theta) \approx 1 \quad \text{at } t/\theta < 1; \quad t < \theta$$
$$\exp(-t/\theta) = 0 \quad \text{at } t/\theta > 1; \quad t > \theta$$

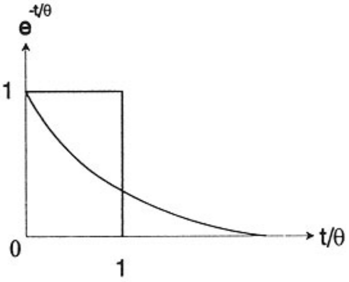

Figure 7.5. Stepwise change of exponential function to calculate a spectrum (first approximation).

The idea of this (first order) approximation is seen from Figure 7.5. The continuous exponential curve is changed by an abrupt step. Eq 7.36 becomes:

$$\varphi(t) \approx \int_{\theta}^{\infty} F(\theta)d\theta \qquad [7.37]$$

In fact, it means that a term on the right side of Eq 7.36 is omitted on the basis that the exponential decay will suppress the input from the function F(θ), assumed to be rather low. The error of this approximation is unknown. Due to this process, a very simple formula for calculation of F(θ) is obtained by differentiating both sides of Eq 7.37 by the lower limit of the integral:

$$F(\theta) = -\frac{d\varphi(t)}{dt} \quad \text{at } t = \theta \qquad [7.38]$$

The idea of this method can be used for higher approximations but the same main disadvantages of uncertain errors still exist.

7.4.2 CALCULATING DISCRETE SPECTRUM

The practice of treating real experimental data of rheological investigations shows that, in fact, any relaxation curve (decay of stresses) can be approximated by the sum of 4-5 or (in the worst case) of 7-8 exponential items. A very limited number of relaxation times is thus needed to describe experimental points with permissible error within scatter of measurements.

Standard computer procedures of minimizing an error in finding constants of some analytical formula are also available. This problem was under discussion from the beginning of application of the linear theory of viscoelasticity to real experimental data and continues to be the focus of interest. The most important goal is to minimize non-linear functional errors to which numerous publications were devoted.[14-18] In this case, it is a sum of N exponents with unknown weights E_i and values of θ_i. In this approach, one begins with N = 1 and increases the number of exponents. Each step permits on to decrease the error of approximation. The last step and the final number of exponents is when an error of approximation becomes lower than permissible error of experiment.

In some theories, the set of relaxation times appears to be dependent but follows the definite rule. For example, the row of relaxation times obeys the following rule:

$$\theta_i = \theta_o^{-ni}$$

where θ_o and n are constants (e.g., n = 2) and i are integers (i = 0, 1, 2, 3...).[19] It limits the possibility to vary the parameters of a relaxation spectrum because there are only two independent parameters (θ_o and n); moreover, since n is a result of molecular model calculations it cannot be treated as a fully independent parameter. Now the relaxation function takes the following form:

$$\varphi(t) = \sum_{i=1}^{\infty} E_i \theta^{-ni} \qquad [7.39]$$

The procedure minimizes error of approximation but the set of constants under search (E_i) is different from the general case based on Eq 7.35.

According to this approach, it is irrelevant to search for a "true" number of exponents (or relaxation times) in a discrete spectrum because the procedure of approximation should only be continued up to the limit of experimental error, after which further effort is inconsequential. The minimal number of exponents which correctly (within the limits of experimental error) describe results of measurements should be used.

Discussion of the relaxation function, $\varphi(t)$, can be almost repeated word for word as regards the creep function, $\psi(t)$. In the latter case, the resulting equation is as follows:

$$\psi(t) = \sum_{i=1}^{\infty} [I_i (1 - e^{-t/\lambda_i})] \qquad [7.40]$$

or in the form of the continuous spectrum:

$$\psi(t) = \int_0^{\infty} \Phi(\lambda)(1 - e^{-t/\lambda}) d\lambda \qquad [7.41]$$

where $\Phi(\lambda)$ is called a **retardation spectrum** or a *distribution of retardation times.*

The introduction of the integral kernel in Eq 7.40 in the form $(1 - e^{-t/\lambda})$ instead of $e^{-t/\theta}$ is explained by the fact that $\psi(t)$ is increasing, not decreasing (as $\varphi(t)$), though its mirror reflection, or elastic recoil function, is also a decreasing function, as is shown in Figure 4.20, curve 1.

The change of an exponent function $e^{-t/\theta}$ for $(1 - e^{-t/\lambda})$ leads to small variations in methods of approximation of spectrum. Instead of the step shown in Figure 7.5, one may write the following (first order) approximate equalities:

$$1-e^{-t/\lambda} \approx 0 \quad \text{at } t/\lambda < 1; \;\; t < \lambda$$

$$1-e^{-t/\lambda} \approx 1 \quad \text{at } t/\lambda > 1; \;\; t > \lambda$$

Graphic interpretation of this approximation is essentially the same as in Figure 7.5, with an exception that the mirror reflection of Figure 7.5 is considered.

Discussion in relation to a relaxation spectrum, including arguments concerning methods of its calculation, holds true for a retardation spectrum.

In real practice, the measurement of relaxation and retardation (or creep) is performed for as wide a time range as possible to cover at least some decimal orders of the argument. It is analogous to determining a flow curve (Chapter 5) in a wide range of shear rates. The linear time scale is changed to logarithmic in order to make experimental results easier to visualize (the same method was used for flow curves in Chapter 5). This conversion is expressed by the following formulas:

$$\varphi(t) = \int_{-\infty}^{\infty} H(\ln\theta) e^{-t/\theta} d\ln\theta \qquad [7.42]$$

and

$$\psi(t) = \int_{-\infty}^{\infty} L(\ln\lambda) e^{-t/\lambda} d\ln\lambda \qquad [7.43]$$

with the following obvious relationships between linear and *logarithmic spectra*

$$H(\ln\theta) = \theta F(\theta) \qquad [7.44]$$

and

$$L(\ln\lambda) = \lambda \Phi(\lambda) \qquad [7.45]$$

The last problem to be discussed in this section concerns the interrelation between distribution of relaxation and retardation times. *They are not equivalent*, though certainly they both originate from the same molecular phenomena and thus are closely related to each other.

The existence of interrelation between relaxation $F(\theta)$ and retardation $\Phi(\lambda)$ spectra can be proven if we take into account that $F(\theta)$ represents a relaxation function, $\Phi(\lambda)$ represents a creep function, and both are connected by Eq 7.33. It is illustrated in Figure 7.6. One can expect that a relationship between spectra $F(\theta)$ and $\Phi(\lambda)$ also exists.[20]

If one of the pair of spectra is continuous, the second one is also continuous, though they are not equivalent. If a relaxation spectrum is discrete, then a retardation spectrum is also discrete. Besides, there is an interesting point rigorously proven in the theory regarding correlation of numbers and positions of lines in a pair of discrete spectra. In viscoelastic liquid ($\eta < \infty$ and $G_\infty = 0$), the number of members (lines) in a relaxation spectrum is larger by one than the number of members in a retardation spectrum, and the lines of a retardation spectrum are arranged between the lines of a relaxation spectrum. For example, in Maxwellian relaxation there is one relaxation time (Eq 7.34) but the retardation spectrum is empty (no lines) and deformation of a Maxwellian viscoelastic liquid at constant stress occurs without delay. In a viscoelastic solid, the number of lines in both spectra is the same.

7.5 DYNAMIC AND RELAXATION PROPERTIES - CORRELATIONS

The dynamic characteristics (components of dynamic modulus and compliance) can be correlated with the relaxation properties of material. Certainly, it can be done based on the fundamental principle of linear superposition. In this section, main theoretical results of correlations between dynamic and relaxation properties are discussed.

The components of the dynamic modulus are expressed through a relaxation function as

$$G'(\omega) = \omega\int_0^\infty \varphi(t)\sin\omega t\,dt \qquad [7.46]$$

The inverse relationships, i.e., solution of Eqs 7.45 and 7.46, have the following form:

$$G'' = \omega\int_0^\infty \varphi(t)\cos\omega t dt \qquad [7.47]$$

For a relaxation function φ(t), which is calculated from components of the dynamic modulus, it has a similar form:

$$\varphi(t) = \frac{2}{\pi}\int_0^\infty \frac{G'(\omega)}{\omega}\sin\omega t dt \qquad [7.48]$$

and

$$\varphi(t) = \frac{2}{\pi}\int_0^\infty \frac{G''(\omega)}{\omega}\cos\omega t dt \qquad [7.49]$$

Two main conclusions can be drawn from Eqs 7.46 to 7.49:

- components of the dynamic modulus can be calculated if a relaxation function was measured (and *vice versa*)
- accuracy of such calculations is limited by the need to find the integrals in these equations in limits from 0 to ∞, and uncertain input of “tails" of functions on the right side of these integrals.

Analogous equations can be established for the components of dynamic compliance. Rigorous calculations give the following results:

$$I'(\omega) = \int_0^\infty \frac{\partial\psi}{\partial t}\cos\omega t dt \qquad [7.50]$$

$$I'' = \int_0^\infty \frac{\partial\psi}{\partial t}\sin\omega t dt \qquad [7.51]$$

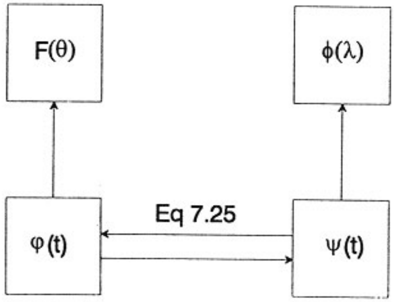

Figure 7.6. Structure of interrelations between relaxation and retardation spectra.

The inverse relationships for a creep function can also be written. They are quite analogous to Eqs 7.48 and 7.49, with an evident change of components of modulus for compliance and relaxation function for a derivative of a creep function.

The same conclusions apply to the possibility of a mutual correlation between dynamic compliance and creep function, as for the correlation between dynamic modulus and a relaxation function as discussed above.

The main sense of all equations given in this section is, first of all, to demonstrate the existence of relationships for all viscoelastic characteristics under discussion (they can be used for mutual calculations), and secondly, to emphasize the fact that all these relationships are represented by the *integral equations with infinite limit*, which complicates practical applications of these relationships.

Figures 7.6 and 7.7 show that components of dynamic modulus and compliance can also be expressed through relaxation (retardation) spectra. The equations below give a final result for $G^*(\omega)$:

$$E'(\omega) = \int_0^\infty F(\theta) \frac{(\omega\theta)^2}{1 + (\omega\theta)^2} \qquad [7.52]$$

$$E'' = \int_0^\infty F(\theta) \frac{(\omega\theta)}{1 + (\omega\theta)^2} \qquad [7.53]$$

Analogous equations can be written for $I^*(\omega)$, and they are

$$I'(\omega) = \int_0^\infty \Phi(\lambda) \frac{1}{1 + (\omega\lambda)^2} d\lambda + I_o \qquad [7.54]$$

$$I'' = \frac{1}{\omega\eta} + \int_0^\infty \Phi(\lambda)\frac{(\omega\lambda)}{1+(\omega\lambda)^2}d\lambda \qquad [7.55]$$

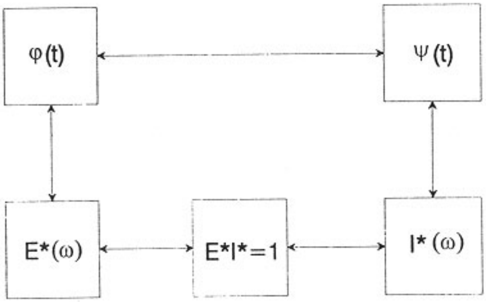

Figure 7.7. Structure of interrelations between relaxation characteristics of a viscoelastic material including dynamic modulus and compliance.

All these relationships have a structure very similar to the equations discussed above. They show that it is possible to establish correspondence between dynamic properties and relaxation spectra, but real calculations are rather complex because of integral equations with infinite limits.

Inverse transforms of Eqs 7.52 to 7.55 cannot be expressed in analytical form for arbitrary dynamic functions. It can be illustrated by constructing the first approximation formula related to relaxation spectrum and dynamic modulus.[22,23] As in Figure 7.5, we change the kernel in the equation for dynamic modulus stepwise:

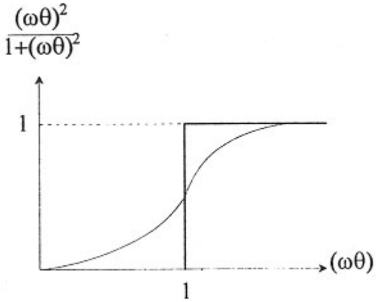

Figure 7.8. Stepwise change of the kernel in the integral equation for dynamic modulus to calculate a spectrum (first approximation).

$$\frac{(\omega\theta)^2}{1+(\omega\theta)^2} \approx 0 \text{ at } \theta < \omega^{-1}$$

$$\frac{(\omega\theta)^2}{1+(\omega\theta)^2} \approx 1 \text{ at } \theta > \omega^{-1}$$

The meaning of this approximation is illustrated in Figure 7.8. Then, Eq 7.51 changes to

$$E' \approx \int_{\omega^{-1}}^\infty F(\theta)d\theta$$

After differentiating it by the lower limit of integral, the following approximate equation for calculating a relaxation spectrum by dynamic modulus is obtained:

$$F(\theta) \approx \frac{\omega^2 dE'(\omega)}{d\omega} \quad \text{at } \theta = \omega^{-1}$$

Quite analogous equations can be written for all other dynamic functions under discussion. Their accuracy is limited by an uncertain input of the “tail” of a function used for calculations which has been cut off because of change in the kernel in the integral equation by a rather rough step approximation – a common feature of all approximations used in solving integral equations applied in the theory of linear viscoelasticity

Equations written in the last two sections and schemes in Figures 7.6 and 7.7 give the positive answer to the main question on the theory formulated above: all viscoelastic characteristics of a material are related to each other and can be mutually calculated. However, this answer is partially positive because of inevitable complications of these calculations, due to the special form of equations connecting all viscoelastic functions.

7.6 RELATIONSHIPS BETWEEN CONSTANTS

In the main definitions and in all equations of the theory of viscoelasticity there are some constants representing limiting cases (at $t = 0$ and $t \rightarrow \infty$) of stresses and deformations. These constants are:

η - viscosity at steady flow (constant when liquid is linear or Newtonian)
I_o - instantaneous compliance
I_∞ - equilibrium compliance
E_∞ - equilibrium modulus
E_o - instantaneous modulus.

Discussion below concentrates on establishing the relationships between these constants and relaxation characteristics of a material, such as creep and relaxation functions, and a relaxation spectrum. To begin, it should be repeated that some of the constants are characteristics for either viscoelastic solid or viscoelastic liquid, which causes relationships between the constants to be different for these two types of viscoelastic materials.

7.6.1 VISCOELASTIC SOLID

The definition of a solid is

$$\frac{1}{\eta} = 0$$

It is a rather formal definition because material with viscosity of the order 10^{20} Pa·s (inorganic glass) is a solid, though formally it is a liquid having very high viscosity. Nevertheless, this formal definition is important for rigorous classification of viscoelastic materials.

Then, for a viscoelastic solid, when stress is preset:

$$I_o = \frac{1}{G_o} = \frac{1}{G_\infty + \varphi(0)} \qquad [7.56]$$

and

$$I_\infty = I_o + \psi(\infty) \qquad [7.57]$$

For a viscoelastic solid when deformation is preset:

$$E_o = I_o^{-1} \qquad [7.58]$$

$$E_\infty = \frac{1}{I_o + \psi(\infty)} = I_\infty^{-1} \qquad [7.59]$$

and

$$E_o - E_\infty = \varphi(0) = \frac{\psi(\infty)}{I_o[I_o + \psi(\infty)]} = \frac{I_\infty - I_o}{I_\infty I_o} \qquad [7.60]$$

7.6.2 VISCOELASTIC LIQUID

The definition of a liquid is

$$\eta < \infty; \quad E_\infty = 0$$

Then, one can derive the following relationships between the constants:

$$E_o = I_o^{-1} = \varphi(0) = \int_0^\infty F(\theta)d\theta \qquad [7.61]$$

All other relationships vanish because $E_\infty = 0$.

Two of the relationships listed above are of special interest: equation expressing instantaneous modulus by "zero" moment and viscosity by " first" moment of a relaxation spectrum:

$$E_o = \int_0^\infty F(\theta)d\theta; \quad \eta = \int_0^\infty \theta F(\theta)d\theta \qquad [7.62]$$

Then, it is possible to determine a certain "average" relaxation time, θ_{av}, as a ratio η / E_o

$$\theta_{av} = \frac{\eta}{E_o} = \frac{\int_0^\infty \theta F(\theta)d\theta}{\int_0^\infty F(\theta)d\theta}$$

Certainly it is possible to define other characteristics of "averaged" relaxation times, such as ratio of two consequent moments of a relaxation spectrum.

7.7 MECHANICAL MODELS OF VISCOELASTIC BEHAVIOR

Theory of viscoelasticity is treated above as a *phenomenological generalization* of ideas concerning delayed effects in deformations or superposition of elastic storage and viscous dissipative losses of energy during deformation. The concepts of relaxation or slow return to the equilibrium state and creep can also be introduced from more general physical reasoning and illustrated by very visual examples.

Let the state of a system be characterized by a certain parameter x and its value corresponding to the equilibrium state by x_∞. Then, let us consider the possible reaction of a system taken out of its equilibrium state. A system always tends to return to the equilibrium state. Let us assume, according to the Maxwell fundamental idea, that the rate of an approach, from any arbitrary state, to the equilibrium state is proportional to the degree of divergence from the equilibrium.

In the language of mathematics, this concept can be written in the form of a kinetic equation

$$\frac{dx}{dt} = -\frac{1}{\theta}(x - x_\infty)$$

where $1/\theta$ is a kinetic factor, characterizing the rate of changes in the state of a system.

The integral of this differential equation is

$$x = x_o e^{-t/\theta} + x_\infty \qquad [7.63]$$

where x_o is an initial value of x.

It is quite evident that if stress is substituted by parameter x, the equation describes mechanical relaxation, with θ being a characteristic time of relaxation of this process and x_∞ the residual stress, which equals zero for liquid.

Now, let us imagine a mechanical model constructed from a combination of a spring and a plunger in a cylinder filled with a liquid (damper), with these two elements connected in series (Figure 7.9). The spring is a model of an ideal Hookean solid and its deformation is described by the equation

$$X_H = \frac{F}{E}$$

where X_H is a displacement of a lower end of a spring from the equilibrium (non-loaded) state, E is the modulus of a spring, and F is the force applied at the bottom of the model, causing its deformation.

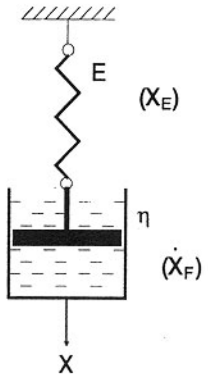

Figure 7.9. Mechanical model of Maxwellian relaxation: spring and a plunger in a cylinder with viscous liquid (damper), connected in series.

A plunger moving in a cylinder filled with viscous liquid (damper) is a model of an ideal Newtonian liquid and its deformation is described by the equation

$$\dot{X}_N = \frac{dX_N}{dt} = \frac{F}{\eta}$$

where dX_N/dt is the rate of displacement of a plunger, η viscous resistance to a movement of the plunger in the cylinder, proportional to viscosity of liquid, F the same force which caused the deformation of the spring.

It is evident that the full displacement of a lower point of the model in Figure 7.9 is a sum of the two components: the displacement of the bottom of a spring and the movement of a plunger. It can be written as follows:

$$X = X_H + X_N$$

and

$$\dot{X} = \dot{X}_H + \dot{X}_N$$

After substituting expressions for displacement of the elements of the model, the equation for deformation of the whole model is obtained:

$$\frac{\dot{F}}{E} + \frac{F}{\eta} = \dot{X} \qquad [7.64]$$

Let us analyze the behavior of the mechanical model in Figure 7.9 (called **Maxwell model**)when the step displacement is set up, or in other words, let us find a *relaxation function of this model*. Integrating Eq 7.64 at the appropriate boundary conditions gives

$$F(t) = X_o E e^{-tE/\eta}$$

or

$$\frac{F(t)}{X_o} = \varphi(t) = E e^{-t/\theta} \qquad [7.65]$$

where X_o is an initial displacement of the bottom of the model, and $\theta = \eta / E$ a constant which can be called a relaxation time.

The complete equivalence of Eq 7.64 to expressions for relaxation of a liquid having a single relaxation time (Eq 7.34) and the Maxwell concept of relaxation as delayed approach to the equilibrium state (Eq 7.63) are quite evident. That is why the model shown in Figure 7.9 is called the model of the *Maxwell liquid*. The rheological equation of state, Eq 7.64, is called the equation of **linear Maxwell viscoelastic liquid**.

The rheological properties of a linear Maxwell viscoelastic liquid are characterized by the following parameters: viscosity, η, instantaneous modulus, E, and the components of dynamic modulus which are expressed as

$$G'(\omega) = E \frac{(\omega\theta)^2}{1 + (\omega\theta)^2}; \quad G'' = E \frac{\omega\theta}{1 + (\omega\theta)^2}$$

and

$$\tan\delta = (\omega\theta)^{-1}$$

Certainly the mechanical model drawn in Figure 7.9 is a model of liquid because equilibrium modulus is zero.

A creep function of a Maxwell liquid is described by the equation

$$\psi(t) = \frac{\varepsilon(t)}{\sigma_o} = \frac{1}{E} + \frac{t}{\eta}$$

This equation shows that, when a constant stress is preset, a step-like deformation equals σ_o / E, and there is no delay in deformation.

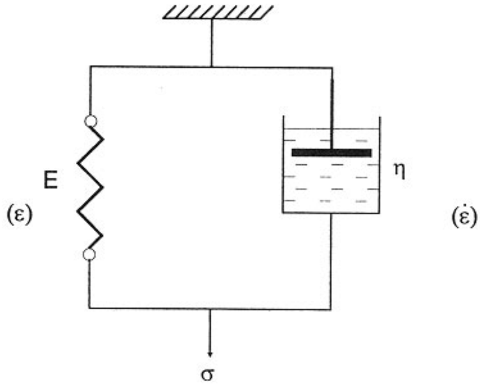

Figure 7.10. Mechanical model of delayed (Kelvin-Voigt) creep: spring and a plunger in a cylinder with viscous liquid (damper) connected in parallel.

The mechanical model, represented in Figure 7.9, reflects the viscoelastic behavior of a single-relaxation-time liquid. In line with phenomenological generalization of a single-time-relaxation in Eq 7.34 to the sum of exponents in Eq 7.35, we can obtain the same result using mechanical models. This aim is reached by the same method of summarizing exponential items, as in Eq 7.35. Indeed, let us join in parallel a number of Maxwell models with different values of parameters. Then, the relaxation process, in this multi-relaxation-time Maxwell model, is described by Eq 7.35 with a set of relaxation times, having different value for every branch of a generalized model.

The rheological behavior of the generalized model is described by an equation of the differential type containing time derivatives of stress and deformation (Eq 7.68).

Another way of constructing mechanical models consists in joining a spring and a plunger moving in a cylinder with viscous liquid (damper), not in series, as in Figure 7.9, but in parallel, as shown in Figure 7.10. This model is called the **Kelvin-Voigt model**. The mechanical properties of both elements in this model are the same as in the Maxwell model, but, contrary to the latter (deformations of the components are added), stresses acting in the branches of a model are added. The following equation describes the rheological properties of the Kelvin-Voigt model:

$$E\varepsilon + \eta\dot{\varepsilon} = \sigma \qquad [7.66]$$

In the standard experiment, when $\sigma = \sigma_o = \text{const}$, the following creep function of the Kelvin-Voigt model takes place:

$$\psi(t) = \frac{\varepsilon(t)}{\sigma_o} = \frac{1}{E}(1 - e^{-t/\lambda}) \qquad [7.67]$$

where σ_o / E is the initial deformation, and consequently $E^{-1} = I_o$ is instantaneous compliance, and $\lambda = \eta / E$ is a retardation time.

It can be easily shown that the Kelvin-Voigt model represents the viscoelastic behavior of a solid, because the model conserves residual stresses equal to $E\varepsilon_o$, where ε_o is an instantaneous deformation. This model represents the properties of a non-relaxing body (relaxation time is equal to infinity).

Generalizing the serially joined elementary models, one obtains the model of viscoelastic solid behavior with a set of retardation times. Creep of the multi-constant Kelvin-Voigt model is described by Eq 7.40.

In a general case deformation properties of any mechanical model constructed from the Maxwell and Kelvin-Voigt elements can be represented by the equation:

$$\sum_{n}^{N} A_n \frac{d^n\varepsilon}{dt_n} = \sum_{m}^{M} B_m \frac{d^m\sigma}{dt^m} \qquad [7.68]$$

where the order (M and N) of sums in Eq 7.68 depends on the structure of a mechanical model, and A_n and B_m are material constants of a model.

Thus, any mechanical model leads to the equation describing mechanical behavior of a material by a differential equation and this is **equation of state of differential type**, contrary to **equation of state of integral type** such as Eqs 7.31 and 7.32. It means that *differential equations correspond to line (discrete) relaxation spectra, while integral equations correspond to continuous spectra*. This difference is not very important because any discrete spectrum can be approximated by a smooth curve and any continuous spectrum can be approximated by a set of lines; nevertheless, this difference exists and can be used in applications for real calculations.

Whether the model represented by Eq 7.68 corresponds to a viscoelastic liquid or to a viscoelastic solid is determined by the junior member of the left-hand sum. If this member is of the zero-th order, i.e., calculation of the sum starts from n = 0, it is a model of a solid. If the zero-th member is absent and the junior member is of the first order (n = 1), it is a model of liquid. For the Maxwell model, N = 1 (there is only one member in the left-side sum) and M = 1. For the Kelvin-Voigt model also, N = 1 (but we have two members in the left-side sum because the junior member corresponds to n = 0) and M = 0 (only one member is present in the right-side sum).

Varying the order of differential operators in Eq 7.68 and values of parameters A_n and B_m, we are able to describe various special cases of viscoelastic behavior of a material with any arbitrary relaxation properties. There is one fundamental limitation: Eq 7.68 describes mechanical properties of a **linear** viscoelastic material and cannot go beyond this limit if some modification of the initial idea is not introduced.

After the Maxwell and Kelvin-Voigt models were proposed, many attempts were performed to apply models to explain the behavior of real physical substances. In this approach, it was thought that the above-discussed models represent not only behavior but also molecular structure of a body. For example, in considering relaxation properties of a very long (polymeric) molecular chain, it was proposed that any part of such chain can be represented by the Maxwell model.

Such an approach opens wide opportunities for constructing models of real materials expressed by combinations of elementary Maxwell and Kelvin-Voigt models. Though some of these structures are very attractive, it is, however, necessary to distinguish between *models of a body structure* and *models of material behavior*, which are not the same (both are related to each other, not quite directly and not in an obvious way). Any mechanical model is a model of behavior, and the stress-deformation relationship, describing movement of elements of a mechanical model, gives equations which can closely approximate deformation behavior of material. The model can be very deceiving because a real body does not consist of springs and dampers.

The equations of differential type, like any other rheological equations, are written for a "point". If deformations are small, time derivatives entering Eq 7.68 are only partial time derivatives and nothing more. If deformations become large, it appears necessary to substitute ε in Eq 7.68 by some measure of large deformation to use their time derivatives as discussed in Chapter 3. This offers a model of a viscoelastic medium capable of large deformations and leads to some new rheological phenomena which can be treated as a weak non-linear effect.

The main goal of any mechanical model is to present a visual **illustration** of the concept of creep, relaxation, and viscoelastic behavior occurring simultaneously, and to demonstrate how rheological equations of differential type can be obtained. The same goal (especially its second part — construction of rheological models of differential type) can be reached by other methods, for example, using models based on analogy to electrical properties. In this case, it is possible to create electrical networks of any complexity consisting of resistors, condensers and capacitors. The time dependencies of electrical current and voltage would also be described by the same differential equations, such as Eq 7.68, and they can be treated as electrical models of viscoelastic behavior. Such models can also be very convenient in representing transient behavior of a viscoelastic medium.

7.8 SUPERPOSITION

The idea of superposition (the discussion in this section must not be confused with the Boltzmann principle of linear superposition expressed by Eqs 7.31 and 7.32) based on the influence of different factors on viscoelastic properties is widely used in practice of investigating behavior of real materials. The basic idea of this approach can be formulated in the following way: the same value of any viscoelastic function can be obtained *either* by changing time (frequency) *or* physical state of material, the latter governed by change in temperature, concentration of components, or other parameters. Sometimes, it can be a very unexpected factor; for example, it can be a duration of exposure of a material to ultraviolet radiation of the Sun (important for predicting long-term behavior of organic glasses in illuminators of air-liners).

The idea of superposition is illustrated in Figure 7.11. Let us have two experimental points for a creep function measured on the same time base, t_1, but at two different temperatures, T_1 and T_2. The value of a creep function, ψ_2, can be obtained in two ways; first, as shown in Figure 7.11, by direct measurement at temperature T_2 during time t_1, and second, at temperature T_1, but with time base t_2. If we know a coefficient a_T, which characterizes temperature dependence of a creep function, we can **shift** the point (t_1, ψ_2) to the position (t_2, ψ_2) as shown by the arrow in Figure 7.11.

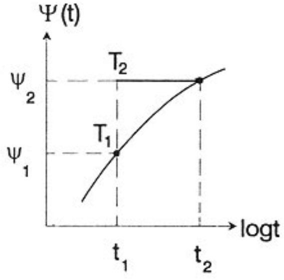

Figure 7.11. Superposition of points of the creep function by its shift along the time scale - an illustration.

The temperature coefficient a_T is

$$a_T = \log \frac{t_2}{t_1} \qquad [7.69]$$

or in a general form

$$a_T = t^* a_T(T) \qquad [7.70]$$

where t* is a constant and $a_T(T)$ is a function characterizing temperature dependence of viscoelastic properties. A very important supposition is that this function is the same for any viscoelastic function; it can be proven by the existence of mutual interrelations between different functions characterizing the viscoelastic behavior of materials.

Now, after shifting the point on the creep function (t_1, ψ_2) into a new position (t_2, ψ_2), we have obtained two points on the isothermal (at T_1) creep curve and we can try to reconstruct the creep function curve as shown in Figure 7.11. In fact, superposing results of measurements of viscoelastic functions on the limited time (frequency) base or "window" (in Figure 7.11) (it is only one point at t_1), one has a possibility to extend the range of experimental determination of this function. It is a very important method because in real experimental practice we rarely have a chance to make measurements beyond the range of 1-10^4 s or 10^{-2}-10^3 Hz, except by using the method of superposition. We can extend this range practically without limit and cover the range of 12-15 decimal orders in time or frequency.

In many real situations, we do not know the temperature coefficient, $a_T(T)$, beforehand. In order to obtain its value, it is not sufficient to measure only one point for every temperature. It is necessary to obtain a relationship with some points having the same values of a viscoelastic function. This approach is illustrated in Figure 7.12. We have two sections of the $G'(\omega)$ dependencies measured at two temperatures. In this case, the temperature coefficient is found as a distance between two curves at a height where the values of the modulus at two temperatures appear to be the same, E'_o.

The **reduced** time-scale is calculated as t/a_T and the reduced frequency scale, as ωa_T. It is possible to find hundreds examples of application of the time-temperature superposition in publications devoted to measuring properties of polymeric materials.[6,7,24] In order to illustrate the strength of this method we shall

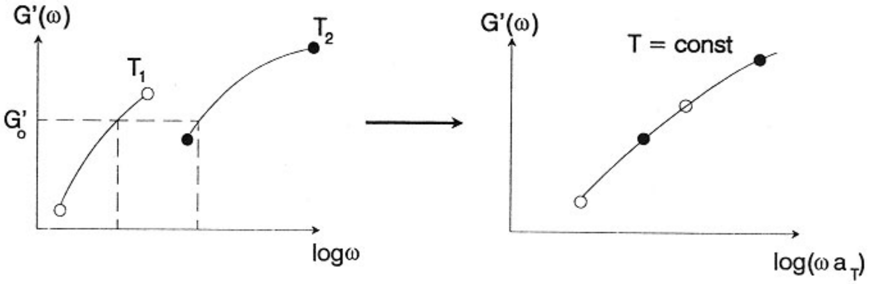

Figure 7.12. Superposition of two portions of the frequency dependencies of dynamic modulus measured at two temperatures.

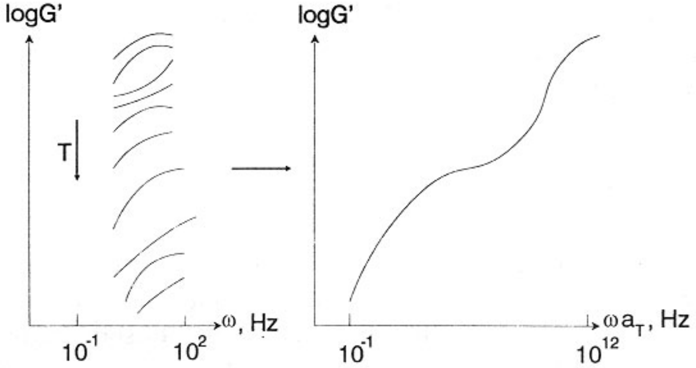

Figure 7.13. Example illustrating superposition of many portions of frequency dependencies of dynamic modulus measured at different temperatures (increasing along the direction of the arrow).

discuss one conditional (but close to reality) example of superposition of dynamic modulus measured at rather limited frequency range (Figure 7.13). The experimental “window” was no wider than 3 decimal orders and therefore only very limited portions of the full $G'(\omega)$ dependence are known. Superposition opens this window and we can now know the values of this dependence in a very wide range of frequencies.

An empirical approach to time-temperature superposition is possible if all neighboring portions of the curve have common points. We do not need to know the $a_T(T)$ function. However, such treatment of data is not always possible, and in many cases, not even convenient. That is why it is important to know the $a_T(T)$ function beforehand.

It was proven experimentally that two possible expressions have general meaning for the $a_T(T)$ function. The first of them is the **Arrhenius-Eyring** exponential **equation**, proposed as an analogue to the kinetic equation for the rates of chemical reactions

$$a_T = Ae^{E/RT} \quad [7.71]$$

where A is a front-factor (coefficient), and E energy of activation of relaxation processes.

It we choose some temperature T_o, as a *reference point* (i.e., if we reduce all experimental data to this selected temperature), then the Arrhenius-Eyring equation can be written as

$$a_T = \exp\left[\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right] \quad [7.72]$$

The second expression for the a_T function, widely used for time-temperature superposition of experimental data in various polymeric materials (it must be emphasized that polymeric materials and polymer-based compositions are the main object for application of superpositions of different type), is the so-called **Williams-Landel-Ferry (WLF) equation**, which can be written as[25-27]

$$\log a_T = \frac{-c_1(T - T_o)}{c_2 + (T - T_o)} \quad [7.73]$$

where T_o is the reference temperature, and c_1 and c_2 are constants depending on the choice of the reference temperature.

If the glass temperature is assumed as a reference temperature the values of these constants appear rather stable: c_1 is close to 17.4 and c_2 to 51.6. But in fact it is a rough approximation and it is preferable to use individual values of the constants which are different for various materials.

As a general rule, it is thought that the Williams-Landel-Ferry equation is true in the temperature range from the glass transition temperature, T_g, up to

$T_g + 100°C$. The Arrhenius-Eyring equation can successfully be used in the range of temperatures approximately at $T > T_g + 100°C$.

If we know the form of temperature dependence of a_T, it allows us not to have to measure the function $a_T(T)$ in the whole range of temperatures but to restrict measurement to some points only in order to verify the constants entering these equations.

Method of superposition is not limited to reduction of data by means of changing temperature only. The state of a material can be changed for different reasons. Variations in content (concentration) of a polymer in a solution is often used to change its relaxation properties. Then we can realize time-concentration superposition, and so on.

The method of superposition, used to reduce experimental data along the time (frequency) scale, is a very powerful possibility to increase the range of observations. At the same time, it must be remembered that the main principle of the method is based on the assumption that in changing the state of a material its relaxation spectrum changes in the same manner for *all* relaxation times, i.e., no new relaxation process appears, no process disappears, and temperature dependencies of all relaxation times in a spectrum are the same. The latter assumption is confirmed by the fact that the temperature dependence of any relaxation time is the same as viscosity; and we know that viscosity is the integral representation of all relaxation times (see Eq 7.62). At the same time, it is a rather strong assumption which may not be fulfilled, especially if superposition is carried out for initial experimental data obtained in a wide temperature range. In fact, many cases are known in which this basic assumption was wrong. One of the most evident examples is a phase transition. If it takes place in the temperature range under discussion, it definitely leads to radical changes in relaxation properties. The danger is rather serious for crystallizable polymers because the process of their crystallization takes place in a wide temperature range.

The second example is that of block-copolymers:[28] the moveability of blocks of different types (i.e., possibility to relax) appears in different temperature ranges and reflects freezing of different relaxation modes. It means that different parts of relaxation spectrum are characterized by different temperature dependencies and direct superposition of all portions obtained at different temperatures is incorrect in principle.

The third example regards mixtures of different components. In this case, it is quite obvious that temperature dependencies of relaxation properties of various components in a mixture, if different, restrict the possibility of superposition of portions of viscoelastic functions measured at different temperatures.

Examples discussed above show that time-temperature superposition is not a universal method and has definite limitations. That is why one must be very accurate in treating experimental data of a newly investigated material by this method, especially if far extrapolation, beyond an experimental window, is attempted.

7.9 APPLICATIONS OF LINEAR VISCOELASTICITY

There are three main lines of applications of the theory of linear viscoelasticity. They are as follows:

- *comparison of different materials* through constants and functions introduced and determined based on the theory
- *calculation* of the response of a material and predicting its behavior in arbitrary deformation using results of standard experiments and their theoretical relationships
- *comparison of predictions of structure and molecular theories* with experimental data.

7.9.1 COMPARISON OF MATERIALS BY THEIR VISCOELASTIC PROPERTIES

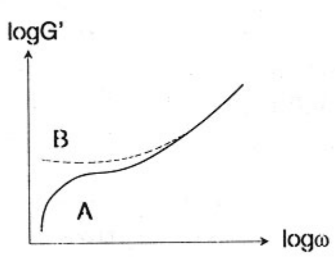

Figure 7.14. Frequency dependencies of dynamic modulus of a polymer melt (A) and a lightly cured rubber (B), prepared from this polymer.

We can think about two ways of comparison of different materials. First, it is possible to estimate the *type* of a material and to determine quantitatively such qualitative definitions as, for example, “solid”, “rigid”, “stiff”, “mild”, “fluid” and so on. Second, it is possible to compare materials of the same type by *values of their constants*; e.g., it is possible to distinguish two rigid materials with different resistance to creep. These possibilities are illustrated below.

As a first example, let us compare typical linear viscoelastic characteristics (frequency dependencies of dynamic modulus) of a polymer melt and a slightly cured rubber prepared from the same material (Figure 7.14). We can see that it is reasonable to select five regions of a frequency dependence of dynamic modulus for a polymer melt. They are called:

I - *flow (or terminal) zone*
II - *transient viscoelastic region*
III - *rubbery plateau*
IV - *transient leathery zone*
V - *glassy zone.*

Certainly, all five parts of the $E'(\omega)$ curve can be observed for a single sample by varying temperature, which results in changing physical (relaxation) states of a material. Then, one can apply the method of frequency-temperature superposition and construct the generalized $E'(\omega)$ dependence by joining segments of the full curve and shift along the frequency axis, such as curve A in Figure 7.14, constructed for a polymer which can melt at high temperatures (or flow at very low frequencies).

The first two regions of the complete $E'(\omega)$ dependence for a cured rubber are absent (curve B in Figure 7.14), though all other three parts stay practically unchanged in comparison with the melt. It means that, based on the measurement of the $E'(\omega)$ dependence for an unknown sample, one may find out that it is a linear polymer which can flow and be processed by regular methods or distinguish it from rubber able to sustain higher temperatures and deformations without irreversible changes of the shape.

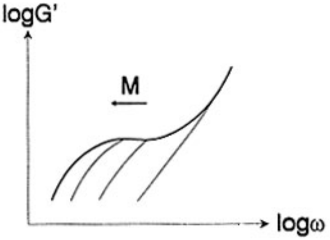

Figure 7.15. Frequency dependencies of dynamic modulus for samples of the same polymer but of different molecular weights. The arrow shows the direction of increasing molecular weight.

The second example concerns the influence of molecular weight (length of a molecular chain). Figure 7.15 shows that, for high molecular weight samples, all five regions are observed in the $E'(\omega)$ curve. Decreasing molecular weight leads to a shift of low-frequency regions (flow and transient viscoelastic zones) of the complete curve but does not affect the height of the rubbery plateau and shape and position of two other regions of the full $E'(\omega)$ dependence. However, with a rather low molecular weight member of the same homologous series, we lose a transient viscoelastic zone (marked as II in Figure 7.14) and rubbery plateau (marked as III in Figure 7.14), though the flow zone and high-frequency (glassy) part of a curve are present.

It shows that we can distinguish between polymers having different molecular weights by measuring their viscoelastic properties and comparing the position of the flow zone and/or the length of a rubbery plateau. It can be used as a relative method of comparison of two polymers by measuring the length of a plateau or frequencies for any arbitrary level of modulus in a flow zone. If molecular weight dependence of these factors was known beforehand (for calibrated series of samples), this approach could have been used as an absolute method of measuring molecular weights of polymers.

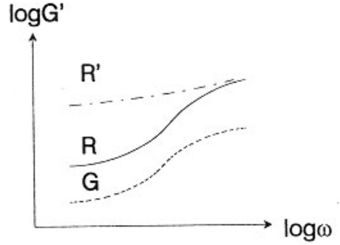

Figure 7.16. Frequency dependencies of a cured rubber (R) and a gel (G) prepared from the same rubber. The influence of higher density of a network of crosslinks (curve R') is also shown.

The third example (Figure 7.16) is a comparison of a cured rubber and a gel. In both cases, the first two regions (I and II in Figure 7.14) of a complete $E'(\omega)$ dependence are absent, such as for sample B in Figure 7.14. Addition of a low molecular weight solvent shifts all other parts of the curve, and in particular, lowers the height of a rubbery plateau during transition from a cured rubber to a gel.

Figure 7.16 also represents the influence of increasing density of network crosslinks in a rubber. This factor is primarily reflected in the height of a rubbery plateau and also in the values of modulus in a glassy state.

Examples shown in Figure 7.16 demonstrate the idea of constructing rubbery materials of different rigidity. Suppose there is a need for a soft rubbery material for eyesight-correcting covers. In this case, we must prepare gels having the required value of rubbery modulus (on the plateau). In another case, we may need a hard rubbery material for heavy tires, and again, properties of material are characterized by the rubbery modulus. Regulating the content of a plasticizer (low molecular weight solvent) and a hardening solid additive, we can reach the necessary combinations of viscoelastic properties in different frequency ranges needed for the application. For example, sealants require definite elasticity in the low frequency range and aircraft tires must be elastic at high frequencies because these products work under quite different conditions, even though both must be elastic in application.

The last series of examples is, in fact, comparison of materials by their viscoelastic properties in relations to different areas of their application. In all these cases (as in many others), the main problem consists in the necessity to formulate special conditions of application in terms of the theory of viscoelasticity and to establish the required level of properties. In real life it can be constants, such as viscosity or modulus, which are integrals (moments) of a relaxation spectrum of a material, or they can be definite values of viscoelastic functions at one or some frequencies or moments of time.

For example, it can be very important to know values of the creep function or the relaxation function on the definite time basis, as already discussed in Chapter 4. In this and analogous situations, one does not need to know the theory of viscoelasticity or to make any calculations, but the application conditions must be reproducible and a simulating experiment should be performed with all necessary standard requirements regarding accuracy and statistics of experimental results. Moreover, in these cases we are not restricted by the limits of linearity because application conditions do not obey any artificial limitations.

Measurements of viscoelastic properties of a material gives a quantitative base for reference to different relaxational states: glassy, leathery, rubbery, and so on. At the same time, it must be remembered that, in fact one does not consider the state of matter but its behavior. If some definite frequency was chosen for measurement of dynamic modulus (for example, standard frequency of 1 Hz), the comparison of various materials under these test conditions is straightforward. On the other hand, the same material can look quite different in other frequency ranges. A typical rubber can behave like a glass at very high frequency, as proven by frequency-temperature superposition. For example, in tire application for aircrafts, the high frequency behavior of rubber must be considered, since a tire must damp vibrations and can suddenly break if it performs like a glassy rather than a rubbery material.

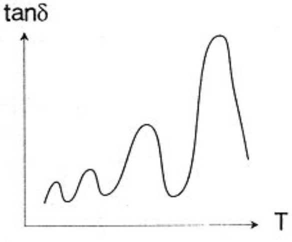

Figure 7.17. Typical temperature dependence of mechanical losses in periodic deformations characterized by loss tangent.

In addition to primary classification of materials in accordance with their main relaxational states, some more precise conclusions can be drawn from measuring the temperature dependence of the loss tangent, tanδ. A typical example of such dependence is shown in Figure

7.17. There are maxima in tanδ and each of them is treated as a relaxational transition. The most intensive high-temperature maximum is called the main or α-transition and identified with glass transition temperature. Others, to the left of the main transition (in the direction of lower temperatures), are marked by letters of the Greek alphabet, starting from β, and are called secondary transitions.

It is accepted that each relaxational transition identified with maximum of tan δ corresponds to the condition

$$\omega\theta = 1$$

where $\omega$is the frequency at which temperature dependence of mechanical losses is measured, and θ is a relaxation time.

During the experiment, the frequency is constant, and by changing temperature, one varies relaxation time. At some temperature, the above-formulated condition is reached and it is a criterion of "transition". It can be argued that this condition corresponds to a maximum of tanδ; in particular, it can be illustrated by a simple mechanical model of viscoelastic behavior including a single relaxation time.

One of the popular approaches to treating experimental data of the type shown in Figure 7.17 relates the tanδ maximum with "freezing" or "defreezing" of molecular movements of different kinds. These data can be used to recognize molecular process according to their position of "transition" along the temperature scale. The other side of this approach is the idea that passing through the temperature where tanδ maximum is achieved, we change the relaxation state and spectrum of a material, and therefore the principle of temperature superposition can be applied in the temperature range between two transitions only.

In measuring temperature dependence of tanδ, we also do not need to know the theory of viscoelasticity. It should be treated as a standard "one-point" (i.e., carried out at one frequency) method of characterizing a material. This method is a bridge for using measurements of viscoelastic properties of a material to understand its molecular structure.

7.9.2 CALCULATION OF THE RESPONSE

This line of application of the viscoelasticity theory is restricted by the linearity requirement, because, at present no non-linear theory of viscoelasticity (see the next section of this chapter) is treated as a solid base for a long-term prediction of behavior of real materials or fits the empirical experimental data.

Within the limits of linear viscoelastic behavior, the problem of calculation of responses to arbitrary loads is completely solved by the Boltzmann superposition principle. The relationships between viscoelastic functions were discussed above. If we know a relaxation spectrum of a material, all other calculations are only a technical problem. The major problem is the accuracy of determination of a relaxation spectrum based on experimental data.

We shall illustrate real limits of calculation by an example concerning relaxation and creep of polycarbonate,[29] a typical engineering plastic widely used in industry. The relaxation curve is approximated by the so-called Kolhrausch function[30]

$$\sigma(t) = Ae^{-\gamma t^{\alpha}}$$

where A, γ and α are empirical constants.

The values of the constants in this formula were found by a computational procedure and they satisfy the condition: points calculated with the set of selected constants according to the Kolhrausch function lie within the limits of possible experimental error. These limits were rather narrow, only about 5%. Then, the creep function was calculated for three possible sets of constants (satisfying the above-formulated requirement). The results are represented in Figure 7.18, where the exact creep function is also drawn (dotted line). A calculated curve can be rather far from the true creep function and the error large. It was dem-

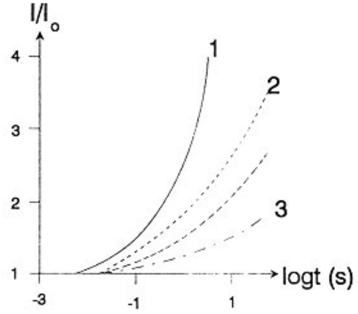

Figure 7.18. The results of calculations of the creep function. The relaxation curve was approximated by the Kolhrausch function with three different sets of constants (curves 1, 2 and 3). Dotted line is an exact creep function.

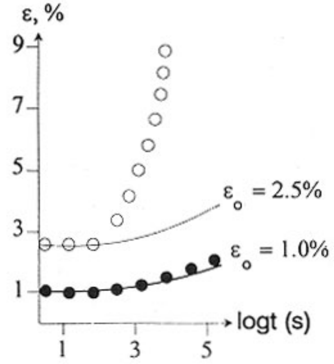

Figure 7.19. Creep of polycarbonate at two levels of stress: initial (instantaneous) deformation was 1% (1) and 2.5% (2). Open marks - experimental points, curves - calculated from a relaxation curve in a linear viscoelastic range. 20°C.

onstrated,[29] that a real relaxation curve can be approximated in different ways and the method of approximation strongly influences the results of calculations. Particularly, the relaxation curve can be approximated by a sum of exponent functions (by discrete relaxation spectrum) and only 5 members are sufficient to cover a wide time range of relaxation.

Another example cited from the results of the above-mentioned investigations of creep and relaxation of polycarbonate demonstrates the effect of non-linearity. Figure 7.19 shows two sets of experimental points (open symbols) measured in creep at different levels of stress (different initial deformations) and curves calculated from a relaxation curve, the latter measured in the range of linear viscoelastic behavior of a material at very low instantaneous deformation. At initial deformation (1%), the behavior of a material in creep is linear and quite well predicted by the theory of linear viscoelasticity from a relaxation curve. But the creep function becomes strongly non-linear even at initial deformation (2.5%), and the experimental points radically deviate from the calculated curve.

It is also worth noting that non-linear effects do not appear from the very beginning of creep; instead, here is some initial period of creep where points lie rather close to the calculated curve. It means that linearity in viscoelastic behavior is limited, not by stress (or deformation) level only but by the time factor, i.e., a material can be linear in a short range of loading and become non-linear in long-range loading. Certainly the duration of this range depends on stress level, as illustrated by experimental data in Figure 7.20. The limit of linear viscoelastic behavior (the limit can be determined with some experimental error, too) is a very strong function of stress. Experimental points in Figure 7.20 can be approximated by an expression

$$t^* = me^{-a\sigma}$$

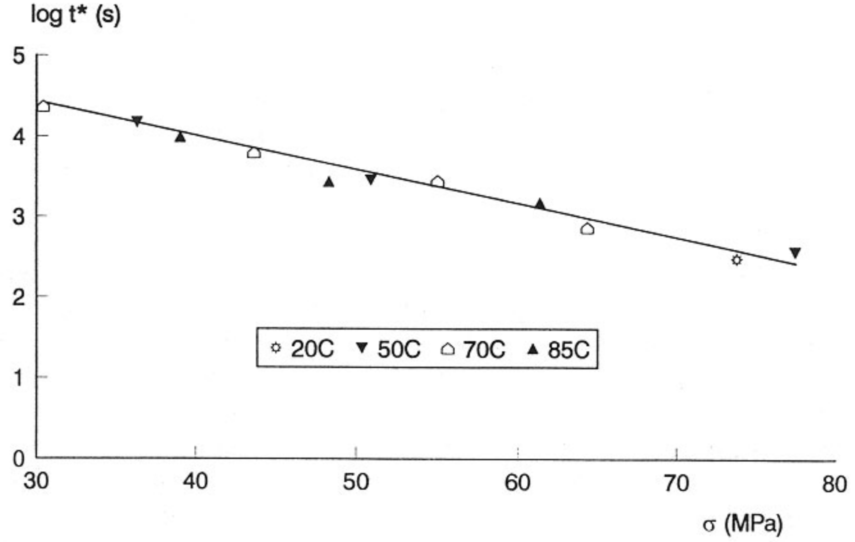

Figure 7.20. Dependence of the time, t*, corresponding to the limit of linear viscoelastic behavior in creep on the level of stresses at different temperatures. Straight line approximating experimental points is an exponential function.

where m and a are empirical constants (the constant a can be called a stress-sensitivity factor, and it equals 0.1 MPa^{-1} for experimental data in Figure 7.20; this value depends on material under investigation).

The example shows that the theory of linear viscoelasticity can be applied in practical calculations but the accuracy of predictions depends on:

- accuracy of initial experimental data
- method used for approximation of experimental points
- confidence of being inside the limits of linearity
- deformation and time ranges for which predictions are made.

All these factors are hard to estimate and this seriously limits the possibilities of calculation based on the linear theory of viscoelasticity. It therefore should be applied only when one is sure that the potential problems, listed above, are not applicable; then the theory of linear viscoelasticity becomes a powerful method of prediction based on limited experimental data.

7.9.3 MOLECULAR THEORIES AND EXPERIMENTAL DATA

Any molecular theory claims to predict the behavior of real materials. One of the broad areas for predictions is viscoelastic behavior, because relaxation effects are inherent to many materials and primarily to polymeric and colloid systems. That is why results of observations of viscoelastic behavior of different materials are widely used for comparison with theoretical predictions based on molecular models of materials.

As a general rule, the theory predicts a relaxation spectrum of a material, and the main question is, which type of experiment is used for comparison with theoretical predictions? Frequency dependence of dynamic modulus is the most widely-used method. It is explained by the fact that this dependence can be measured relatively simply in a very wide range of its argument.

A very important peculiarity of this line of applications of linear viscoelasticity, which is not important in other cases, is the necessity to have reliable results of measurements of viscoelastic functions and their application to very well characterized objects. The last requirement is especially important but in many cases, it is quite difficult to have sufficient information about a sample needed for formulation and use of a molecular theory, rather than to simply measure viscoelastic properties of the material. This is a main additional limitation in comparison of experimental data with molecular theories. Nevertheless, the reference to viscoelastic properties of a material is widely-used in modern theoretical speculations.

7.10 NON-LINEAR VISCOELASTICITY. INTRODUCTION

Theory of linear viscoelasticity is a rather rare example of a specialized and closed theoretical approach to describing behavior of a material. It has a rigid mathematical structure, set of theorems, conclusions, and it can be used for practical calculations of stress-deformation relationship in arbitrary regimes of deformations (loading). The theory has two main limitations which were mentioned above. One of them is the necessity to use initial experimental data for calculations, which can be determined only in a limited range of an argument and with some experimental error. It can lead to errors in calculations which can be much larger than an error of initial measurement, and as a rule, this error cannot be estimated at all. It is a natural inherent limitation of the theory.

The second limitation is of a more fundamental nature which severely restricts capabilities of the theory, especially in applications for technical purposes. That is a *limitation of linearity*. Some possible definitions of the limits of linear viscoelastic behavior were introduced in discussing fundamental experiments of viscoelasticity (relaxation, creep, periodic oscillations). This is independence of viscoelastic functions and constants, appearing in the theory, on the level of stresses and/or deformations. All these requirements are, in fact, reflections of the concept of independence of a relaxation spectrum of a material to external influences.

Many non-linear effects are observed in deformations of viscoelastic materials. The main effects were listed and discussed in Chapter 4, and some main types of non-linearity, with their inherent causes, formulated. The points below are designed to illustrate fundamental reasons for non-linear phenomena:

- *weak (geometrical)* non-linear effects due to possibility of large deformations of medium
- *strong (structural)* non-linear effects caused by changes in relaxation properties (spectrum) of a medium under external influence
- *breaking (phase)* non-linear effects, which are results of phase or relaxational transitions caused by deformations. This physical cause leads to significant change in relaxation properties of a media, not related to the properties corresponding to the initial state of a material.

All types of non-linear effects can be found in deformations of viscoelastic materials. Consequently, in constructing rheological equations of state for **non-linear viscoelastic materials**, we must take into account these levels of non-linearity. Certainly, effects of the lower level are always present when non-linear effects of higher level are observed. One can expect that strong non-linear phenomena related to gradual changes in a relaxation spectrum will be accompanied by large deformations, and so on. Moreover, the transition from one level of non-linearity to the next, as a rule, is not abrupt, especially if we bear in mind that the majority of real materials are multi-component and conditions of transition are different for components of a material. Certainly the threshold for transition is different for various materials.

For example: which deformations can be called *large*? The general answer is: these which are comparable with 1 (i.e., 100%). But we saw that even at deformation of an order of 2.5% (i.e., 0.0025) the behavior of polycarbonate in creep appears to be non-linear (Figure 7.19). Moreover, non-linear effects in deformation of highly filled polymeric[31,32] or colloidal plastic disperse systems[33] (colloidal dispersion of naphthenate aluminum in low-molecular-weight solvent)[34] become quite obvious at deformations of about 0.1%. It is explained by the existence of a very rigid structure of a solid compound, destroyed at this deformation and leading to change in relaxation spectrum and strong non-linear effect, such as, for example, non-Newtonian flow and dependence of dynamic modulus on amplitude of deformations.

It has already been mentioned (Chapter 4) that strong and phase non-linear phenomena are kinetic effects because changes in a relaxation spectrum and phase transitions occur in time. These time-effects superimpose on viscoelastic time-effects, and the rheological approach must be combined with a kinetic one in order to understand what happens to a material and to explain and describe what we observe in the case of “non-linear effects”.

The last concluding remark in this Introduction to non-linear viscoelasticity is: even though there is a complete theory of linear viscoelasticity, no such non-linear theory exists, and maybe cannot exist, but there can be many theories of non-linear viscoelastic behavior which seem to explain various non-linear phenomena. At the same time, no theory exists capable of covering *all* non-linear cases because of the diversity of causes of non-linear effects. For example, it is convenient to use a flow curve equation for a non-Newtonian flow for applied calculations for transportation of a liquid in pipes, neglecting that a flow curve is only a consequence of some more general rheological equation of state not known.

7.10.1 LARGE DEFORMATIONS IN NON-LINEAR VISCOELASTICITY

The starting point for developing the concept of viscoelastic behavior in non-linear range is the Boltzmann-Volterra equation (7.31). It is the most general representation of viscoelastic response at infinitesimal deformations. The next step regards the use of large (finite) deformations discussed in Chapter 3.

It is convenient to use two tensors for large deformations: the Cauchy - Green tensor, C_{ij}, and the Finger tensor, C^{-1}_{ij}, both are functions of two time moments: an “initial” moment of time when a point of a body is in its reference state and a current moment of time, i.e., the moment when deformations C_{ij} and C^{-1}_{ij} are measured relative to the reference state. In many cases, the initial (reference) state is assumed to be isotropic at the point, although it is not always true. For example, liquid crystalline polymers and reinforced plastics are very important exceptions (or to be more exact, they form another case) because these media are inherently anisotropic materials and rheological description of their properties and behavior needs special theoretical understanding.

The idea of large deformations and their role in rheological behavior of real materials can be illustrated by an example of simple shear. For this purpose let us write the components of the Cauchy - Green and Finger tensors for unidimensional simple shear in the plane x_1 - x_2. Assuming that deformations at the reference state are absent and that shear at the moment, t, equals γ, we can write the components of the Cauchy - Green and Finger tensors as follows

$$C_{ij}(t) = \begin{vmatrix} 0 & \gamma & 0 \\ \gamma & \gamma^2 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad \text{and} \quad C_{ij}^{-1} = \begin{vmatrix} -\gamma^2 & \gamma & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

Then, we need to formulate the Boltzmann superposition principle for large deformations. One of the possible ways to do it is to use a form of rheological equation of state of **rubber-like liquid** as proposed by Lodge:[35]

$$\sigma_{ij}(t) = \int_0^t C_{ij}^{-1} m(t - t')dt' \qquad [7.74]$$

where m(t - t′) is called the **memory function**.

It is easy to show that the memory function is directly related to the relaxation function by the following equations:

$$\varphi(t) = \int_t^\infty m(s)ds; \quad m(t) = -\frac{d\varphi(t)}{dt} \qquad [7.75]$$

These equations show that the memory function is the same as for the linear viscoelasticity limit and it does not depend on deformation. Using the measure of large deformation, instead of infinitesimal deformation, we come to some new results: presence of diagonal members in the C_{ij}^{-1} tensor leads to the prediction of the Weissenberg effect. It appears here as a natural consequence of finite deformation, and it is really a second order effect because predicted normal stresses are proportional to γ^2. Then, using different combinations of the tensors C_{ij} and C_{ij}^{-1}, one can reach correct sign and value of normal stresses (within the limits of weak non-linearity). The statement "using different combinations" shows that there are various possible paths for generalization of the linear theory of viscoelasticity and we have no formal ground for unambiguous choice of either version.

The second power of normal stresses in elastic deformation is a weak non-linear effect resulting from large deformation of a material, which is true for a viscoelastic solid and liquid as well. The model of rubber-like liquid predicts some new effects besides normal stresses in shear, important as reflections of weak non-linearity. The first one is time dependence of tensile stress observed in uniaxial extension performed at constant rate of deformation. For linear viscoelastic liquid at constant rate of extension (and at constant rate of shear), one expects that stress will grow to the limit of steady flow with constant (Newtonian in shear and Trouton at extension) viscosity, and such level is reached at $t \to \infty$.

To illustrate what happens to rubber-like liquid, it is convenient to operate with a single-relaxation-time model (a relaxation spectrum degenerates to a single line relaxation time, θ) because this model gives very spectacular results. Theory shows that in uniaxial extension of such viscoelastic (or rubber-like) liquid, stress dependence on rate of deformation at $t \to \infty$ is[36]

$$\sigma(\dot{\varepsilon}) = \frac{3\eta\dot{\varepsilon}}{(1-2\dot{\varepsilon}\theta)(1+\dot{\varepsilon}\theta)} \qquad [7.76]$$

At *very low* rates of deformation (and the words "very low" mean that the Weissenberg Number, $We = \dot{\varepsilon}\theta << 1$), we reach the limit of linear viscoelasticity: the Trouton Law for extensional viscosity. Indeed, at $We \equiv \dot{\varepsilon}\theta << 1$

$$\lambda = \frac{\sigma}{\dot{\varepsilon}} = 3\eta$$

Increase in the rate of deformation leads to the growth of elongational viscosity, as can be derived from Eq 7.76, so the theory predicts increasing extensional viscosity. However, the most intriguing result can be obtained at $We \to 0.5$. Eq 7.76 predicts, in this case, an unlimited growth of stress, which is physically impossible. In fact, it means that at $We > 0.5$, *steady* elongational flow becomes impossible, resulting in rupture of a stream to overcome some critical rate of deformation, determined by the criterion We = 0.5.[37,38]

If a (linear) relaxation spectrum is not represented by a single but rather a set of relaxation times, the expression for stress dependence on rate of deformation becomes more complex, resulting in preclusion to reach a steady flow regime of extension at sufficiently high rates of deformation. In the general case, the critical value (equal to 0.5) of the Weissenberg Number must be calculated through the maximum relaxation time from a spectrum. Moreover, if a relaxation spectrum of a material is continuous and stretches up to infinity, then the state of steady uniaxial flow becomes impossible at any low rate of deformation.

The prediction of unlimited growth and thus the rupture of material in uniaxial extension is very important because the model of rubber-like liquid explains impossibility of increase in extension rate; for example, in the process of fiber spinning (very much desired in technological practice) beyond the definite threshold: a liquid jet would break, which helps to realize even weak non-linearity as a result of large elastic deformations in order to observe this effect.

Now, let us discuss the next interesting and important phenomenon predicted by the model of viscoelastic (rubber-like) liquid. This is **constrained recoil** of such a liquid after cessation of shear deformation, γ_r, which is a function of time. *Recoverable deformations*, $\gamma_r(t)$, accompany flow of viscoelastic liquid and can be measured after sudden (jump-like) cessation of flow. Recoverable deformations at $t \to \infty$, so-called ultimate (or "equilibrium") recoil, γ_∞, are calculated as

$$\gamma_\infty = \frac{\tau}{E_o} = \frac{\eta\dot{\gamma}}{E_o} \qquad [7.77]$$

where η is viscosity (Newtonian viscosity for linear viscoelastic liquid) and E_0 modulus of elasticity.

It is possible to prove that γ_{el} can also be calculated by means of the so-called **Lodge equation**:

$$\gamma_{el} = \frac{\psi_1\dot{\gamma}}{\eta} = \frac{\sigma_{11} - \sigma_{22}}{2\sigma_{12}} \qquad [7.78]$$

where

$$\psi_1 = \frac{\sigma_{11} - \sigma_{22}}{2\dot{\gamma}^2}$$

is called coefficient of the first difference of normal stresses (see also p. 74). Then, one can write a new relationship between material constants of a rubber-like liquid

$$\psi_1 = \frac{\eta^2}{E_o} \qquad [7.79]$$

The normal stresses can be expressed as a function of the moments of a relaxation spectrum because both components in Eq 7.79 are such moments (see Eq 7.62). Then normal stresses appear in the model of rubber-like liquid also as a second-order effect, which can be connected with relaxation properties of medium.

7.10.2 RELAXATION PROPERTIES DEPENDENT ON DEFORMATION

There is a great variety of non-linear models which take into account the second level of non-linearity, i.e., changing relaxation properties as a function of deformations.[39-41] If we go by the way of generalization of Eq 7.74, we can assume that m(t) is a function not of time only but also of deformation. Because a memory function is a material parameter of matter, its dependence on deformation must certainly be expressed through invariants of the deformation tensor.

Then, we can write

$$\sigma_{ij} = \int_0^t C_{ij}^{-1} m[(t - t');I_1;I_2]dt' \qquad [7.80]$$

where I_1 and I_2 are invariants of the C_{ij}^{-1} tensor.

Eq 7.80 is a natural generalization of a model of a rubber-like liquid. However, practical applications of Eq 7.80 meet with a major difficulty which is common for non-linear models of such type. It is a problem of determining a memory function with its uncertain dependencies on invariants of the deformation tensor. To overcome this difficulty, Wagner[42] proposed the use of a rather old observation obtained from investigation of deformation of crosslinked rubbers. It was known that in many practically important cases, a relaxation function (or a relaxation modulus) at large deformations can be treated as a product of two independent functions: the first one is a time-dependent memory function and the second is a function of deformation (or in more general case, a function of invariants of the deformation tensor), i.e., it is possible to separate the dependence of a memory function on its arguments into two different dependencies based on a limited number of arguments:

$$m(t,I_1,I_2) = m_o(t)h(I_1,I_2) \qquad [7.81]$$

where $m_0(t)$ is a linear-limit memory function, and $h(I_1, I_2)$ is called a damping function, and the latter reflects the influence of deformation on relaxation properties of material.

It is rather difficult to separate the influence of both invariants on damping function, $h(I_1,I_2)$, because in simple (standard) experiments the two invariants cannot be changed independently. There are some experimental result related to large deformations in shear where a single measure of deformations, γ, can be used. Wagner[42] and Laun[43] demonstrated that a damping function can be approximated by a single exponent

$$h(\gamma) = e^{-n\gamma}$$

and Soskey and Winter[44] and Larson[45] showed that experimental data can be satisfactory fitted, if we express a damping function by a power law

$$h(\gamma) = \frac{1}{1 + a\gamma^b}$$

Parameters a, b, and n in these expressions are empirical constants.

Other versions of a "non-linear" memory function are also known and their generalization, as a function of invariants, can be found in the literature. For our discussion, the most interesting is, first of all, the existence of the dependence of relaxation properties on deformations, and secondly, the rather strong influence of deformations, regardless of whether they are expressed by an exponential or a power function.

Eq 7.80 is able to predict strong non-linear phenomena. One can obtain the expression for non-Newtonian viscosity, which is written as

$$\eta(\dot{\gamma}) = \int_0^\infty \varphi(t') \frac{d}{d\dot{\gamma}}[\dot{\gamma}h(\dot{\gamma})]$$

The final form of the dependence of non-Newtonian viscosity on rate of shear is determined by the structure of a damping function. Regardless of its exact expression, one may state that the influence of shear appears more strongly on the long-term side of a spectrum than at shorter relaxation times. In this sense, we can say that shearing suppresses slow relaxation processes (they do not have enough time to occur) and this phenomenon increasingly envelopes the part of a relaxation spectrum (from the long-term side), the higher the rate of deformation is.

Eq 7.81 proposed by Wagner[42] is popular in rheological literature because, in the form used in Eq 7.80, it can describe many experimental data on non-linear relaxation in the range of large deformations. Eq 7.80 also predicts non-quadratic dependence of normal stress on shear rate at high rates of deformation, i.e., it demonstrates that at high rates of deformation, the Weissenberg effect reflects not only weak but also strong non-linearity, as well.

Though Eq 7.80, with separation of arguments, as in Eq 7.81, looks very attractive for describing various rheological phenomena, there are at least two principle contradictions of theoretical predictions based on this approach and experimental facts. First is the wrong prediction concerning the second difference of normal stresses: according to Eq 7.80, it equals zero, whereas, in fact, it is not; second is the prediction of monotonous growth of normal stresses in transient shearing deformations, whereas, in fact, an overshoot takes place. It proves that this approach is not universally acceptable.

The next step in understanding and describing non-linear viscoelastic behavior is connected with so-called the **K-BKZ model** of rheological behavior,[46,47] which incorporates both measures of large deformations, the Cauchy - Green, C_{ij}, and Finger, C_{ij}^{-1}, tensors. Again, there is some ambiguousness in constructing rheological models because both measures of large deformations can enter rheological model as arbitrary form, but they allow one to select combinations which give the best fit of experimental data.

Different forms of the K-BKZ equation exist. If we explore the idea of separation of arguments in a memory function, as discussed above, we may come to the following, relatively simple, expression for the K-BKZ model:

$$\sigma_{ij} = \int_0^t m(t - t')[2\frac{\partial W}{\partial I_1} C_{ij}(t') - 2\frac{\partial W}{\partial I_2} C_{ij}^{-1}(t')]dt' \qquad [7.82]$$

where W is an elastic potential depending on the invariants of the deformation tensor, and this elastic potential is essentially the same as used in the theory of elastic (rubbery) solids (see Chapter 6).

An elastic energy potential function in Eq 7.82 depends on the deformation and therefore on time. The dependence $W(I_1,I_2)$ must be determined experimentally like a damping function in Eq 7.81. There is a vast number of publications devoted to experimental probing of the predictive strength of this model and determining elastic potential function. Meanwhile, the main advantage of Eq 7.82 over Eq 7.80 is in prediction of the non-zero second difference of normal stresses. Freedom in combinating measures of deformations and dependency of elastic potential on invariants of the deformation tensor provides great possibilities to use the K-BKZ model to fit numerous experimental data and describe various special effects in behavior of different rheological media.

Both equations (Wagner and K-BKZ) explore an idea of the influence of the deformation on a memory function and thus on a relaxation spectrum of a material, but using it in a simplified form through separation of inputs of time and deformation. It allows one to single out the linear limit of relaxation function. Certainly, it is a particular case, but an important one. Moreover, transition to a more general (and more complex) model of non-linear viscoelastic behavior, as a rule, makes these equations almost unrealistic for practical applications.

There are many other, different approaches to constructing non-linear rheological equations of state for viscoelastic materials. We do not intend to review all published theoretical ideas; only fundamental and applicable approaches were discussed above. It is also worth mentioning that there are numerous attempts to take into consideration weak (due to finite deformations) and strong (due to deformational changes of a relaxation properties) non-linear phenomena, but non-linear effects of the third level (phase non-linearity) do not appear in rheological equations. However, the idea of fracture appears in many cases, even as a result of a weak non-linearity as discussed for high rates of extension of a rubber-like liquid.

In the conclusion of this section, we shall shortly discuss the applied purposes of non-linear theories of viscoelasticity. They are essentially the same as those of the linear theory, but their applied value is even more pronounced because real technical applications and technological operations take place at high rates of deformation and reach large deformations. On the other hand, at present an applied meaning of non-linear theories is very limited. This is explained by difficulties in determining material functions used in theories and the low reliability of their predictions for experimental conditions other than those used to determine material functions.

A large number of investigations were performed to verify the correctness of prediction of qualitative or (better) quantitative results of simple fundamental experiments (simple shear, uni- and biaxial extension, transient regimes of shear and extension) by different theories, but seldomly to solve applied technical problems. Only empirical or semi-theoretical equations for steady non-linear phenomena, such as non-Newtonian flow of liquids or long-term creep of solids and long-term prediction, including extrapolation, are rather widely used for solving applied problems.

7.11 CONCLUDING REMARKS

Viscoelasticity is a combination of viscous dissipation and storage of deformation energy. The phenomenon is common for practically all materials, though its importance and potential possibility to observe viscoelastic effects is determined by the ratio of inherent time-scale (time of relaxation) and characteristic time of deformation. Various effects explained by viscoelastic behavior are often observed and are important for polymeric materials in the form of melts, solutions, and colloidal dispersions, solids and reinforced plastics, rubbers and foams. The main reason for its presence is their wide relaxation spectra, causing the same order of value as duration of loading (deformation) to always exist.

There are three fundamental experiments which are treated as reflections of viscoelastic behavior of a matter:

- **creep** - delayed development of deformations under action of constant force (or stress)
- **relaxation** - slow decay of stresses at preserving constant deformation
- **periodic oscillations** - harmonic changing of stresses or deformations with relative shift of deformation in relation to stress.

These experiments can be carried out in any geometrical configuration of deformation, primarily at shear or uniaxial extension-compression.

The experiments allow one to find material characteristics of matter - **creep function**, **relaxation function**, **dynamic modulus** (and **compliance**), **instantaneous modulus**, **equilibrium modulus** and **viscosity**. If these material functions do not depend on the level of deformation (and stress), material has a **linear viscoelastic behavior**; in the opposite case, material is a **non-linear viscoelastic body**.

For linear viscoelastic materials, the **principle of superposition** (Boltzmann principle) is valid. According to the principle, reaction of a material to all consequent deformations (or stresses) are independent and previous deformation does not influence the reaction of the material to the next one. Mathematical expression of this principle is done by a pair of the **Volterra equations**.

Creep and relaxation functions can be represented as sums (or at a limit as an integral) of exponential items, and exponents in these expansions are **relaxation** and **retardation spectra**. Calculation of **relaxation times** in a spectrum is based on solving integral equations. In principle it can be done unambiguously if a creep or a relaxation function are known exactly in a full range of time, from zero to infinity. Since this is impossible, we are compelled to use approximate methods in solving integral equations, based on analytical approximation and extrapolation of experimental data. However, accuracy of these methods is limited by the unavoidable scatter of experimental points and the ambiguity of their extrapolation beyond the experimental time or frequency "window".

Characteristics of a linear viscoelastic behavior of a material are interrelated to each other by algebraic or integral equations and can be mutually recalculated. That is why the *linear theory of viscoelasticity* is a closed theory, containing all necessary equations in order to estimate mechanical behavior of a material in arbitrary stress-deformation situation based on measurements of any fundamental characteristic of viscoelastic properties of a material.

There is an important method of extending the experimental time (frequency) "window" based on the idea of *superposition of experimental data* obtained at different temperatures or concentration in multi-component systems at some other external factors, which should not be confused with the Boltzmann principle of superposition. This method is based on the idea that the same value of any viscoelastic function can be reached either by changing time (frequency) scale or varying a value of an external factor (temperature, concentration and so on). This experimental method allows us to separate parts of time-dependent curves by their shift along the time-scale and thus to obtain a curve over a much wider range of arguments than can be realized in a direct experiment.

The method of superposition is related to the idea that the dependencies of relaxation times in a spectrum are the same for all of them, and thus this principle is not applicable if dependencies of different relaxation times in a spectrum on an external factor (for example on temperature) are different.

The theory of linear viscoelasticity is used for:

- *obtaining objective characteristics of a material*, which can be correlated with their molecular structure and/or content
- *verification of conclusions from molecular theories* which give grounds for understanding the molecular structure of a material and intermolecular interactions
- *calculation of mechanical behavior of a material* in arbitrary regimes of their exploitation (but at rather low levels of stresses).

The theory of linear viscoelasticity works well only within the limit of infinitesimal deformations. In increasing deformations, fundamental assumptions of the theory, and primarily the principle of linear superposition, become inadequate. The theory requires generalization because numerous effects observed at large deformations are definitely related to viscoelasticity of a material and are especially important in real technological practice.

The methods of generalization of the classical theory of linear viscoelasticity can differ, depending on the proposed and assumed mechanism of **non-linearity**. Consequently, various theories of **non-linear viscoelasticity** were developed. The first step consists of the introduction of a measure of large deformations instead of infinitesimal ones, which causes ambiguity of predictions of non-linear viscoelastic effects.

The concept of **rubber-like liquid** (viscous liquid, capable to store large elastic or reversible deformations in flow) allows us to explain phenomena related to weak non-linear behavior, such as existence of normal stresses in shear flow, which is an effect of the second (quadratic) order. Moreover, this model predicts that at sufficiently high rates of uniaxial extension, a steady state flow becomes impossible and a stream is broken, due to unlimited increase of stresses.

The concept of rubber-like liquid is not sufficient to understand and to describe the strong non-linear effects; for example, non-Newtonian viscous flow of viscoelastic liquids. We need to explore the idea of *changing (or modification) of relaxation properties* (or in general sense of changing spectrum) of a matter due to large deformations as an inherent reason of strong non-linear effects. It can be done on the basis of different theoretical or experimental considerations and then we may arrive at different predictions concerning rheological behavior of a material.

Efforts of numerous researches are directed primarily to comparison of predictions of various existing non-linear theories with results of some principle experiments in uni- or biaxial deformations. This offers the a possibility to find material functions characterizing non-linear viscoelastic properties of a material. However, general theories of viscoelasticity are rarely used for solving concrete applied problems. Only directly measured non-linear characteristics are used for these purposes. For example, non-Newtonian flow curves are used to solving tube transportation problems, and a creep function measured at high (non-linear) range of stresses is used for predicting long-term deformations of real engineering materials.

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NOMENCLATURE

A	Front-factor (empirical coefficient)
A	Intensity of heat dissipation (in viscous flow)
A	Surface area (in shear)
A_n	Rivlin-Ericksen tensor of the n-th order
a, b	Semi-axes of an ellipsis
a, b, c	Initial length of edges of a pipe
a^*, b^*, c^*	Length of edges of a pipe after deformation
a_{ij}	Components of the gradient of velocity
a_T	Coefficient of temperature reduction
B	Width of a channel
B	Transverse size of a plane
B	Bulk modulus of compressibility
B_n	White-Metzner tensor of the n-th order
b	Ratio of rotation speeds of two coaxial cylinders
b	Width of a rectangular crosssection
C_1, C_2	Constants in the Mooney-Rivlin equation
C_{ij}	Components of the Cauchy-Green tensor
C_{ij}^{-1}	Components of the Finger tensor
C_{mf}	Dimensionless coefficient of viscous friction
c_1, c_2	Constants in the WLF equation
D	Diameter of a tube
D_i	Invariants of the rate of deformation tensor
D_{ij}	Components of the rate of deformation tensor
d	Linear size (in particular, diameter of a tube)
d_{ij}	Components of the infinitesimal deformation tensor
d_i	Principal values of the infinitesimal deformation tensor
$d_{ij}^{(dev)}$	Deviatoric part of the d_{ij}-tensor
E	Energy of activation
E	Modulus of elasticity (Young modulus)
E^*	Complex (dynamic) modulus
E'	Real component of dynamic modulus (storage modulus)
E''	Imaginary component of dynamic modulus (loss modulus)
E_a	Apparent modulus of elasticity
E_i	Partial moduli
E_i	Invariants of the tensor of large deformations

E_C	Elastic modulus in compression
E_T	Elastic modulus in extension
E_o	Initial (instantaneous) modulus
E_o	Absolute value of the dynamic modulus (in periodic oscillations)
E_∞	Equilibrium modulus
F	Normal force
F_f	Resistance force due to viscous friction
F_i	Force (in various situations)
F_n	Normal force
F_p	Resistance force due to pressure
$F_{p,1}$	Component of F_p related to action of pressure on a surface
$F_{p,2}$	Component of F_p related to action of pressure on a bottom
F_s	Stokes force at movement of a ball through a liquid
F_y	Force at the point of yielding
F_σ	Tangential force
$F(\theta)$	Relaxation spectrum
f	Deflection
f_{max}	Maximal deflection
G	Shear modulus
G_i	Constants in the theory of rubber elasticity
G_∞	Equilibrium modulus
g	Gravitational constant
g_{ij}	Components of the gradient of relative displacement
H	Maximal sagging
H	Distance
H	Height (in various situations)
$H(\ln\theta)$	Logarithmic relaxation spectrum
h	Gap (constant or current) between two parallel surfaces
h	Height of a rectangular cross-section
h_o	Initial distance between two approaching disks
$h(t)$	Damping function (in non-linear viscoelasticity)
I	Axial moment of inertia
I_i	Invariants of the stress tensor
I^*	Complex dynamic compliance
I'	Real component of dynamic compliance
I''	Imaginary component of dynamic compliance
I_i	Partial compliance
I_i	Invariants of stress tensor
I_p	Polar moment of inertia
I_o	Instantaneous compliance
I_x	Moment of inertia relative an x-axis
I_∞	Equilibrium compliance
K, K_n	Geometrical factors
K_c	Geometrical factor for flow along the axis between two coaxial cylinders

K_{el}	Geometrical factor for an elliptic cross-section
$K_{(n)}$	Hydrodynamic factor for a “power” liquid
k_{ijkl}	Components of the tensor of moduli (for an anisotropic solid)
L	Length (of a tube, bar)
L	Height of two coaxial cylinders
$L(\ln\lambda)$	Logarithmic retardation spectrum
l	Distance from the top of a penetrating body to the bottom of a vessel
l	Length (of a sample)
l_o	Initial length of a sample
M	Torque
M_y	Torque at the point of yielding (in flexure)
M_z	Torque around the z-axis
$m(t)$	Memory function (in viscoelasticity)
n	Exponent of the power law in various rheological equations
n_i	Components of a vector showing the orientation (direction)
P	Moving force (in the Stokes problem)
P	Resistance force (in the lubrication theory)
p	Hydrostatic pressure
p^*	Pressure corresponding to elastic-to-plastic transition
p_o	Pressure at the edge crosssection of a confusor (or at the outer free surface)
Q	Volumetric output (flow rate)
Q_D	Volume output due to drag flow
Q_p	Volume output due to pressure gradient
q	Distributed load (in Figure 2.12)
R, R_i	Radius in various situations (of a tube, cylinder, sphere)
R_i	Radius of an inner cylinder
R_h	Radius of a hole (on a cross section of a bar)
R_o	Radius of an outer cylinder
R_o	Initial radius
r	Radius-vector, current radius, radial coordinates
r	Distance between two points in continuum
r_i	Components of radius-vector
r_o	Radius of the edge cross-section of a confusor
r_o	Radius of a hole
r, z, θ	Cylindrical coordinates
S	Area (of a surface in extension)
S_p	Static moment of a plastic zone
s	Distance between two points
T	Total force
T	Characteristic time of deformation (flow)
T	Duration of an oscillation cycle
T, T_i	Temperature (in various situations)
T_g	Glass temperature
T_o	Reference temperature

t	Current time
t^*	Time characterizing limit of linear viscoelasticity
t^*	Time constant
t_i	Time (in various situations)
t_{inh}	Characteristic inherent time (of a material)
t_{obs}	Time of observation
u_i	Components of displacement vector
V	Velocity (average velocity)
V_x, V_z	Components of the velocity vector
V^*	Dimensionless velocity
V_{max}	Maximal velocity (at the axis of a channel)
V_w	Velocity of a moving wall of a channel
V_i	Velocity of an inner cylinder
V_o	Velocity of an outer cylinder
V_o	Volume-averaged velocity
v_i	Volume
v_i	Components of the velocity vector
W	Work (produced during a cycle of periodic deformations)
W	Elastic potential
w_{ij}	Components of the vorticity tensor
X_i	Components of the vector of body forces
X_H	Displacement of a Hookean spring
X_N	Displacement of a Newtonian damper
X_o	Initial displacement (of a Maxwellian model)
x	Parameter
x_o	Initial value of x
x_∞	Equilibrium value of x
x, y, z	Cartesian coordinates
x_i	Coordinates of the Cartesian coordinate system
z^*	Distance from a neutral axis to a border of a plastic zone
A, B, C, K, M, a, k, m, n, p	Empirical constants of different equations

De	Deborah Number
Re	Reynolds Number
Re_R	Reynolds Number related to the radius of a tube
Re^*, Re^{**}, Re_*	Characteristic values of the Reynolds Number
T	Taylor Number
We	Weissenberg Number

α	Angle (in different meanings); constant in various equations
α	Coefficient of linear thermal expansion
α	Dimensionless eccentricity of two coaxial cylinders
α_o, α_{max}	Different values of an angle

β	Dimensionless coordinate
β	Angle (various meanings)
β^*	Critical value of an azimuthal angle in formation of vortices
γ	Magnitude of shift (in simple shear)
γ	Gradient of displacement
γ	Empirical constant (in the Kolhrausch function)
γ	Deformation in simple shear
γ_z	Recoil strain (recoverable deformation in shear)
γ_∞	Ultimate recoil ("equilibrium" recoverable deformation in shear)
$\gamma = \cos\alpha$	Value used in the solution of the hydrodynamic problem of converging flow
$\gamma = \cos\alpha_o$	Value used in the solution of the hydrodynamic problem of converging flow
$\dot{\gamma}$	Rate of deformation (shear rate)
$\dot{\gamma}_w$	Rate of deformation (shear rate) at a wall
$\dot{\gamma}_{w,N}$	Rate of deformation (shear rate) at a wall in flow of Newtonian liquid
$\dot{\gamma}_{w,VP}$	Rate of deformation (shear rate) at a wall in flow of visco-plastic medium
Δl_i	Elongation
ΔP	Pressure drop (pressure difference at the ends of a tube)
Δr	Change of a radius
ΔV	Change of volume
δ, δ_o	Width of thin elements (covers, gaps, and so on)
δ	Difference of radii of two coaxial cylinders
δ	Outstripping factor (in rolling)
δ	Phase (loss) angle
δ_{ij}	Kronecker delta (the unit tensor)
ε	Relative change in the distance between two points
ε	Eccentricity of two coaxial cylinders
ε	Ratio of the gap width between coaxial cylinders to the radius of an inner cylinder;
ε	Tensile strain
ε_f	Residual deformation
ε_v	Relative change of volume
ε^H	Hencky measure of deformations
ε_{ij}	Components of the tensor of deformations
ε_o	Instantaneous deformation
ε_0	Amplitude of deformation (in periodic oscillations)
ε^*	Engineering measure of deformation
$\dot{\varepsilon}$	Rate of axial deformation (gradient of velocity in extension)
ζ	Dimensionless radius
η	Shear viscosity (Newtonian, apparent)
η_o	Initial (zero shear) viscosity
η_c	Cross-viscosity (in Rivlin's equation)
η_p	Plastic (Bingham) viscosity
η_s	Viscosity calculated by the Stokes formula
η^o	Viscosity of a liquid droplet

η^*	Complex dynamic viscosity
η'	Real component of dynamic viscosity (or dynamic viscosity)
η''	Imaginary component of dynamic viscosity
θ	Angle (in different meanings); angle coordinate
θ, θ_i	Relaxation time
θ_{av}	Average relaxation time
θ_{ij}	Components of the rotations (turns)
λ	Draw (extension) ratio
λ	Elongational (Trouton) viscosity
λ	Characteristic retardation time
λ	Dimensionless coefficient of friction
λ, λ_i	Retardation time
λ_R	Dimensionless coefficient of friction calculated through the radius of a tube
μ	Poisson ratio
ξ	Depth of penetration
ξ	Dimensionless ratio of volume output
ρ	Density
ρ	Radius of curvature of a bar
ρ_l	Density of a liquid
ρ_s	Density of a solid
ρ^o	Density of a liquid droplet
σ	Stress; shear stress
σ_E	Normal stress in extension; tensile stress
σ_e	Conventional (engineering) stress
σ_i	Stress at the surface of an inner cylinder
σ_{ij}	Components of the stress tensor
$\sigma_{ij,\alpha}$	Components of the stress tensor at a plane inclined by an angle α
σ_o	Stress at the surface of an outer cylinder
σ_w	Shear stress at the wall of a channel
σ_y	Yield stress; yield point
σ_{yE}	Yield stress in simple shear
σ_o	Amplitude of stress (in periodic oscillations)
σ_o	Conventional stress (in uniaxial extension)
σ_1, σ_2	First and second differences of normal stresses
σ_i	Principle values of the stress tensor
σ_∞	Stored part of stress (in relaxation)
Φ	Decay of stress function
$\Phi(\lambda)$	Retardation spectrum (spectrum of retardation times)
φ	Relaxation function
φ	Angle of turn
φ_{max}	Maximal angle of turn
φ_{sp}	Relative angle of twisting (turn)
Ψ	Delayed deformation function
Ψ_1, Ψ_2	First and second normal stress coefficients (in Weissenberg effect) according

	to recommended Nomenclature
ψ_1, ψ_2	First and second normal stress coefficients (in Weissenberg effect) according to Eq 4.11
ψ	Creep function
ω	Frequency
ω	Angular velocity
ω_i	Rate of rotation of the inner cylinder
ω_o	Rate of rotation of the outer cylinder
α, λ	Empirical constants
α, β, γ	Dimensionless geometrical parameters

SUBJECT INDEX