Molecular Theory and Modeling
Chemical Engineering, 698D

Edward J. Maginn
University of Notre Dame
Notre Dame, IN 46556 USA

Contents

Preface

> If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generations of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis (or the atomic fact, or whatever you wish to call it) that all things are made of atoms-little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence, you will see, there is an enormous amount of information about the world, if just a little imagination and thinking are applied.
> *Richard P. Feynman*

This course is intended mainly for graduate students or advanced undergraduates in chemical engineering. It is also appropriate for students with backgrounds in physics, chemistry or other fields that can make use of statistical mechanics, molecular theory and simulations. The emphasis of the course will be the *application* of the principles of statistical mechanics to the solution of problems of interest in engineering and the sciences. Necessarily, there is a significant amount of mathematics and theory involved, and the first half of the class is devoted to the development of the basic machinery of statistical mechanics. By no means is the treatment given here complete, however, so when appropriate additional references are given where the interested student may seek out additional details. The second half of the course deals with solving statistical mechanical models numerically through use of *molecular simulations*. A number of practical issues associated with molecular simulations are touched on, and examples from the some of my research (and other's) are used to illustrate some of the more important points. Again, a comprehensive treatment is not intended or possible, but the course and notes should give you enough information to pursue the topics introduced here in greater detail.

Regarding these notes: the notes you are reading are NOT intended to serve as a textbook. These are simply a collection of notes that I have prepared over the last two years that provide a basis for our class discussions. Thus the writing may not appear coherent in some sections, and you may find lots of typos along the way. I will try to point out mistakes as I encounter them - if you find errors, please bring them to my attention!

I suggest you purchase the textbook by Richard Rowley *Statistical Mechanics for Thermophysical Property Calculations*. This book is very easy to read and may help you grasp the material better than these notes or my lectures alone. In addition, a number of books have been placed on reserve in the Engineering Library in Fitzpatrick Hall. You should make use of these books in your studies to help clarify issues and reach a deeper understanding of topics which interest you.

I am indebted to a number of people who introduced me to this field. Much of the material in these notes can be traced back to old course notes of mine. In particular, I would like to acknowledge the work of Prof. Doros Theodorou and Prof. Arup Chakraborty, who co-taught a class at Berkeley in 1991 entitled “Molecular Theory for Chemical Engineers”. I also benefitted greatly from statistical mechanics courses taught by Prof. David Shirley in 1991 and Prof. David Chandler in 1992.

Chapter 1

Outline and Scope

1.1 Definitions

The course will be broken down into two parts. In the first part, we will develop the essential components of *statistical mechanical theory* to handle the second part of the class, *molecular simulation*. We will use the following definitions when discussing these topics.

Statistical Mechanics is the formalism that provides the link between the microscopic states of matter and observed macroscopic properties. To actually compute macroscopic properties, we have two basic choices. First, we can develop **Statistical Mechanical Theories**. These are rigorous theories that provide an exact relationship between the properties of interest and the microscopic details of the system. Typically, an exact analytical solution is impossible for all but the simplest models. Thus, we *approximate reality* by constructing simple models which can be solved with pencil and paper (or minimal amounts of computation). On the other hand, we can use **Molecular Simulations** to attack the problem. Molecular simulations are a numerical solution of the *full* statistical mechanics. These simulations are *exact* within the numerical accuracy of the computer that is used. Unfortunately, Nature is so complex that formulating the problem with all the required details makes for calculations that are prohibitively long. Molecular simulations take *lots* of computer time! To get around this, we often make approximations to the statistical mechanical models, although these approximations are usually much less severe than are those made in solving purely theoretical formulations. In practice, we use both of these tools interchangeably, and there is no clear division. The advent of fast, inexpensive computers has invigorated the area of molecular simulation, such that these simulations are being carried out in a number of corporate as well as academic research groups.

1.2 Synopsis

In a nutshell, the following major topics will be covered:

1. Equilibrium statistical mechanics: systems in thermodynamic equilibrium

   There are $\mathcal{O}10^{23}$ microscopic variables (degrees of freedom) in a macroscopic system, but a thermodynamic description involves only a handful of degrees of freedom. This remarkable reduction is a consequence of statistical laws that govern the behavior of many–body systems. We will discuss these laws in the initial part of the class.

2. Nonequilibrium statistical mechanics: systems kept off equilibrium

   This isn't often treated in statistical mechanics classes, but it turns out to be very useful when conducting simulations. Thus, we will formulate the statistical mechanics of systems where a perturbing field drives the system away from equilibrium. The formalism relies upon "irreversible thermodynamics", and is the molecular foundation for transport phenomena and chemical kinetics.

3. Statistical mechanical theories

   Having discussed the fundamentals, we will touch on various theoretical approaches that are used to understand the behavior of systems. These theories provide a rigorous formalism for predicting macroscopic behavior. An exact analytical solution is impossible for all but the simplest molecular models so approximations are employed involving *simplified models* (i.e. molecular shape, spatial arrangement, interactions, etc.) and simplified *mathematical formulation* (i.e. Gaussian statistics, etc.). Oftentimes, we do both! Given these approximations, closed–form solution can be solved either analytically or numerically. Typically, good approximations yield good results and modest computational effort.

4. Molecular simulations

   The last topic to be discussed involves the solution of the *full* statistical mechanics. When done properly, *exact* solution of the molecular model is obtained. People often refer to this approach as "computer experiments" that track organization and mode of motion of molecules. The macroscopic manifestation of molecular phenomena are monitored during a simulation. My view is that simulations are just another tool, such as a new spectroscopy, that can be useful in the proper situation. Its main value is its flexibility and that it becomes more powerful with each passing year, as computational speed continues to double every 18 months. The main advantages of molecular simulations are that one can make *property predictions* by constructing a model that faithfully mimics reality. No less importantly, one can also rigorously test molecular theory. That is, an *exact* numerical solution of a model can be obtained to test if the analytic solution obtained from your theory is correct. The main disadvantage of the technique is that it is computationally intensive. Consequently, you are typically limited to short simulation times and length scales. However, one can minimize computational requirements by utilizing various "tricks", using parallel computing techniques, or by invoking approximations which are generally less severe than those required in statistical mechanical theories.

Purpose of the course: To provide *exposure* to some fundamental and applied aspects of statistical mechanics useful in chemical engineering research and practice. This is relevant as Chemical Engineering has been moving toward a more molecular–level approach to problem solving for several years in response to tighter environmental controls (conversion, waste, use), growth of specialty markets and increased competition in commodity markets.

A rough outline of the topics to be covered is given below. Note that this may change according to the interests of the class. In Part 1 of the class, we will develop the basis of statistical mechanics, emphasizing only the essential features necessary to understand how many modern problems are being addressed with these techniques. The following items will be covered:

1.3 Outline of Statistical Mechanics Section

1. From Hamiltonian Dynamics to Statistical Mechanics
   - classical mechanics
   - phase space
   - Liouville equation
   - ergodicity and mixing in phase space
2. Introduction to Equilibrium Statistical Mechanics
   - ensembles: microcanonical, canonical, grand canonical
   - connection with thermodynamics
3. Elementary Statistical Mechanics of Fluids

  - Ideal Gas
  - Mean Field Approximations
  - Applications (e.g. isotherms)

4. Distribution Functions in Monatomic Fluids
  - Pair Distribution Functions

5. Integral Equation Theories

In the second half of the class, we will introduce molecular simulations and cover both theoretical and practical topics associated with their use. The outline below will be more or less followed:

1.4 Outline of Molecular Simulation Section

1. Why use molecular simulations?
   - Difficulty in applying statistical mechanics to "real" problems
   - Relationship between molecular simulation, experiment, and continuum theories
2. Construction of a molecular model
   - molecular representation
   - potentials
   - model system
3. Monte Carlo methods
   - Importance sampling
   - Markov chains
   - Metropolis algorithm
   - Monte Carlo in different ensembles
4. Molecular Dynamics
   - Equations of motion
   - Integration algorithms
   - Molecular systems
   - Constraint dynamics
   - Extended ensembles
   - Structure from MD
   - Transport properties (Green-Kubo relations, linear response theory)
   - Nonequilibrium statistical mechanics, nonequilibrium MD
5. Brownian Dynamics
   - Brownian motion
   - Langevin equation, Fokker-Planck
6. Transition–State Theory

Chapter 2

Introduction

> A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.
> *Albert Einstein*

2.1 Historical Perspective

Before embarking on the details of a topic, it is often useful to spend just a little time seeing where the subject came from. The seeds of statistical mechanics were sown in the early nineteenth century, when classical thermodynamics was developed. Through the "laws" of thermodynamics, scientists and engineers had a conceptual tool that enabled them to design and analyze the processes that sparked the industrial revolution. The efficiency of devices such as steam engines and power plants could be described and predicted using this formalism. Later, thermodynamics was extended to a host of other situations, including the description of chemical and phase equilibrium. Interestingly, classical thermodynamics makes no assumption about the nature of matter, and yet it still works fine!

It was only about 100 years ago that people really started to question what makes up the substances around us. The atomistic view of matter was not widely accepted, although people like van der Waals and Boltzmann made convincing arguments for the existence of atoms. In his Ph.D. thesis of 1873 entitled "On the Continuity of the Gaseous and Liquid States", van der Waals writes

> We have therefore to explain why it is that particles attracting one another and only separated by empty space do not fall together: and to do this we must look around for other causes. These we find in the motion of the molecules themselves, which must be of such a nature that it opposes a diminution of volume and causes the gas to act as if there were repulsive forces between its particles.

van der Waals then goes on to propose the first cubic equation of state, which is still taught in every thermodynamics class. He correctly identified the two key concepts that are essential in understanding fluid behavior: (1) matter is made of molecules that are always moving about, and (2) the molecules have both attractive and repulsive forces between them, which governs the fluid behavior. Although we now know all this fairly well, it was a remarkable conceptual breakthrough at the time.

People realized then that, if fluid behavior was determined by the way in which particles move about and interact, then there must be some link between the behavior of these particles and classical thermodynamics. What was the link? In other words, if the microscopic interactions of molecules governs macroscopic properties, how do we go about calculating what those properties are? To the deterministic thinkers of that day, the task looked impossible. How do you track the movement of 10^{23} particles? Even with today's supercomputers, calculating the interactions between that many particles would take roughly as much time as the universe has been in existence. We simply can’t do it. Ironically, because there are *so many* molecules in a macroscopic fluid element, we actually don’t have to track all the particles. Just as actuaries and pollsters rely on small samples of huge populations to accurately predict death rates and election outcomes, so too are we able to say something about the *average* properties of materials by studying small samples. Following all the particles with classical mechanics isn’t necessary. Instead, all we need to do is figure out the *statistical* behavior of the system, and we can determine macroscopic properties. Hence the name *statistical mechanics*. It was Ludwig Boltzmann who provided this important link between classical thermodynamics and statistical mechanics when he reinterpreting the Second Law in terms of molecular probability. Boltzmann was the one who stated that entropy was proportional to the logarithm of the number of quantum states available to the system (we’ll get into this later). That constant of proportionality is now called Boltzmann’s constant, and we now recognize him as the father of statistical mechanics. Unfortunately for Boltzmann, he died before ever seeing his ideas accepted, but his famous equation is inscribed on his tombstone forever reminding us that he was right.

2.2 Link Between Microscopic and Macroscopic

The methods used to go from a statistical description of molecules to macroscopic properties are complex, and computational difficulties have limited the use of statistical mechanics in engineering applications. Historically, statistical mechanical treatments have only been possible of idealized systems, but much progress has been made in the last ten to twenty years, so that now fairly complex (and thus interesting) systems can be studied with these methods. Conceptually, however, the connection is quite simple, as shown in Figure 2.1. What we will do in this class is show practical ways in which we can make this link.

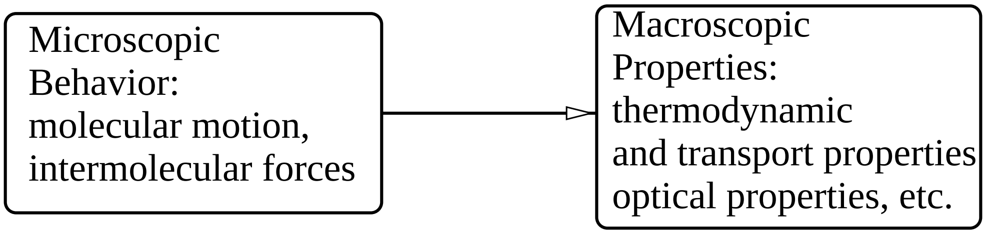

Figure 2.1: Statistical mechanics provides the conceptual link between the microscopic behavior of molecules and the macroscopically observable properties of a material.

2.3 Practical Problems

The next issue we need to address before getting into details is *when* would one like to perform calculations of this type or do this kind of modeling? In other words, what are we interested in calculating and why? Aside from the fact that the field is fun and intellectually pleasing (reason enough for academics!), there are several practical problems that people are trying to address with statistical mechanics/simulations. We will talk briefly about two such problems: rational material design and thermophysical property estimation. Part of this class will be devoted to helping you find applications relevant to your interests or thesis research.

2.3.1 Material Design

Statistical mechanics plays a central role within the hierarchy of approaches for first principle design of engineering materials. An alternative design process, utilizing a “shotgun” approach, is called *combinatorial chemistry* of *combinatorial synthesis*. The tools discussed in this class are also applicable to this process, as some guidance on the molecular level can greatly reduce the number of “trials” one makes and thus can help focus the search for new materials in the combinatorial approach.

The following figure depicts a rational design “hierarchy” strategy. We see that *quantum mechanics* is the most fundamental step in the process, taking information on the chemical constitution of matter and yielding the following type of information

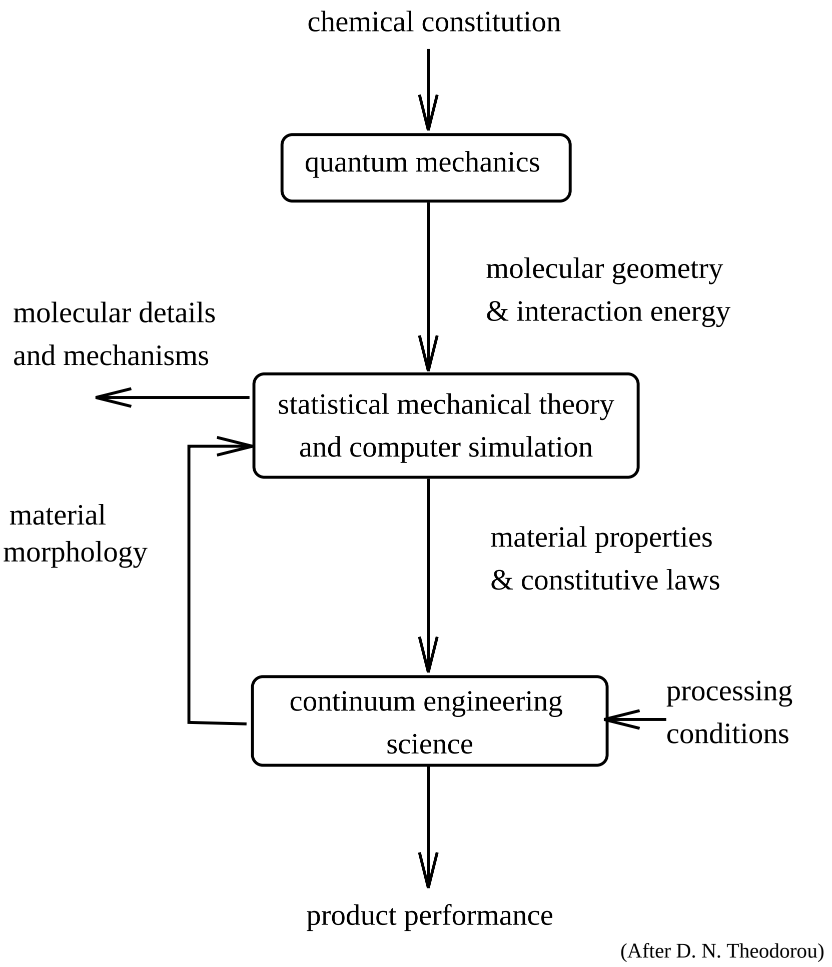

Figure 2.2: Hierarchy of approaches for the rational design of materials (after D. N. Theodorou)

- potential energy of interactions between atoms and molecules as a function of spatial configuration
- molecular geometry resulting from interactions

Given these inputs from quantum mechanics, *statistical mechanics* provides a framework for predicting properties. Note, however, that we may obtain these inputs from other sources, such as experiment. The kind of properties we can get from statistical mechanics include:

- Thermodynamic properties, such as
  - phase diagrams
  - volumetric behavior
  - heat capacity

  - solubility
  - sorption isotherms
  - surface and interfacial tension
- Mechanical properties, such as
  - elastic moduli
  - toughness
  - strength
- Transport and rheological properties, such as
  - viscosities
  - diffusion coefficients
  - thermal conductivities
  - relaxation times
- Chemical properties, such as
  - reaction rate constants
  - equilibrium constants
- Constitutive laws governing materials (i.e. polymer rheology)
- Molecular organization and motion
  - mechanisms underlying macroscopic behavior
  - insight for “what if” questions

All of these properties are useful in and of themselves. We can compare the results of our calculations with experimental measurements to assess how well our model does in capturing physical reality. If the models are good, we can then use the calculations in a *predictive mode* to help us determine properties for systems where experiments are difficult, expensive, or impossible. Once the properties of interest are determined, we then use *continuum engineering science* to move to longer length scales and longer time scales. This enables us to carry out calculations necessary for actual materials and/or process design. These areas include fields traditionally studied by engineers and chemists, including

- thermodynamics
- transport phenomena
- continuum mechanics
- rheology
- chemical and catalytic kinetics

A rational design strategy whereby the input to continuum models is derived *completely* from quantum and statistical mechanics does not exist – and probably never will completely exist for many areas! *However*, parts of this strategy are being developed and used in industry. Recent advances have helped make this possible in:

- molecular–based drug design

- coatings
- catalysis

Many parts of this strategy have been established qualitatively. We typically call this “experience” or “insight”. The techniques discussed in this class will help formalize how we obtain this type of molecular insight. In addition to the usefulness in the design process, traditional experimental investigations are complemented, enhanced, and interpreted through use of theory and simulations. My main point here is that, *even for someone who considers themselves to be purely an experimentalist*, statistical mechanical methods are important and should be considered in your work!

2.3.2 Thermophysical Property Estimation

Another area where statistical mechanical theory and simulation is making a big impact is in the estimation of thermophysical properties. This is really a subset of the rational design process mentioned above, but it is so important that I want to emphasize its use in a separate section. To carry out design calculations, the engineer needs thermophysical properties. That is, we need to know heats of formation, viscosities, densities, phase diagrams and a whole host of other properties. Many of these properties have been measured and tabulated for pure substances. We have much less information regarding mixtures. In addition, there are huge gaps in the data outside relatively mild laboratory conditions. That is, we often have no information regarding thermophysical properties under extreme conditions, because experiments in this regime are often too difficult. We are often left no choice but to estimate thermophysical properties when performing preliminary calculations. (We still must measure many of these properties before a final design is carried out, but the ratio of final designs to preliminary designs is a small number. Thus, there is a big incentive for us to be able to estimate properties with reasonable accuracy in a way much cheaper than experiment). The traditional approach is to develop models to help us predict properties (or worse, we extrapolate existing data - a dangerous thing to do!). Examples of these models include the large number of activity coefficient models or equations of state which help us predict vapor-liquid equilibrium behavior. As you know, these models don’t always work, and typically require some experimental data as input.

To make models more predictive, people have developed *group contribution* methods. A good example is the UNIFAC method for predicting activity coefficients. While this method sometimes work, sometimes it doesn’t. Is there another alternative?

People have been working on methods whereby *molecular simulations* could be used to help predict thermophysical properties of materials. We will discuss exactly how this is done later, but the vision is that an engineer could access a corporate database and ask for a thermophysical property (i.e. the viscosity of a hydrocarbon mixture). If experimental data were available, it would be given to the person. If no data exists, a simulation could be conducted on the company computer using either first-principles or empirical forcefields, and an estimate would be generated. Obviously, if your job is to figure out how to do the simulations to get the estimate then you need to know the content of this course. However, even if you are accessing such information, you should know how it gets generated so that you can have a better idea of its accuracy and the shortcomings of the methods.

2.4 Review of Some Mathematics and Statistics

We will make use of a number of concepts from statistics. This section serves as a review and a way of introducing nomenclature. For additional details, see McQuarrie, *Statistical Mechanics*. Much of what follows comes from McQuarrie, as well as Rowley and *Introductory Statistical Mechanics* by Bowley and Sanchez.

2.4.1 Probability

The everyday meaning of the word “probability” has to deal with the odds of a particular outcome. For example, we speak of probability as meaning “What are the odds the Packers will win this Sunday or that a given horse will win a race?” This is not the interpretation of probability we will be using.

We will think of probability in two ways. The first is the *classical notion of probability* in which we assign, a priori, equal probabilities to all possible outcomes of an event. The second notion is *statistical probability,* which is a measure of the relative frequency of an event.

Classical Probability

The rule for setting the classical probability is simple: count all the points in a given sample space and assign them equal probabilities. If there are W points in the sample space, then the probability of each point is $1/W$. Thus,

$$p_i = \frac{1}{W} \tag{2.1}$$

For example, if we toss a coin, there are two possible outcomes: heads or tails. The probability of getting a heads is just $1/2$, since $W = 2$. If we tossed the coin N times, there would be 2^N possible outcomes (we count each outcome separately, remember, even though we may not be able to distinguish one “head” from another). The probability of any one event for this situation is thus

$$p_i = \frac{1}{2^N} \tag{2.2}$$

What we have done in this case is to enumerate all possible *simple events* and assign equal probabilities to each. A simple event is simply the outcome of a trial that doesn’t depend on any other event. The flipping of a coin is about as close as we can come to a simple event. Does the concept of a classical probability always work? Let’s apply it to the prediction of the sex of a baby. There are two possible outcomes for a baby’s sex: boy or girl. Using classical probability, we would anticipate that $p_{boys} = 0.5$, since in the absence of any other information we assume that both possible outcomes are equally likely. If we look at the records, however, we find that $p_{boys} \approx 0.51$ for most countries. More boys are born than girls. What’s wrong with our approach? An even more extreme case can be found if you use classical probability to predict the weather. Let us predict the probability that it will rain in San Diego on any given day. Since there are two possibilities, that it rains or that it doesn’t, we might naively assume that $p_{rain} = 0.5$. If you’ve ever been to San Diego, you know this is clearly wrong, for it rains only a few days out of the year. The source of difficulty here is that whether it rains or a boy is born depends on a number of events acting together. These are not simple events, but are instead *compound* events. Compound events are made up of a collection of simple events. Clearly, we should test experimentally our a priori assignment of probabilities.

Statistical Probability

Statistical probability is concerned with the experimental method of assigning probabilities to events by measuring the relative frequency of occurrence. Using a modification of our baby analogy, let’s say we want to know what the probability is that a baby born in the U.S. will have blue eyes, brown eyes, or green eyes. One way of determining this is to go out and count babies. Let’s say a roving group of graduate students goes to a number of hospitals around the U.S.[1] The graduate students come back after having examined 1000 babies and they report that 601 of the babies had brown eyes, 251 of the babies had blue eyes, and 148 had brown eyes. We could then assign probabilities in the following way:

$$p_{brown} = 0.601,\ p_{blue} = 0.251, and\ p_{green} = 0.148$$

The advisor of these students isn’t satisfied, however, and tells them to go out and count more babies. They cheerfully agree and count 9000 more babies. Now their sample size is 10,000. They obtain the following:

$$n_{brown} = 6,205,\ n_{blue} = 2,688,\ n_{green} = 1,107$$

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[1] Let’s forget about local variations in the population, and assume that the U.S. is completely homogeneous for the time being. Of course this is a terrible assumption, but this example is only for illustrative purposes!

Their revised probabilities are :

$$p_{brown} = 0.6205,\ p_{blue} = 0.2688, and\ p_{green} = 0.1107$$

Mathematically, the relative frequencies are written as (n_i/N), where n_i is the number of occurrences and N are the total number of samples or trials. If the relative frequencies tend toward a constant as N goes to infinity, then this limit is defined as the *statistical probability*, p_i, given as

$$p_i = \lim_{N\to\infty}\left(\frac{n_i}{N}\right) \tag{2.3}$$

In practice, (n_i/N) will fluctuate, but should converge to a well-defined limit as N gets very large. For random events, the fluctuations in the statistical probability diminish as $N^{-1/2}$; thus the larger N becomes, the more accurately we know p_i. We see that the graduate students probably jumped the gun by assigning probabilities too soon after only 1000 babies. Hopefully, after many more trials they would see values converge and would assign a probability according to eqn 2.3.

For many simple systems such as dice and cards, it is an axiom that the observation of well defined events tends to a limit and that a definite probability can be assigned. Las Vegas has thrived using this axiom. Of course, this is an act of faith, because we can never take an infinite number of trials, but apparently a large number is close enough to make a fortune!

Now, here is a key point: statistical probabilities are only accurate when the same event occurs many times, so that the ratio (n_i/N) can converge. This is why speaking of the "probability" of the Packers beating the Vikings in football doesn't have the same meaning as our stricter definition of probability. The Packers/Vikings contest will only occur once. The next time the teams play, it may be on a different field, with different weather and different players. Another key point: statistical probabilities only have meaning when the ratio (n_i/N) tends to a limit. You may ask what is the statistical probability the Dow Jones Industrial Average will close at 7800 tonight. The market moves up and down, but is not apparently converging on a particular value. Even though it is the same market, it is drifting (we hope up), and not converging. Therefore statistical probabilities have no meaning in this context.

Axioms of Probability Theory

There are three axioms we must identify in probability theory. First, suppose we have a set of probabilities p_i. In the case of classical probability, we have W simple events each with a probability $p_i = 1/W$. In the case of statistical probability, $p_i = n_i/N$, with N going to infinity. In both cases, *the probabilities are positive numbers, or zero*. This is the first axiom: all probabilities are either zero or positive numbers.

The second axiom is that *the probabilities are less than or equal to one*.

The third axiom concerns compound events. Let us say that p_i is the probability that event i occurs, and p_j is the probability that event j occurs. If both events cannot occur in a single trial, then the events are said to be *mutually exclusive*. The third axiom is that for mutually exclusive events, the probability of either event i occurring or j occurring is

$$p_{i+j} = p_i + p_j \tag{2.4}$$

where the notation p_{i+j} refers to the probability that either event i *or* j occur. For example, let's say we draw a card from a pack of cards. The card can't be the ace of spades *and* the jack of hearts. These are exclusive events. The probability of getting *either* the ace of spades or the jack of hearts in a single draw is just

$$p_{AS+JH} = p_{AS} + p_{JH} \tag{2.5}$$

In general, a set $(1, 2, \ldots, r)$ of mutually exclusive events has a set of individual probabilities $(p_1, p_2, \ldots, p_r)$. The third axiom states that the probability that one of these events occurs during a single trial is

$$p = p_1 + p_2 + \cdots + p_r \tag{2.6}$$

Question: Consider an ideal die with 6 sides. What is the statistical probability of rolling an even number? What is the statistical probability of rolling a number less than 4? What is the chance that either or both occur? Are these events mutually exclusive?

Independent Events

The probability that two independent events will occur is the product of their individual probabilities. That is, if the probability of event i is p_i and the probability of *independent* event j is p_j, then the probability that both event occur must be

$$p_{i,j} = p_i p_j \tag{2.7}$$

As an example, the probability of rolling a 6 on a single die is

$$p_6 = \frac{1}{6}$$

Let's say you have just rolled a 6. What is the probability of rolling another 6? For this particular trial, it is again

$$p_6 = \frac{1}{6}$$

However, if you ask what is the probability of rolling two consecutive 6s, where now we consider the two rolls as a single "trial", then the probability is

$$p_{6,6} = p_6 p_6 = \frac{1}{36}$$

Generalizing this, we can have r independent events, each with individual probability $p_1, p_2, \ldots, p_r$. The probability that they all occur in a single trial is

$$p = p_1 p_2 \cdots p_r \tag{2.8}$$

2.4.2 Counting

In statistical mechanics, we have to know how to "count" the number of ways things can be arranged, combined, or permuted. Here are some basic formulas we will use.

Arrangements

The number of ways of arranging n dissimilar objects in a line is $n! = n \times (n-1) \times (n-2) \cdots \times 2 \times 1$. If there are n objects, p of which are identical, then the number of different ways these can be arranged are $n!/p!$. For example, we can arrange the letters A,B,C,D in 24 different ways ($4!$). However, we can only arrange the letters A,A,B,C in 12 different ways. We can generalize this to the case when we have n objects we wish to arrange in a line, where we have p objects of one kind, q objects of another kind, r of another and so on. The number of arrangements in this case is $n!/p!q!r! \cdots$.

Permutations

Let us now say we wish to know how many ways can we arrange r objects out of a total of n objects. We call this the *permutation* of r objects out of n. It is given by the following formula

$$_nP_r = \frac{n!}{(n-r)!} \tag{2.9}$$

As an example of how this works, say we have 5 letters A,B,C,D,E and we wish to know the number of ways of choosing 2 of the 5 letters. The first choice can be any 1 of 5 (i.e. "B") but the second choice can be only 1 of 4 (i.e. "C"). This selection then forms a single permutation of the 5 letters, and has the "value" BC. Assuming that the two choices are independent of each other, the number of permutations can be explicitly worked out. The result for this particular case follows from eqn 2.9

$$ {}_5P_2 = \frac{5!}{(5-2)!} = 20 $$

Combinations

In many situations, we don't care about the order with which the selections are made. For example, if we have our letters A-E as above, we might wish to consider BC as being equivalent to CB. We must therefore divide out the degenerate cases from eqn 2.9. We call this the number of *combinations* of r objects out of n, and the general formula for this is

$$ {}_nC_r = \frac{n!}{r!(n-r)!} \tag{2.10} $$

The number of combinations of two-letter pairs from five total is now 10, whereas the number of permutations is 20.

Molecules of the same kind are indistinguishable, so we will use combinations to count the number of unique, distinguishable arrangements. We can generalize the result in eqn 2.10 to account for different states. For example, let us say we have 10 total letters. We wish to place three of them in box one, five in box two and the remaining two in box three. How many ways can this be done? Let's try to derive a general formula using this specific case.

The first three letters can be chosen with

$$ {}_{10}C_3 = \frac{10!}{3!(10-3)!} $$

number of ways; the second five can be chosen in

$$ {}_7C_5 = \frac{7!}{5!2!} $$

ways; the final two are chosen in

$$ {}_2C_2 = \frac{2!}{2!0!} $$

number of ways. Recalling that $0! = 1$, and recognizing that each of these events is *independent*, we arrive at the total number of ways of making the choices as

$$ W = {}_{10}C_3\,{}_7C_5\,{}_2C_2 = \frac{10!}{3!5!2!} $$

We see that, in general, the number of arrangements for N items with n_i in each state i is

$$ W = \frac{N!}{n_1! \times n_2! \times n_3! \times \cdots} \tag{2.11} $$

where the denominator implies a division by all $n_i!$. We will use eqn 2.11 to work out the total number of ways energy can be arranged between different quantum states.

2.4.3 Distributions

Let's suppose that our team of graduate students now wants to determine how tall the average American adult male is. To do this, they go out and start measuring adult males. They measure 100 men, and arrive at an average height using the following formula

$$\langle h \rangle = \frac{1}{N} \sum_{i=1}^{N} h_i \tag{2.12}$$

where $\langle h \rangle$ is the average height, N is the total number of men (samples) measured, and h_i is the result of measurement i. They obtain a value of $\langle h \rangle = 67.4$ inches. The raw data are plotted in Figure 2.4.3

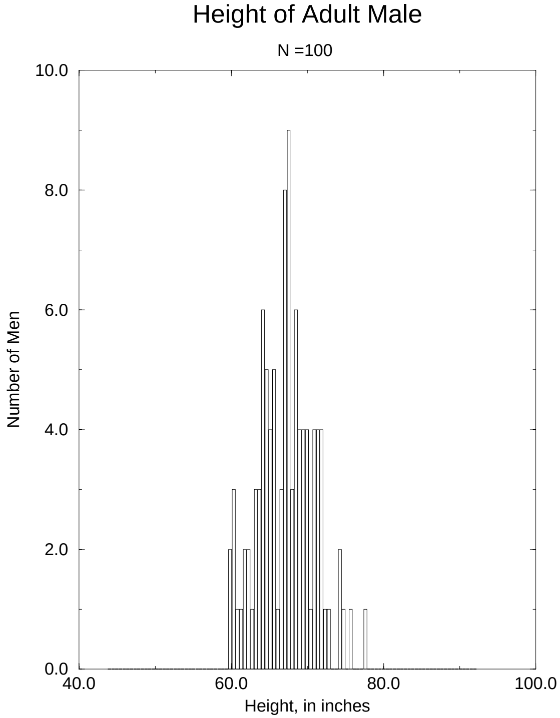

Figure 2.3: Distribution of heights with 100 samples.

What the students don't tell you is that the resolution of their ruler is only about 1/2 an inch, so the heights were actually *binned* as shown in the histogram of Figure 2.4.3. Thus, the *actual* formula used to get the mean was

$$\langle h \rangle = \frac{\sum_{i=1}^{nbins} n_i h_i}{N} \tag{2.13}$$

where $N = \sum_{i=1}^{nbins} n_i$, the sum over all the bins of the number of men having a height within some discrete bin width. Notice that, in the limit of $N \to \infty$, eqn 2.13 goes to the following

$$\langle h \rangle = \sum_{i=1}^{nbins} p_i h_i \tag{2.14}$$

where p_i is the *statistical probability* that a man is of height h_i.

The graduate students are so excited by their results, that they take additional samples with $N = 1000$ and $N = 100,000$; the results are shown in Figures 2.4 - 2.5.

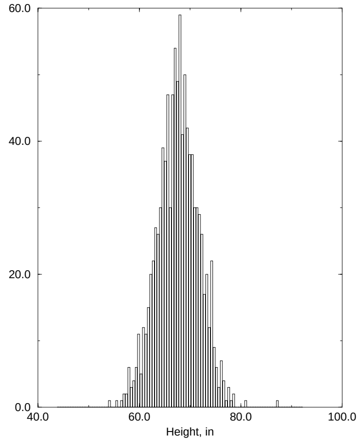

Figure 2.4: Distribution of heights with 1000 samples.

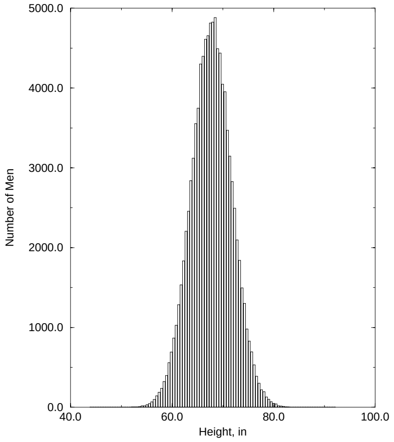

Figure 2.5: Distribution of heights with 100,000 samples.

These results show that as the number of samples increases, the distribution becomes smoother and smoother. Said another way, as the number of samples in each bin gets larger, the statistical probabilities associated with each bin become more and more certain. If our ruler has very fine resolution dh (instead of 1/2 inch), we could replace p_i, the probability of being in bin i by $p(h)dh$, where dh is the differential "bin width" or resolution of our ruler, and $p(h)$ is a smooth function of h. The continuous curve $p(h)$ is called a *probability density distribution*. The sum over the bins becomes an integral, such that

$$\sum_{i=1}^{nbins} p_i = 1 \tag{2.15}$$

becomes

$$\int_{-\infty}^{+\infty} p(h)dh = 1 \tag{2.16}$$

We write the above equation in the general case; for the example we were talking about, the lower limit would obviously be zero. Note that $p(h)$ must be a probability *density* distribution with units of $(h)^{-1}$.

The distribution which fits the data in Figure 2.5 is the most important probability distribution in statistical mechanics, and one you are familiar with. We call it a *Gaussian* or *normal* distribution, and it is defined by

$$p(h) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{1}{2}\left(\frac{h- < h >}{\sigma}\right)^2\right] \tag{2.17}$$

Only two parameters are needed to define this distribution: the mean value, $< h >$, and the standard deviation, σ. Let us now set out to more formally define the concepts of discrete and continuous distributions.

Discrete Probability Distributions

Let $F(x)$ be the value of a discrete function at x. If there are M possible values of F $(F(x_1), F(x_2), \ldots F(x_M))$ with corresponding probabilities P $(P(x_1), P(x_2), \ldots P(x_M))$ then

$$\langle F(x) \rangle = \frac{\sum_{j=1}^{M} P(x_j) F(x_j)}{\sum_{j=1}^{M} P(x_j)} \tag{2.18}$$

$P(x)$ is a *discrete distribution* and $F(x)$ is a *discrete random variable*. Since P is a probability, we know it is normalized.

$$\sum_{j=1}^{M} P(x_j) = 1 \tag{2.19}$$

$$\langle F(x) \rangle = \sum_{j=1}^{M} P(x_j) F(x_j) \tag{2.20}$$

Continuous Distributions

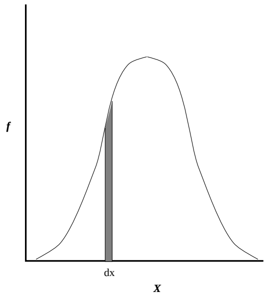

Figure 2.6: An example of a continuous distribution

Let f represent a *continuous distribution function* of events that depend on x. Let $\rho\, dx$ be the probability of an event occurring in the infinitesimal region dx.

$$\rho\, dx = \frac{f\, dx}{\int_{-\infty}^{+\infty} f\, dx} \tag{2.21}$$

ρ is the *probability density*. Again, we have normalized *probabilities* $\int_{-\infty}^{+\infty} \rho\, dx = 1$. Averages with continuous distributions are calculated as follows:

$$\langle F \rangle = \frac{\int F\, f(x)\, dx}{\int f(x)\, dx} \tag{2.22}$$

Moments

If $F(x) = x^M$, then $\langle F(x) \rangle$ is the Mth moment of the distribution $P(x)$. We normally work with *central moments*, however. If $F(x) = (x - \langle x \rangle)^M$, then $\langle F(x) \rangle$ is the Mth central moment of $P(x)$. Using Rowley's nomenclature, we define the Mth central moment as

$$\mu_M \equiv \langle (x - < x >)^M \rangle \tag{2.23}$$

We see that $\mu_0 = 1$, $\mu_1 = 0$, and $\mu_2 = \sigma^2$, the *variance*. The square root of the variance is called the *standard deviation*, and measures the *spread* of the distribution. The *coefficient of skewness*, α_3, is related to the third central moment and is typically normalized with respect to the standard deviation: $\alpha_3 = \mu_3/\sigma^3$. The *coefficient of kurtosis* is defined as $\alpha_4 = \mu_4/\sigma^4$. These coefficients measure the shape of the distribution. A positive α_3 means the distribution is skewed to the right; a negative α_3 means the distribution is skewed to the left. A large α_4 corresponds to a high, narrow peak.

Gaussian distribution

We have already encountered a Gaussian distribution. Using the symbols for this section, the Gaussian distribution has the form

$$P(x) = \frac{1}{(2\pi\sigma^2)^{1/2}} \exp\left[\frac{-(x - \langle x\rangle)^2}{2\sigma^2}\right] \tag{2.24}$$

Question: What are the first four central moments of the Gaussian distribution?

Binomial and Multinomial Distributions

When we introduced the concept of counting, we discussed *combinations*. The number of combinations of r objects out of a total on n was given by eqn 2.10. This equation is the equation for the coefficients of a *binomial distribution*[2]. Similarly, the number of orderings for groupings of more than two particles are the coefficients of a *multinomial distribution*. That is, the distribution density of N things taken $n_1, n_2, \ldots n_r$ at a time is

$$\frac{N!}{n_1! n_2! \cdots n_r!} = \frac{N!}{\prod_{j=1}^{r} n_j!} \tag{2.25}$$

where the term in eqn 2.25 is known as a *multinomial coefficient*. Note that $n_1 + n_2 \cdots n_r = N$. An important feature of multinomial distributions is that the variance goes to zero as N becomes large. In fact, the variance narrows so rapidly that the peak narrows to a single value. In the limit of an infinite N, the distribution collapses to a single spike. In this limit, then, the entire distribution *may be replaced by the maximum term*. We will make use of this property extensively later on.

2.4.4 Stirling's Approximation

From the above discussion, it is clear that we will encounter factorials of very large numbers quite often. **Question**: What is $N!$ if $N = 10^{23}$? It is awkward to calculate factorials of very large numbers directly, but we can develop an asymptotic approximation valid for large N.

$N!$ is a product, but $\ln N!$ is a sum.

$$\ln N! = \sum_{m=1}^{N} \ln m$$

If we plot x vs $\ln x$ as a continuous curve, and also plot $\ln x$ as a series of rectangles, we see that $\ln x$ forms an envelope for the rectangles. $\ln x!$ is the sum of the area of all rectangles (see Figure 2.7).

For small x, $\ln x$ is a poor approximation of the area of the rectangles. However, as x becomes large, the envelope becomes a very good approximation for the area of the rectangles. For very large N, we may write

$$\ln N! = \sum_{m=1}^{N} \ln m \approx \int_1^N \ln x \, dx = N \ln N - N \tag{2.26}$$

where eqn 2.26 is valid only for large N. Eqn 2.26 is called *Stirling's equation*, and will be quite useful later on.

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[2] See McQuarrie for a brief discussion of binomial and multinomial expansions.

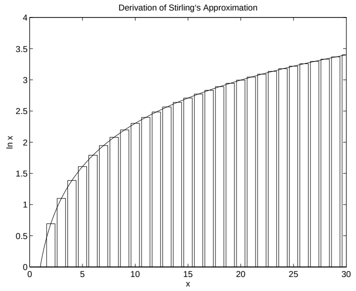


Figure 2.7: Graphical depiction of Stirling's approximation (after McQuarrie)

2.4.5 Lagrange Multipliers

Finally, we need to know how to maximize equations subject to constraints (in particular, we will do this for eqn 2.25). Consider $f(x_1, x_2, \ldots, x_r)$, where the variables are connected by other equations, such as $g_1(x_1, x_2, \ldots, x_r) = 0$, $g_2(x_1, x_2, \ldots, x_r) = 0$, etc. The g_1, g_2, etc. are a series of *constraints*. Were it not for the constraints, the extremum of f would be found by

$$df = \sum_{j=1}^{r} \left(\frac{\partial f}{\partial x_j} \right)_0 dx_j = 0 \tag{2.27}$$

The zero subscript reminds us that eqn 2.27 is zero only when the r partial derivatives are evaluated at the extremum of f. The value of each x_j at the extremum is x_j^0.

With *no* constraints, each dx_j could be varied independently and for df to be zero, $\partial f / \partial x_j = 0$ for all j. The result would be r equations, from which the value of the r x_j^0 could be obtained. With one constraint ($g(x_1, x_2, \ldots, x_r) = 0$), we wish to find the conditional extremum, at x_j^0 subject to the imposed constraint. We have an additional equation relating the x's (which are now not all independent)

$$dg = \sum_{j=1}^{r} \left(\frac{\partial g}{\partial x_j} \right)_0 dx_j = 0 \tag{2.28}$$

This equation serves as a constraint that the dx_j must follow, making one of them depend on the other $r-1$. This equation must also be satisfied at the conditional extremum, since g is a constant. There are a few ways to proceed; in the Lagrange method, one multiplies eqn 2.28 by a parameter λ and adds the result to eqn 2.27

$$\sum_{j=1}^{r} \left(\frac{\partial f}{\partial x_j} - \lambda \frac{\partial g}{\partial x_j} \right) dx_j = 0 \tag{2.29}$$

The dx_j are *still* not independent, but eqn 2.28 is an equation giving one of the dx_j in terms of the other $r-1$ independent ones. Let the dependent dx_j be given by dx_μ.

Define λ such that the coefficient of dx_μ in eqn 2.29 vanishes:

$$\frac{(\partial f / \partial x_\mu)_0}{(\partial g / \partial x_\mu)_0} = \lambda \tag{2.30}$$

where the subscript indicates that the partial derivatives are evaluated at values of x_j such that f is at an extremum under the constraint of eqn 2.28.

The result is a sum of $(r-1)$ terms in eqn 2.29 involving the independent dx_j's, which can be varied independently such that

$$\left(\frac{\partial f}{\partial x_j} \right)_0 - \lambda \left(\frac{\partial g}{\partial x_j} \right)_0 = 0 \tag{2.31}$$

for $j = 1, 2, \ldots, \mu - 1, \mu + 1, \ldots, r$

Combine these $r - 1$ equations with our choice for λ, and we arrive at

$$\left(\frac{\partial f}{\partial x_j}\right)_0 - \lambda \left(\frac{\partial g}{\partial x_j}\right)_0 = 0 \tag{2.32}$$

for *all* j.

This gives r equations and r unknowns (the values of x_j at the extremum). Since the solution depends on λ, we actually obtain as roots $x_j(\lambda)$. That is, $(\partial f/\partial x_\mu)_0$ and $(\partial g/\partial x_\mu)_0$ are evaluated at values of x_j that maximizes (or minimizes) f; these derivatives are known in terms of λ using eqn 2.32.

What is λ?

λ is typically determined from physical arguments (see later), and can be found by using the constraint $g(x_j(\lambda)) = 0$.

If there is more than one constraint, the process is similar. We obtain a Lagrange multiplier for each constraint, and proceed as above to get

$$\frac{\partial f}{\partial x_j} - \lambda_1 \frac{\partial g_1}{\partial x_j} - \lambda_2 \frac{\partial g_2}{\partial x_j} - \cdots = 0 \tag{2.33}$$

Chapter 3

Elementary Concepts in Mechanics and Phase Space

3.1 Generalized Coordinates

Consider a system with a large number of degrees of freedom: i.e. N molecules of a monatomic fluid in a 3-D volume. In the *quantum mechanical* description, the state of the system is described by the wave function, $\mathbf{\Psi}$, which represents the displacement of a wave as it fluctuates with position and time: $\mathbf{\Psi} = \mathbf{\Psi}(\mathbf{q}, t)$. $\mathbf{\Psi}$ is a function of the configuration of all constituent nuclei and electrons, represented by $\mathbf{q}$. Note that bold face type will be used throughout to represent vectorial quantities. In principle, we can solve for this wave function through the Schrödinger equation, subject to the appropriate boundary conditions. Solving for $\mathbf{\Psi}$ then gives expectation values for any mechanical property. This is the subject of a course on quantum mechanics, and so will not discussed in detail here. However, we will refer to quantum mechanics from time to time, as it is somewhat easier to derive statistical mechanical formalisms by invoking concepts from quantum mechanics.

In *classical mechanics*, the state of the system is described by the set of generalized coordinates, $\mathbf{q}^N$, which represents the position of all the atoms, and the set of generalized momenta of the atoms, $\mathbf{p}^N$. We know from the uncertainty principle that we cannot know both the position and momentum of a species exactly, but for most systems we are interested in, we can ignore this effect. (Note: there are some systems for which quantum effects *are* important in determining macroscopic behavior. A good example is the diffusion of hydrogen, especially at lower temperatures.) By way of example, a system could be described using Cartesian position vectors,

$$\mathbf{q}^N = \mathbf{r}^N \tag{3.1}$$

where $\mathbf{r}^N$ represents the $3N$ Cartesian components of position and

$$\mathbf{p}^N = m\mathbf{v}^N \tag{3.2}$$

where $\mathbf{v}^N$ is the $3N$ Cartesian components of molecular velocity. Variables other than Cartesian coordinates can also be used. For example, in Figure 3.1 a commonly-used set of generalized coordinates re used to describe the conformation of a linear molecule made up of four “beads”. This can be thought of as a crude representation of *n*-butane.

Using generalized coordinates, we locate the position of the first atom at Cartesian position $\mathbf{r}_1$. Rather than specify $\mathbf{r}_2$ for atom 2, however, we can equivalently place it by defining two *Eulerian angles*, Ψ_1 and Ψ_2, and a bond length, ℓ_1. Ψ_1 can range between 0 and 2π, while the limits on Ψ_2 are between 0 and π. Similarly, atom 3 could be located with a Cartesian vector $\mathbf{r}_3$, but we can also locate it by specifying: a third Eulerian angle, Ψ_3, which defines the rotation about the axis of the bond between atoms 1 and 2; a bond length ℓ_2; and a *bond angle*, θ_1. Atom 4 is placed by defining a *torsion (or dihedral) angle*, ϕ_1, bond length ℓ_3 and bond angle θ_2. Subsequent

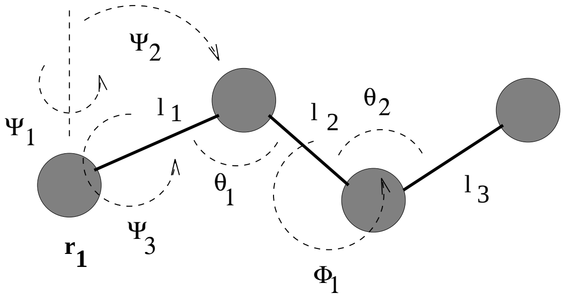


Figure 3.1: Schematic showing one type of generalized coordinate system

atoms i can be defined with ϕ_{i-3}, θ_{i-2} and ℓ_{i-1}. The complete set of generalized coordinates is specified by the vector $\mathbf{q}^N$

$$\mathbf{q}^N = (\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N) \tag{3.3}$$

where $\mathbf{q}_1 = \mathbf{r}_1$, $\mathbf{q}_2 = \Psi_1$, Ψ_2, ℓ_1, etc. We will denote the coordinates of the atoms in the most general sense as $\mathbf{q}^N$.

Before going on, you may rightly ask why we would go to all this trouble to define a generalized coordinate system, when it is easier to think in Cartesian space? The answer is simple: we know things like bond lengths and bond angles from spectroscopy measurements. When we later develop models for the molecular geometry of these systems, we want to be able to refer to these generalized coordinates. These are the natural degrees of freedom of interest to us; knowing the relative Cartesian coordinates of adjacent atoms in a molecule isn't as useful as knowing the bond lengths, angles, etc.

The *total configurational degrees of freedom* of a classical system are made up of configuration space, given by

$$\mathbf{q}^N = (\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N) \tag{3.4}$$

and momentum space

$$\mathbf{p}^N = (\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N) \tag{3.5}$$

As mentioned above, simultaneous specification of position and momentum is permitted in the classical limit (i.e. uncertainty principle limits are unimportant compared to magnitude of $\mathbf{p}^N$ and $\mathbf{q}^N$).

We now define the *state vector* or *system point* or *representative point* as

$$\mathbf{x}^N \equiv (\mathbf{q}^N, \mathbf{p}^N) = (\mathbf{q}_1, \mathbf{q}_2 \ldots, \mathbf{q}_N; \mathbf{p}_1, \mathbf{p}_2 \ldots, \mathbf{p}_N) \tag{3.6}$$

The 6N–dimensional set from which $\mathbf{x}^N$ takes a value is called the *phase space* of the system. The phase space is an important concept, and is given the special symbol $\mathbf{\Gamma}$. A point on $\mathbf{\Gamma}$ represents a microstate of the entire system. A **KEY POINT** to understand is the following: if $\mathbf{x}^N$ is known at one time, *it is completely determined for any other time (past and present)* through the classical equations of motion. We can illustrate this, as in Figure 3.2. As time goes by, the state vector moves in 6N–dimensional phase space, tracing a trajectory on it. The trajectory is a 1–dimensional line, with each point corresponding to an instant in time. We can describe this using classical mechanics.

3.2 Review of Classical Mechanics

3.2.1 Newtonian Mechanics

Newton's equations of motion are commonly written as

$$\frac{d\mathbf{p}}{dt} \equiv \dot{\mathbf{p}} = \mathbf{F} \tag{3.7}$$

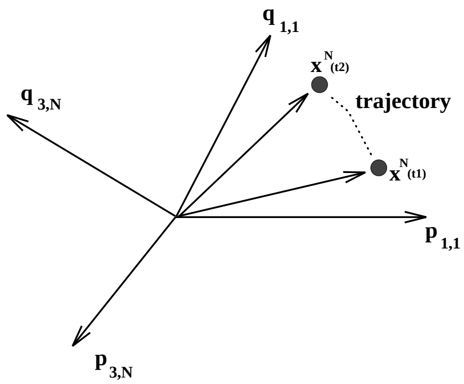


Figure 3.2: The above figure shows a schematic representation of the movement of the system point $\mathbf{x}^N(t)$ in a 6N–dimensional phase space from time t_1 to later time t_2. Only 4 of the 6N axes spanning phase space are shown. (After Reichl, L. E. *A Modern Course in Statistical Physics*)

where the dot above the momentum vector refers to a time derivative, and where **F** is the force vector. This simply states that the rate of change of momentum equals the applied force. If mass is independent of time, then we obtain

$$\frac{d\mathbf{p}}{dt} = m\frac{d\mathbf{v}}{dt} = m\ddot{\mathbf{r}} = m\mathbf{a} \tag{3.8}$$

where the two dots now represent the second derivative with respect to time and the acceleration vector has been defined.

If $\mathbf{F} = \mathbf{F}(x, y, z)$, eqn 3.7 is a set of 2nd order differential equations in (x,y,z) whose solution, given initial conditions, gives (x,y,z) as a function of time. Eqn 3.7 is an *equation of motion*. Recall that you used Newton's classical equations of motion to solve elementary physics problems, like computing ballistic trajectories, etc. If we think of a system with many interacting particles, the equations become much more difficult to solve, but in principle they can be solved by direct application of the equations of motion.

In the Newtonian formulation, the total energy of the system is made up of the *potential energy*, $\mathcal{V}$, and *kinetic energy*, K. For conservative systems (i.e. non-dissipative), the kinetic energy depends only on particle velocities and mass, though the following equation

$$K = \sum_{i=1}^{N} \frac{m_i v_i^2}{2} \tag{3.9}$$

while the potential energy is assumed to depend only on particle *position*: $\mathcal{V} = \mathcal{V}(\mathbf{q})$. Thus the total energy, which is given the symbol H, for reasons that will become apparent momentarily, is found from

$$H(\mathbf{q}, \mathbf{v}) = K + \mathcal{V} \tag{3.10}$$

The force between pairs of particles in a conservative system is given by

$$\mathbf{F} = -\nabla_{\mathbf{q}}\mathcal{V} \tag{3.11}$$

The standard Newtonian equations are fine in Cartesian coordinates, but become unwieldy in other coordinate systems. This is important, as we have said we would like to use generalized coordinate systems to describe molecules. An example of the problem with the Newtonian formulation is given in Rowley's book, and is sketched out in the following example.

Example: Computing Planetary Orbits

The gravitational potential and force between two objects of mass M and m is given by

$$\mathcal{V} = -\frac{MmG}{r} \tag{3.12}$$

$$\mathbf{F} = -\nabla_{\mathbf{r}}\mathcal{V} = -\frac{MmG\mathbf{r}}{r^3} \tag{3.13}$$

where $\mathbf{r}$ is the vector between the masses M and m. We can then write eqn 3.8 for the little mass as

$$m\ddot{\mathbf{r}} + -\frac{MmG\mathbf{r}}{r^3} = 0 \tag{3.14}$$

In Cartesian coordinates, the x and y components of the position vector $\mathbf{r}$ in the above equation are

$$\ddot{x} + \frac{MGx}{r^3} = 0, \quad \ddot{y} + \frac{MGy}{r^3} = 0$$

with $r^2 = x^2 + y^2$. It is easiest to solve this problem by changing coordinate systems. We use polar coordinates, where

$$x = r\cos(\theta) \quad y = r\sin(\theta)$$

After some manipulation, we arrive at the final form of the equations in polar coordinates

$$m\ddot{r} = m\dot{\theta}r - \frac{MmG}{r^2} \tag{3.15}$$

We see that in polar coordinates, a second force term arises that we call the centrifugal force. This is annoying, however, because the form of the equations of motion depends on what coordinate system we use! That is, the equations of motion in polar coordinates do not look like the equations of motion in Cartesian coordinates. There must be a better way!

We'd like to write the equations of motion in a form that is *independent* of the choice of coordinate system. That is, we wish to write

$$m\ddot{\eta} = \mathbf{F}_\eta \tag{3.16}$$

where η is some generalized coordinate system. We'd like to avoid coordinate transformations if possible. It turns out that there are two popular formulations of the equations of motion that *are* independent of coordinate system. We refer to these formulations as *Lagrangian* mechanics and *Hamiltonian* mechanics.

3.2.2 Lagrangian Mechanics

Let's consider a single particle; generalizing to multiple particles simply involves the use of vectors instead of scalars. Let K be the kinetic energy of the system. In Cartesian coordinates

$$K(\dot{x}, \dot{y}, \dot{z}) = \frac{m}{2}[\dot{x}^2 + \dot{y}^2 + \dot{z}^2] \tag{3.17}$$

Let $\mathcal{V}$ be the potential energy of the system, which is assumed to only be a function of position; i.e. $\mathcal{V} = \mathcal{V}(x, y, z)$. For a conservative system

$$F_x = -\frac{\partial\mathcal{V}}{\partial x} \tag{3.18}$$

so that

$$m\ddot{x} = -\frac{\partial\mathcal{V}}{\partial x} \tag{3.19}$$

or generally

$$m\ddot{r} = -\nabla_r \mathcal{V} \tag{3.20}$$

Now let's introduce a function L called the *Lagrangian*

$$L(x,y,z,\dot{x},\dot{y},\dot{z}) \equiv K(\dot{x},\dot{y},\dot{z}) - \mathcal{V}(x,y,z) \tag{3.21}$$

We then can write

$$\frac{\partial L}{\partial \dot{x}} = \frac{\partial K}{\partial \dot{x}} = m\dot{x} \tag{3.22}$$

$$\frac{\partial L}{\partial x} = -\frac{\partial \mathcal{V}}{\partial x} = F_x \tag{3.23}$$

Newton's equations of motion then become

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) = \frac{\partial L}{\partial x} \tag{3.24}$$

Similar expressions hold for the other Cartesian directions so that in general

$$\frac{d}{dt}(\nabla_{\dot{\mathbf{r}}} L) = \nabla_{\mathbf{r}} L \tag{3.25}$$

The advantage of the Lagrangian formulation is that it is independent of coordinate system, so that if (x,y,z) are transformed to (q_1, q_2, q_3)

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) = \frac{\partial L}{\partial q_j}, \;\; j = 1,2,3 \tag{3.26}$$

That is, eqn 3.26 is of the form of eqn 3.16, which satisfies our goal of arriving at equations of motion that are independent of coordinate system.

Notice that eqn 3.26 comprises 3 second order differential equations. To solve them, we must specify initial velocities as

$$(\dot{q}_1(0), \dot{q}_2(0), \dot{q}_3(0))$$

and initial positions as

$$(q_1(0), q_2(0), q_3(0))$$

Given these initial conditions and eqn 3.26, all future and past trajectories can be determined. Note that for N particles, there are 3N Lagrange equations and 6N initial conditions.

3.2.3 Hamiltonian Mechanics

Now that we have achieved our goal of writing a set of equations of motion that are independent of coordinate system, why go on? It turns out that the *Hamiltonian* equations of motion are more convenient to use in some cases than the Lagrangian formulation. We will therefore proceed to derive the Hamiltonian form of the equations of motion. Starting with eqn 3.22, we can write the generalized momentum as

$$p_j = \frac{\partial L}{\partial \dot{q}_j}, \;\; j = 1,2,3,\ldots,N \tag{3.27}$$

We say that the generalized momentum is *conjugate* to the generalized position q_j. We now define the Hamiltonian of a 1–particle system as

$$H(p_1,p_2,p_3,q_1,q_2,q_3) = \sum_{j=1}^{3} p_j \dot{q}_j - L \tag{3.28}$$

Notice that H is a function of generalized *momenta* and generalized coordinates, whereas L is a function of generalized coordinates and *velocities*. Assuming that K is quadratic in generalized velocities we can write

$$K = \sum_{j=1}^{N} a_j(q_1, q_2, q_3)\dot{q}_j^2 \tag{3.29}$$

If we again assume that $\mathcal{V}$ is only a function of generalized positions, then

$$p_j = \frac{\partial L}{\partial \dot{q}_j} = \frac{\partial K}{\partial \dot{q}_j} = 2a_j\dot{q}_j \tag{3.30}$$

Recall, however, that $H = \sum_{j=1}^{N} p_j\dot{q}_j - L$, so

$$H = \sum_{j=1}^{N} 2a_j\dot{q}_j^2 - L = 2K - K + U \tag{3.31}$$

$$H = K + U \tag{3.32}$$

You can easily show by partial differentiation of eqn 3.32 that

$$\frac{\partial H}{\partial p_j} = \dot{q}_j \tag{3.33}$$

$$\frac{\partial H}{\partial q_j} = -\dot{p}_j \tag{3.34}$$

Eqns 3.33 and 3.34 are Hamilton's equations of motion. They constitute 6N 1st order differential equations, and require 3N initial positions ($\mathbf{q}(0)$) and 3N initial momenta ($\mathbf{p}(0)$) to solve. It can be shown that if $L \neq L(t)$ then $\frac{dH}{dt} = 0$. Since $H = K + U$, this means the system is *conservative* (i.e. energy is conserved).

Why do we use a Hamiltonian? There are two main reasons. First, just like in Lagrangian mechanics, **Hamiltonian mechanics are independent of coordinate system**. This means if we change coordinates from the set $(q_1, q_2 \cdots)$ to $(q'_1, q'_2, \cdots)$, and also change the conjugate momenta from $(p_1, p_2 \cdots)$ to $(p'_1, p'_2, \cdots)$, where p' is defined in terms of q' by $p'_i = \frac{\partial K}{\partial \dot{q}_i}$, the element of volume in (q, p) space is equal to the element of volume in (q', p') space

$$dq_1 dq_2 \cdots dp_1 dp_2 \cdots = dq'_1 dq'_2 \cdots dp'_1 dp'_2 \cdots$$

That is, the Jacobian of the transformation $(q, p) \rightarrow (q', p')$ is unity. In addition, H is total energy, a quantity of great interest in quantum and statistical mechanics.

To emphasize again, given $H(\mathbf{x}^N) = H(\mathbf{p}^N, \mathbf{q}^N)$, knowledge of $\mathbf{x}^N(t_1)$ enables $\mathbf{x}^N(t_2)$ to be uniquely determined for all t_2 ($t_2 < t_1$ and $t_2 > t_1$). **Hamiltonian dynamics are completely time reversible** (see Goldstein, H.; *Classical Mechanics*).

3.3 Phase Space and Ergodicity

We have now shown that the Hamiltonian of a conservative system equals the total energy, which is a constant. This means that $H(\mathbf{x}^N) = H(\mathbf{p}^N, \mathbf{q}^N) = E$, E being a constant, is a 6N-1 dimensional hypersurface in phase space, on which the system must lie if its energy is constant and equal to E. (One degree of freedom is removed by the constraint that energy must be constant). This allows us to make two interesting observations regarding Hamiltonian trajectories in phase space:

1. Distinct trajectories on a constant energy hypersurface will never cross.

   Let $\mathbf{x}_A^N(t_1)$ and $\mathbf{x}_B^N(t_1)$ be state points of two systems characterized by the same Hamiltonian in phase space at time t_1, such that $\mathbf{x}_A^N(t_1) \neq \mathbf{x}_B^N(t_1)$. Then, **the trajectories traced by systems A and B in phase space will never cross at all future (and past) times**.

   Proof: If the two systems crossed at t_2, then by integrating Hamilton's equations of motion backward in time to t_1, the systems would have to be at the same state point. That is, $\mathbf{x}_A^N(t_1) = \mathbf{x}_B^N(t_1)$, which violates our initial proposition. Thus, the trajectories traced by A and B may never cross.

2. The trajectory traced by a conservative system on a constant energy hypersurface as time evolves can never intersect itself. It *can* form a closed loop, however. Pictorially, we can represent these ideas as follows:

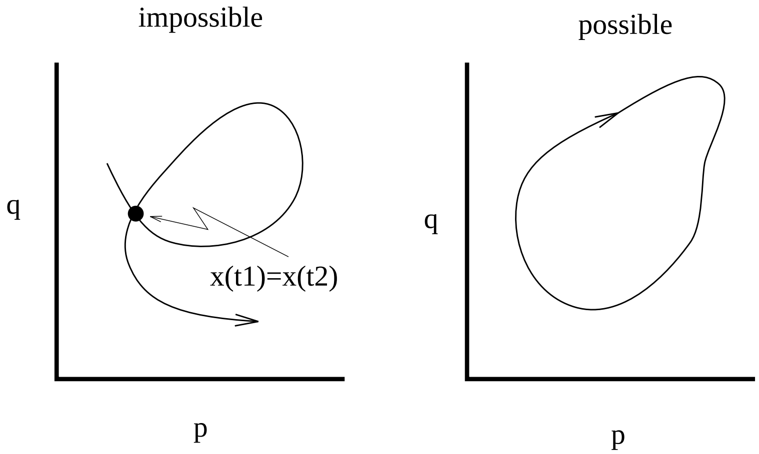


Figure 3.3: Phase space trajectory that crosses itself (left, unallowed) and a trajectory that forms a loop (right, allowed)

Proof: Assume the trajectory crosses, so that $\mathbf{x}^N(t_1) = \mathbf{x}^N(t_2)$ for $t_2 > t_1$ (see Figure 3.4). If a closed loop is not formed, we can always locate a point $\mathbf{x}^N(t_0)$, $t_0 < t_1$ and $(t_1 - t_0) < (t_2 - t_1)$. (i.e. $\mathbf{x}^N(t_0)$ does not lie on the loop).

But this is impossible!

- Start at $\mathbf{x}^N(t_1)$ and integrate backward in time for $(t_1 - t_0)$. We reach $\mathbf{x}^N(t_0)$.
- Start at $\mathbf{x}^N(t_2)$ and integrate backward in time for $(t_1 - t_0)$. We reach a point between $\mathbf{x}^N(t_1)$ and $\mathbf{x}^N(t_2)$ that is *necessarily* distinct from $\mathbf{x}^N(t_0)$. Trajectory may not cross itself, unless it forms a single loop.

  Do you see why a single loop is allowed?

3.4 Probability Density and the Liouville Equation

As stated earlier, measured macroscopic quantities such as pressure, temperature and density arise from molecular interaction and motion. We can't *detect* the relationship between molecular motion and macroscopic properties. In addition, we can't detect differences between systems existing in different microstates (distinct state vectors) but satisfying the same macroscopic conditions, such as volume and energy. That is to say, a system under certain macroscopic conditions is not a single state, but rather is an *infinite number of states* on the same energy hypersurface. In other words, when we have a material under certain conditions, it consists of a *collection* of systems,

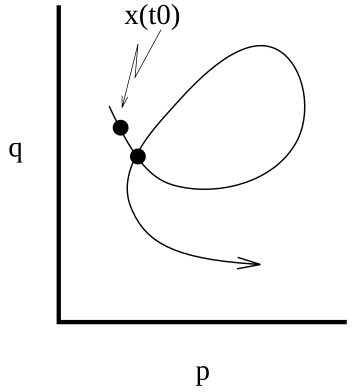


Figure 3.4: Schematic showing why trajectories on a constant energy hypersurface may never cross themselves as time evolves.

identical in composition and macroscopic conditions, but existing in different microstates. Such a collection of systems was termed an **ensemble** by J. W. Gibbs. We'll say more about ensembles later, but for now all we'll say is that an ensemble corresponds to a large number of state points $\mathbf{x}^N = \mathbf{x}^N(\mathbf{p}^N, \mathbf{q}^N)$ in phase space.

3.4.1 Probability Density

At any given time, we can describe an ensemble by a probability density $\rho(\mathbf{x}^N, t)$ of phase space. By definition:

$$\rho(\mathbf{x}^N, t)\ d\mathbf{x}^N \equiv \rho(\mathbf{p}^N, \mathbf{q}^N)\ d\mathbf{p}^N d\mathbf{q}^N \tag{3.35}$$

where

$$\rho(\mathbf{x}^N, t) = \rho(\mathbf{p}_1, \cdots, \mathbf{p}_N; \mathbf{q}_1, \cdots, \mathbf{q}_N) d\mathbf{p}_1, \cdots, d\mathbf{p}_N d\mathbf{q}_1, \cdots, d\mathbf{q}_N \tag{3.36}$$

Physically, eqn 3.35 defines the probability that state point $\mathbf{x}^N$ lies within volume element $\mathbf{x}^N$ to $\mathbf{x}^N + d\mathbf{x}^N$ at time t. Note that an ensemble is *completely specified* by $\rho(\mathbf{x}^N, t)$!

Some characteristics of ensemble probability densities:

1. Probability densities are normalized

$$\int_\Gamma \rho(\mathbf{x}^N, t) d\mathbf{x}^N = \int_\Gamma \rho(\mathbf{p}^N, \mathbf{q}^N) d\mathbf{p}^N d\mathbf{q}^N = 1 \tag{3.37}$$

   where the integral takes place over all of phase space, Γ.

2. The probability of finding the state point in a small region R of Γ–space at time t is:

$$P(R, t) = \int_R \rho(\mathbf{p}^N, \mathbf{q}^N, t) d\mathbf{p}^N, d\mathbf{q}^N \tag{3.38}$$

   That is, to find $P(R, t)$, we simply integrate the probability density over R.

Now, we wish to see how the probability density evolves. The result will be an important equation called the Liouville equation. This equation is simply a conservation equation for probability. As such, I will show a derivation that is probably most familiar to engineers, who have derived general conservation equations in the study of fluid mechanics. Many alternative derivations are possible!

3.4.2 Evolution of Probability Density – Engineering Approach

As time evolves, the state points constituting the ensemble move along trajectories. We can think of the state points as particles or fluid elements moving in 3–dimensional space. The question we wish to answer is: How does the probability density evolve with time? To answer this, we simply need to derive the "continuity" equation for $\rho(\mathbf{x}^N, t)$ using a fluid mechanics approach.

Let V be an arbitrary 6N–dimensional closed domain in phase space, S be a (6N-1)–dimensional "surface", $\dot{\mathbf{x}}^N$ be the 6N–dimensional vector $(\dot{\mathbf{p}}^N, \dot{\mathbf{q}}^N)$, and let $\mathbf{n}(\mathbf{p}^N, \mathbf{q}^N)$ be the vector locally normal to S at $(\mathbf{p}^N, \mathbf{q}^N)$ (see Figure 3.5).

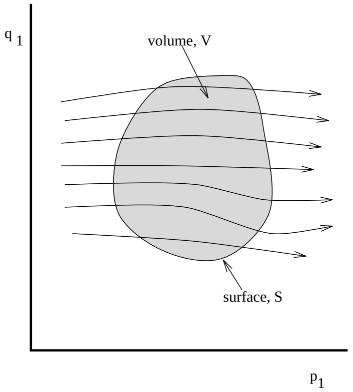


Figure 3.5: Flow of state points through a region V with surface S.

Continuity requires that state points are neither created nor destroyed, so the net number of state points leaving S per unit time equals the rate of decrease of state points in volume V.

$$\oint_S \mathbf{n} \cdot \dot{\mathbf{x}}^N \rho(\mathbf{x}^N, t) dS = -\frac{\partial}{\partial t} \int_V \rho(\mathbf{x}^N, t) d\mathbf{x}^N \tag{3.39}$$

We can use the divergence theorem to convert the surface integral into a volume integral. Define the operator

$$\nabla_{\mathbf{x}^N} \equiv \left(\frac{\partial}{\partial \mathbf{p}_1}, \cdots, \frac{\partial}{\partial \mathbf{p}_N}, \frac{\partial}{\partial \mathbf{q}_1}, \cdots, \frac{\partial}{\partial \mathbf{q}_N} \right)$$

Then continuity becomes

$$\int_V \left[\nabla_{\mathbf{x}^N} \cdot (\rho(\mathbf{x}^N, t) \dot{\mathbf{x}}^N) + \frac{\partial}{\partial t} \rho(\mathbf{x}^N, t) \right] d\mathbf{x}^N = 0 \tag{3.40}$$

From eqn 3.40 and the use of Hamilton's equations, you can show that

$$\nabla_{\mathbf{x}^N} \cdot \dot{\mathbf{x}}^N = 0 \tag{3.41}$$

Eqn 3.41 is entirely analogous to the incompressibility condition in fluid mechanics, $\nabla \cdot \mathbf{v} = 0$. It shows that the collection of state points in an ensemble flow as an *incompressible fluid* as a result of Hamilton's equations of motion.

From eqn 3.41, we get that

$$\dot{\mathbf{x}}^N \cdot \nabla_{\mathbf{x}^N} \rho + \frac{\partial \rho}{\partial t} = 0 \tag{3.42}$$

Again, this is analogous to the continuity equation for fluid mechanics

$$\mathbf{v} \cdot \nabla \rho + \frac{\partial \rho}{\partial t} = 0$$

It is common to use the substantial or total time derivative

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \dot{\mathbf{x}}^N \cdot \nabla_{\mathbf{x}^N}$$

so that continuity becomes

$$\frac{D\rho}{Dt} = 0 \tag{3.43}$$

Let's pause for a moment and look at the physical interpretations of the equations we just derived. Eqn 3.42 states that at a fixed point in phase space, the time rate of change of the ensemble probability density will be related to the density gradient through a continuity equation. Eqn 3.43 says that, moving along a representative point in Γ–space, the density of state points in the immediate vicinity will be constant.

Given this, we can use Hamilton's equations in eqn 3.42 to obtain

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{N} \left(\frac{\partial H}{\partial \mathbf{p}_i} \cdot \frac{\partial}{\partial \mathbf{q}_i} - \frac{\partial H}{\partial \mathbf{q}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) \rho = 0 \tag{3.44}$$

Eqn 3.44 is the *Liouville* equation, and is arguably the most fundamental equation in statistical mechanics. That is because, given an ensemble with a specified Hamiltonian, the Liouville equation completely specifies the evolution of the probability density of the ensemble in phase space. The Liouville equation is often expressed in other equivalent forms, such as

$$\frac{\partial \rho}{\partial t} + \hat{H}\rho = 0 \tag{3.45}$$

or

$$i\,\frac{\partial \rho}{\partial t} = \hat{L}\rho \tag{3.46}$$

where

$$\hat{H} = \sum_{i=1}^{N} \left(\frac{\partial H}{\partial \mathbf{p}_i} \cdot \frac{\partial}{\partial \mathbf{q}_i} - \frac{\partial H}{\partial \mathbf{q}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) \tag{3.47}$$

and

$$\hat{L} = -i\hat{H} \tag{3.48}$$

$\hat{H}$ is the Poisson bracket operator and $\hat{L} = -i\hat{H}$ is the Liouville operator, a Hermitian operator.

The Liouville equation provides a time reversible description of the evolution of a classical dynamical system. If the direction of time is reversed, the Liouville operator changes sign and the equation retains its form. **Question:** How does a system decay irreversibly to an equilibrium probability distribution if it follows the Liouville equation and such an equation is time reversible? The problem of obtaining an irreversible decay from the Liouville equation is one of the central problems of statistical physics.

3.5 Ergodicity and Mixing in Phase Space

Having reviewed classical mechanics and derived the evolution equation for the probability density of an equilibrium system, we now turn our attention to a the question posed at the end of the last section. In particular, we will concern ourselves with the topic of *ergodicity*.

Let us restrict our attention to conservative systems evolving under the constraint of constant energy. We know that the state vectors of such a system form a *constant energy hypersurface* corresponding to energy E. The "area" of such a hypersurface can be written as

$$\Sigma(E) = \int_{\Gamma} \delta(H(\mathbf{x}^N) - E)\, d\mathbf{x}^N \tag{3.49}$$

where $\delta(H(\mathbf{x}^N) - E)$ is a Dirac delta function that selects points on the E–hypersurface. Thus the 6N–dimensional integral is converted to a (6N-1)–dimensional integral over the hypersurface.

A fundamental assumption of equilibrium thermodynamics (an assumption, I should add, that is well supported by our experience) is that isolated systems prepared under arbitrary initial conditions evolve to a state of equilibrium. At equilibrium, macroscopic properties are time–independent. Thus, we expect that for an ensemble of such systems, the probability density, $\rho(\mathbf{x}^N, t)$ will decay to the *equilibrium probability density,* $\rho^{eq}(\mathbf{x}^N)$.

Now, we just derived an expression for the evolution of the probability density, so we expect that the evolution of $\rho(\mathbf{x}^N, t)$ will be described by this equation (the Liouville equation, eqn 3.44). Moreover, $\rho^{eq}(\mathbf{x}^N)$ will be a stationary (time–independent) solution of the Liouville equation. That is, $\rho^{eq}(\mathbf{x}^N)$ will characterize an *equilibrium ensemble* under the given external constraints.

As an example, consider the case where a number of gas molecules are injected into an initially empty, rigid container (see Figure 3.6. Collisions with the container walls are elastic, but the gas molecules interact *with each other*. If the walls are insulated, the system can be considered *isolated*. An ensemble of such systems would be characterized by $\rho(\mathbf{x}^N, 0)$, the *initial probability distribution* of the system. This probability density is highly localized in a small region of phase space. As time evolves, we expect that collisions will make the system explore the entire volume, *and* that the molecules will assume a velocity distribution. Our experience suggests that $\rho(\mathbf{x}^N, t)$ will decay to $\rho^{eq}(\mathbf{x}^N)$, so that the molecules will become uniformly smeared over the (6N-1)–dimensional hypersurface. However, there is nothing in the Liouville equation (eqn 3.44) which suggests such an irreversible decay! Using Hamiltonian mechanics, we could start with the phase point on the right of Figure 3.6 and integrate the equations of motion backward in time (with infinite accuracy), only to arrive at the highly ordered point on the left. Our experience tells us, however, that this will "never"[1] happen. We expect an "irreversible" decay to equilibrium.

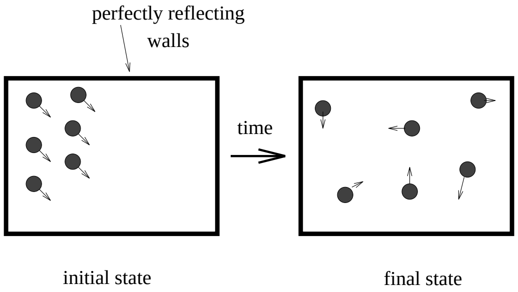


Figure 3.6: An isolated system of N interacting particles in a container decays to equilibrium

This can only mean that *the origins of decay to equilibrium do not come from Newtonian (i.e. classical) mechanics*, but from the nature of the interactions encountered in physical systems. The study of the conditions under which irreversible decay is observed is an intriguing problem in statistical mechanics and mathematics, but will only be touched on here. This is more in the realm of chaos theory and nonlinear mathematics. The key concepts which we will address in the context of this class are the following:

- ergodic flow
- mixing flow

3.5.1 Ergodic Flow

The flow of state points on the energy hypersurface is defined to be *ergodic* if almost all points $\mathbf{x}^N(\mathbf{p}^N, \mathbf{q}^N)$ on the surface move such that they pass through every small finite neighborhood on the energy surface. That is, each state

---

[1] OK, almost never!

point, excluding a set of points of measure zero, follow a trajectory that will pass arbitrarily close to any other point on the energy hypersurface.

Below we sketch out the **Ergodic Theorem** (Birkhoff, 1931).

Consider an integrable function $f(\mathbf{x}^N)$ of the state point $\mathbf{x}^N$ on a hypersurface with fixed energy E. The *phase average* of the function $f(\mathbf{x}^N)$ is

$$\langle f \rangle_{NVE} = \frac{1}{\Sigma(E)} \int_{\Gamma} \delta(H(\mathbf{x}^N) - E) f(\mathbf{x}^N)\, d\mathbf{x}^N \tag{3.50}$$

$$\langle f \rangle_{NVE} = \frac{\int_{\Gamma} \delta(H(\mathbf{x}^N) - E) f(\mathbf{x}^N)\, d\mathbf{x}^N}{\int_{\Gamma} \delta(H(\mathbf{x}^N) - E)\, d\mathbf{x}^N} \tag{3.51}$$

where the subscript NVE refers to constant *n*umber of particles, *v*olume of the system, and *e*nergy. This defines the microcanonical ensemble, as we will discuss shortly. The important point is to recognize that the phase average is taken by averaging over all state points on the constant energy hypersurface.

We can also define a *time average* of f

$$\langle f \rangle_t = \lim_{t \to \infty} \frac{1}{t} \int_{t_0}^{t_0 + t} f(\mathbf{x}^N(t))\, dt \tag{3.52}$$

where now the average is taken over a series of “snapshots” as the system evolves with time *at equilibrium*.

We say that a system is ergodic if for all phase functions $f(\mathbf{x}^N)$, the following statements are true:

1. The time average of eqn 3.52 exists for almost all $\mathbf{x}^N$ (all but a set of measure zero).

2. When the time average exists, it is equal to the phase average; that is $\langle f \rangle_t = \langle f \rangle_{NVE}$

In physical terms, the ergodic theorem says that two things are true. First, the phase space trajectory of almost any representative point on the E–hypersurface passes arbitrarily close to almost any other point on the hypersurface. That is, given sufficient time, the trajectory will cover all of the E–hypersurface. Second, to compute an average of f, we can do two things:

1. Ride on a single trajectory and experience all regions of phase space ($\langle f \rangle_t$).

2. Take a snapshot of the E–hypersurface at a given time and tally all representative points in it ($\langle f \rangle_{NVE}$).

The ergodic hypothesis states that either way of averaging is equivalent.

In Figure 3.7, a schematic diagram of a two-dimensional constant energy hypersurface is shown. The lines trace out paths on the generalized position, generalized momentum surface. We see that some of the lines meander along the surface (but never crossing!), while others form closed loops. Recall that we have already shown that trajectories on a constant E–hypersurface of phase space can appear as either non–crossing lines or closed loops. Does this diagram represent an ergodic system? No! The system shown in Figure 3.7 is clearly non–ergodic. If the system were ergodic, practically all the lines shown would be sections of a single long trajectory. That trajectory, which would span the entire E–hypersurface, would have to be a loop. Imagine if a trajectory started on a point within a closed loop. In such a case, it would be impossible for that trajectory to explore all (or nearly all) of the phase space. Instead, it would get “trapped” in a localized region of the energy hypersurface. Clearly, a time average of such a trajectory would *not* represent the phase average.

The time required to traverse an “ergodic loop” is the Poincaré recurrence time or the Poincaré cycle. For a system of N particles, the Poincaré cycle is of the order e^N. For macroscopic systems, ($N \approx 10^{23}$), this is an enormously long time. By way of reference, the age of the universe is $\approx 10^{10}$ years. From my standpoint, this is an infinite amount of time!

It is easy to come up with Newtonian trajectories that are non–ergodic. For example, in Figure 3.8, a single particle with momentum $\mathbf{p}$ traveling between two perfectly reflecting walls in a three–dimensional box displays

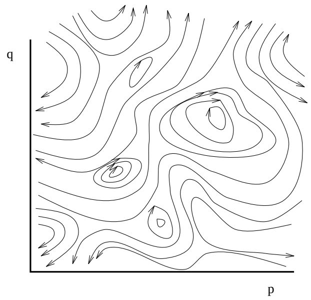


Figure 3.7: Schematic of trajectories on a two–dimensional constant energy hypersurface. If this were an ergodic system, all trajectories would be sections of the same loop. (After Allen and Tildesley).

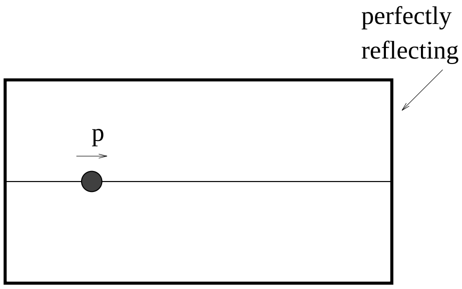


Figure 3.8: An example of a non–ergodic flow in phase space.

non–ergodic behavior. Note that for this example, only a single particle that does not interact with the walls is chosen. What will happen for this particular case? The energy of the particle is constant ($E = \frac{p^2}{2m}$) at all times. The particle will travel on the line between the two walls forever. The configuration space *available* consists of the entire box volume and the momentum space *available* consists of all orientations of $\mathbf{p}$ consistent with the constant energy constraint. The probability density of an ensemble of such particles set initially to travel along the same direction with the same momentum $\mathbf{p}$ would be a periodic function of time, and would never reach a stationary equilibrium limit. (Question: what would happen if we placed two particles in the box that could interact with each other over finite distances? Or, what if we allowed the particle to interact with an atomistic wall?)

3.5.2 Mixing Flow

It turns out that ergodic flow is not a sufficient requirement for an arbitrary ensemble probability density $\rho(\mathbf{x}^N, t)$ to decay to a stationary equilibrium probability density $\rho^{eq}(\mathbf{x}^N)$. Why? There is no guarantee that the swarm of particles in an ergodic system defining $\rho(\mathbf{x}^N, t)$ will disperse itself on the E–hypersurface as time goes by; it may retain its integrity and wander around as a whole such that the whole swarm visits the entire hypersurface. A stronger requirement than ergodicity is required to guarantee the decay to equilibrium. This is the requirement that the flow of state points through phase space be *mixing*.

One can show that if $\rho(\mathbf{x}^N, t)$ is a nonstationary probability density for a mixing system and $f(\mathbf{x}^N)$ any dynamical function, then in the limit of long time,

$$\begin{aligned} \langle f(t) \rangle &\equiv \int_\Gamma f(\mathbf{x}^N)\rho(\mathbf{x}^N, t)\delta(H(\mathbf{x}^N) - E)\, d\mathbf{x}^N \\ &\overset{t\to\infty}{\to} \frac{1}{\Sigma(E)} \int_\Gamma f(\mathbf{x}^N)\delta(H(\mathbf{x}^N) - E)\, d\mathbf{x}^N \end{aligned} \tag{3.53}$$

In other words, the time–dependent probability density *spreads out* with time and ultimately evolves into the stationary equilibrium ensemble distribution. If $H(\mathbf{x}^N) = E$, then $\rho_{NVE}(\mathbf{x}^N) = \frac{1}{\Sigma(E)}$; otherwise, $\rho_{NVE}(\mathbf{x}^N) = 0$. Mixing flow is ergodic, but ergodic flows are not always mixing. Mixing flow is *chaotic* and causes any initial probability distribution to spread through phase space. State points which are initially close to one another spread out exponentially with time, and soon arrive at entirely different parts of the energy hypersurface.

Ergodicity and mixing behavior have been proved for some simple systems (such as hard spheres). For most systems in nature, interparticle interactions are sufficiently many and complex that Hamiltonian dynamics leads to ergodic and mixing behavior. Thus, ergodicity is an excellent working hypothesis in statistical mechanics. We must be careful, however. There are some systems (such as glasses) that by their very nature are prevented from sampling their equilibrium states. We must be aware of these special cases.

Chapter 4

Equilibrium Ensembles

What we wish to do in this chapter is set up a statistical mechanical framework. From this framework, we hope to derive the laws of macroscopic thermodynamics from a fundamental set of postulates governing the microscopic state of the system. Most important to us for this class is the form of the expressions for thermodynamic quantities, such as equations of state, heat capacities, etc. We want to show how these observable quantities are obtained from nothing more than molecular interactions. Besides these macroscopic quantities, we can also obtain important microscopic details such as molecular organization, motion, and structure.

A central concept is the *equilibrium ensemble*. We have already been introduced (briefly) to the constant energy (microcanonical) ensemble, and the name has cropped up in our earlier discussions. We now define the word ensemble formally: *An equilibrium ensemble describes the equilibrium probability density distribution in phase space of a system subject to given external constraints*. Different ensembles correspond to systems having different constraints. Depending on the system, one of several different ensembles may lend itself to the types of properties to be calculated. *All ensembles* yield the same thermodynamic behavior.

4.1 Basic Postulates

Before introducing the various ensembles, we state two postulates which we will use.

Postulate 1: Ergodic Hypothesis: Given enough time, a system will sample all microstates consistent with the constraints imposed. That is, time averages are equivalent to ensemble averages. (We have already addressed this concept). Mathematically, we have

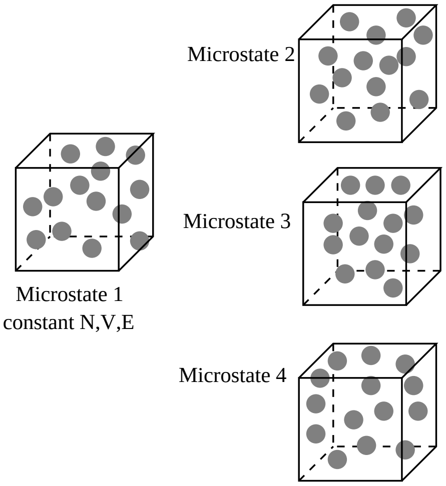
$$\langle x \rangle = \frac{\sum_i x_i \rho_i}{\sum_i \rho_i} = \lim_{t \to \infty} \frac{1}{t} \sum_i x_i \Delta t_i \tag{4.1}$$

where ρ_i is the probability density of state i. **Postulate 2**: Equal a Priori Probabilities: All microstates having the same energy are equally probable. (We use this postulate to construct distribution functions based solely on energetics). Mathematically,

$$\rho_i = \rho_i(E_i) \tag{4.2}$$

4.2 Microcanonical Ensemble

Given these two postulates, we now proceed to describe describe the **Microcanonical (NVE) Ensemble**. The microcanonical ensemble is an equilibrium ensemble with constraints of constant number of particle, volume, and energy (NVE). It is an *isolated* system. Microstates are discrete in a quantum mechanical description, and so is the probability distribution of the microstates. That is, we have microstate probabilities, not probability densities of phase space.



Imagine a system comprised of N molecules in a volume V with total energy E. Referring to Figure 4.2 we can think of this microstate as being like microstate 1, in which all the molecules are arranged in a certain way. Now imagine that we rearrange the molecules in a different way (in reality, take the molecules to another point in phase space so that they have different positions and/or momenta), but keep the external constraints of constant volume, number of molecules and energy fixed. Perhaps microstates 2,3 and 4 are such states. An *ensemble* is simply a collection of a large number of such states that satisfy the external constraints. Because each state is in the microcanonical ensemble, the “walls” surrounding each microstate would be impermeable to energy transfer, impermeable to the addition or deletion of molecules, and they would be rigid to maintain a constant volume. We say that such a system is *isolated*. Under this condition, we could imagine the molecules in each microstate “box” would happily move about on a constant energy hypersurface, exploring a different region of phase space. As the molecules change their positions and/or momenta, they probe a different microstate. One way of tracking these molecules would be to integrate the Hamiltonian (or Newtonian) equations of motion, since we know these equations conserve energy. We can imagine that if we change any of the external constraints, we would get a completely different set of microstates (or configurational “snapshots”).

To formalize these concepts, let $W(N,V,E)$ be the number of microstates with energy between E and $E-\delta E$, where δE is characteristic of the limits of our ability to specify the exact energy level. Equal a priori probabilities means that for a given microstate ν

$$P_\nu^{NVE} = \begin{cases} \frac{1}{W(N,V,E)}, & \text{if } E-\delta E < E_\nu < E; \\ 0, & \text{otherwise.} \end{cases} \tag{4.3}$$

where P_ν^{NVE} is the probability of a microstate, not an energy level. The probability of an energy level, E_ν, is found by multiplying P_ν^{NVE} by the degeneracy of that level.

Classically, microstates form a continuum in phase space. We have an equilibrium probability *density*, $\rho^{NVE}(\mathbf{p}^N, \mathbf{q}^N)$, given by

$$\rho^{NVE}(\mathbf{p}^N, \mathbf{q}^N) = \begin{cases} \frac{1}{\Sigma(N,V,E)}, & \text{if } E-\delta E < H(\mathbf{p}^N, \mathbf{q}^N) < E; \\ 0, & \text{otherwise.} \end{cases} \tag{4.4}$$

where

$$\Sigma(N,V,E) = \int_{\Gamma'} d\mathbf{p}^N d\mathbf{q}^N \tag{4.5}$$

The shorthand notation Γ' refers to the region of phase space where $E-\delta E < H(\mathbf{p}^N, \mathbf{q}^N) < E$. Note that the dimensions of ρ^{NVE} are $(pq)^{-3N}$, which is consistent.

In the classical formulation, we define a dimensionless quantity that corresponds to the number of microstates in the quantum mechanical formulation:

$$W(N,V,E)=\frac{1}{h^{3N}N!}\Sigma(N,V,E)=\frac{1}{h^{3N}N!}\int_{\Gamma'}d\mathbf{p}^N d\mathbf{q}^N \tag{4.6}$$

The prefactor $1/(h^{3N}N!)$ simply ensures consistency between classical and quantum mechanical pictures. The h^{3N} tells us there is a lower limit to the resolution with which we can define state points, and makes W dimensionless. The $N!$ arises from the indistinguishability of molecules (correct "Boltzmann counting").

Now, it turns out that the microcanonical ensemble, while perhaps easiest to understand, isn't the most useful ensemble. The reason is that we rarely perform experiments in the lab in which the density and energy are kept constant. However, because the standard equations of motion are at constant energy, the NVE ensemble is the most natural ensemble for conducting molecular dynamics simulations (more on this later). We will shortly develop the canonical ensemble (constant volume, number of particles and *temperature*), and show the link between this ensemble and the others. For now, though, we can make a few links between the statistical mechanical statement of the microcanonical ensemble and classical thermodynamics.

4.2.1 Connection With Thermodynamics

We make the connection between statistical mechanics and classical thermodynamics through the entropy. Let us assume that there are $W(N,V,E)$ possible microstates (or more properly, quantum states) available to our system. We now invoke Boltzmann's hypothesis, that *the entropy of a system is related to the probability of its being in a quantum state*. The probability of each state is $p=1/W$, if there are W quantum states. We can express Boltzmann's hypothesis as

$$S=\phi(W) \tag{4.7}$$

where $\phi(W)$ is some unknown function of W.

To determine $\phi(W)$, we use an approach due to Einstein. Consider two systems A and B which are not interacting so they are independent of each other. Their entropies are

$$S_A=\phi(W_A) \tag{4.8}$$

and

$$S_B=\phi(W_B) \tag{4.9}$$

Instead of considering the two systems separately, we could just as well think of them as a single system with entropy S_{AB} and probability $p_{AB}=1/W_{AB}$. The total entropy is then the sum of the entropies of the two systems

$$S_{AB}=S_A+S_B=\phi(W_{AB}) \tag{4.10}$$

We can say this because the sum of the independent systems is the sum of their individual entropies. This just means that entropy is an *extensive* variable. Because the two systems are independent, the total number of states available is $W_{AB}=W_AW_B$, so that

$$\phi(W_{AB})=\phi(W_AW_B)=\phi(W_A)+\phi(W_B) \tag{4.11}$$

The solution to eqn 4.11 is $\phi(W)=k_B\ln(W)$, where k_B is a universal constant. Thus we see that Boltzmann's hypothesis leads to a mathematical expression for the entropy involving a universal constant k_B called the *Boltzmann constant*

$$S(N,V,E)\equiv k_B\ln W(N,V,E) \tag{4.12}$$

This is an extremely important equation, from which we can derive all thermodynamics.

To illustrate the power of this equation and the way in which statistical mechanics can be used, consider the following simple derivation[1] We will think of a dilute gas as consisting of N non-interacting molecules moving in a volume V. Imagine that we specify the position of each molecule by sub-dividing the total space into cells, each of volume ΔV. The number of ways of placing one particular molecule in the volume is $W = V/\Delta V$. Since each molecule is non-interacting, the number of ways of arranging N molecules is $(V/\Delta V)^N$. Hence, according to eqn 4.12, the entropy is

$$S = k_B \ln(V/\Delta V)^N = N k_B \ln(V/\Delta V) \tag{4.13}$$

We see from this expression that the entropy depends on our choice of the cell volume, ΔV. However, this is arbitrary, because remember that we are most concerned with *differences* in entropy. Thus, as we change the volume of the system, V, but kept the cell volumes constant, the difference in entropy between the initial and final state would be

$$\Delta S = S_f - S_i = N k_B \ln(V_f/V_i) \tag{4.14}$$

which we see is independent of ΔV.

From classical thermodynamics, we know that the pressure of a system is given by

$$P = T\left(\frac{\partial S}{\partial V}\right)_U \tag{4.15}$$

Using this equation with our expression for the entropy of our dilute gas, we obtain

$$P = \frac{N k_B T}{V} \tag{4.16}$$

One can use the same arguments to derive an expression for the osmotic pressure of molecules in solution. The van't Hoff equation, which has the same form as eqn 4.16, results.

While eqn 4.16 is not exactly revolutionary, we do see how the connection with thermodynamics can be made. In addition, we have obtained an expression for the Boltzmann constant, namely $k_B = R/N_A$, where R is the gas constant and N_A is Avagadro's number. Of course, the van't Hoff equation and the ideal gas law were known before Einstein's time, so one could argue that the above derivation is no big deal. However, as should be apparent, we can relax our assumption of non-interacting molecules and try to account for the finite size of the molecules and intermolecular interactions. The results of such efforts are increasingly sophisticated *equations of state* that attempt to capture the P-V-T behavior of fluids. This represents an active area of research to this very day.

In addition to the ideal gas law, we can define a temperature. Recall that

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = 1/T \tag{4.17}$$

where we are loosely using E and U equivalently. Thus, we see that

$$\beta \equiv (k_B T)^{-1} = \left(\frac{\partial \ln W}{\partial E}\right)_{N,V} \tag{4.18}$$

The thermodynamic condition that temperature is positive requires that $W(N, V, E)$ be a monotonic increasing function of E.

4.2.2 Second Law of Thermodynamics

We can make other connections with thermodynamics. In this section, we will briefly show how the Second Law can be obtained from eqn 4.12. For additional details, see Chandler, *Introduction to Modern Statistical Mechanics*.

We start from a variational statement of the Second Law: The entropy of an isolated system at equilibrium is at a maximum with respect to the imposition of any internal constraint on the system. Internal constraints couple to extensive variables, but do not change the value of those extensive variables.

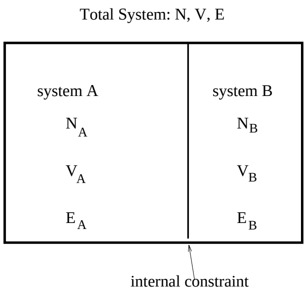


Figure 4.1: System with an internal constraint

To illustrate this concept, consider a system at equilibrium, with fixed N, V, E (fig 4.1). An internal constraint is imposed so as to divide the system into two subsystems, A and B. The total number of molecules, volume and energy are given by: $N_A + N_B = N$, $V_A + V_B = V$ and $E_A + E_B = E$. The set of microstates accessible to the partitioned system is necessarily less than the system could assume without the constraint. Thus,

$$W(N, V, E) > W(N, V, E; constraint) \tag{4.19}$$

and

$$S(N, V, E) > S(N, V, E; constraint) \tag{4.20}$$

Eqn 4.20 is the variational statement of the second law. The equilibrium state is the state at which $S(N, V, E; constraint)$ has its global maximum.

Question: Consider a system with energy E partitioned with $E_1^{initial}$ and $E_2^{initial}$ in subsystems 1 and 2 (See Figure 4.2). What is the final partitioning of energy? That is, at equilibrium, what must be true about the values E_1 and E_2?

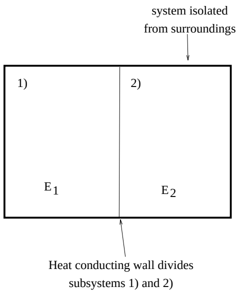


Figure 4.2: Example of partitioned system which will maximize entropy

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[1] This derivation was originally put forth by Einstein in his "miracle year", 1905.

4.2.3 Third Law of Thermodynamics

The Boltzmann equation (eqn 4.12) establishes an absolute scale for entropy. At absolute zero, a perfect crystalline substance localizes in the lowest–energy quantum microstate (the "ground state"). Excitations into higher energy states are impossible. Thus,

$$W(N, V, E) = 1 \tag{4.21}$$

$$S = k_B \ln W(N, V, E) = 0 \tag{4.22}$$

Equation 4.22 is the third law.

4.3 Canonical Ensemble

When we introduced the microcanonical ensemble, we thought of individual systems having a fixed number of particles, volume and energy. Now imagine a collection of systems (ensemble) with the same number of particles and volume, *but the energy is allowed to fluctuate*. Energy can be passed from one system to its neighbors, so that the energy of each system fluctuates. Each system is in thermal contact with the remainder, which acts as a heat bath for the system. This can be represented by Figure 4.3. The ensemble is made up of a collection of cells, each with rigid, impermeable walls (hence constant N and V) that can exchange heat with one another (constant T). The entire collection is brought to a fixed energy and then made adiabatic. Thus, the *entire system* can be treated as an NVE system, but each cell is at constant NVT. Remember: T is constant for each replicate (cell), but the energy of each cell fluctuates. This ensemble is called the *canonical ensemble*. The name comes from the fact that a system in contact with a heat bath is said to be in its canonical state. The word "canonical" is derived from the word canon, which means a rule or law. Canonical therefore means conforming to a general rule or standard. In our context then, canonical means a standard. Most experimental systems are in contact with heat baths, so this is a more natural ensemble than the microcanonical ensemble. In fact, the canonical (NVT) ensemble is the workhorse of statistical mechanics.

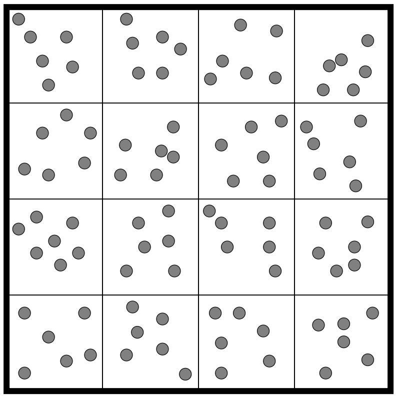

Figure 4.3: Depiction of the canonical ensemble. Each cell has a constant volume and occupation, and the temperature is fixed. However, the energy of each cell can fluctuate.

Our goal is to obtain the probability distribution and partition function for this ensemble. We start by assuming that we have $\mathcal{N}$ members of a canonical ensemble. Each member represents the whole macroscopic system of N molecules in a particular microscopic state. Let $\mathcal{N}_i$ represent the number of ensemble members in state i having energy E_i. Then we know that the sum over all members in each state i will give the total number of members:

$$\mathcal{N} = \sum_i \mathcal{N}_i \tag{4.23}$$

In addition, the total energy is

$$E = \sum_i \mathcal{N}_i E_i \tag{4.24}$$

We seek to determine the number of possible states (ensemble members) among the various microscopic states. For *any* of these distributions, we know the probability of finding $\mathcal{N}_j$ ensemble members in the jth state is:

$$\rho_j = \frac{\mathcal{N}_j}{\mathcal{N}} \tag{4.25}$$

This doesn't help much, since this is just the probability of any distribution j. We need to replace $\mathcal{N}_j$ with the expectation value $\langle \mathcal{N}_j \rangle$ determined from all combinations of the $\mathcal{N}$ ensemble members.

We assume equal *a priori* probabilities (that is, equal probabilities for energetically degenerate states). To get the distribution function, we determine the number of ways of distributing $\mathcal{N}$ things, $\mathcal{N}_j$ at a time.

$$f = \frac{\mathcal{N}!}{\prod_i \mathcal{N}_i!} \tag{4.26}$$

This is the multinomial distribution function (eqn 2.25). This distribution function can be used to get $\langle \mathcal{N}_j \rangle$ and the probability of $\mathcal{N}_j$ systems in microstates j.

It turns out that the degeneracy of microstates leading to the same thermodynamic state is huge. As we saw before, this enables us to replace the actual distribution function f with its maximum term, f^*, without loss of accuracy. Therefore, we can write

$$\rho_j = \frac{\langle \mathcal{N}_j \rangle}{\mathcal{N}} = \frac{1}{\mathcal{N}} \frac{\sum_{\mathcal{N}} \mathcal{N}_j^* f^*}{\sum_{\mathcal{N}} f} \tag{4.27}$$

$$\rho_j = \frac{1}{\mathcal{N}} \frac{\mathcal{N}_j^* f^*}{f^*} = \frac{\mathcal{N}_j^*}{\mathcal{N}} \tag{4.28}$$

Eqn 4.28 tells us that the probability of state j can be found by finding the maximum of the distribution, f^*. The maximum of $\ln f$ will also give f^*, so we maximize $\ln f$ using Lagrange's method of undetermined multipliers. Our constraints are given by eqns 4.23 and 4.24.

$$F = \ln f + \alpha(\mathcal{N} - \sum_i \mathcal{N}_i) + \beta(E - \sum_i \mathcal{N}_i E_i) \tag{4.29}$$

$$F = \ln \mathcal{N}! - \sum_i \ln \mathcal{N}_i! + \alpha(\mathcal{N} - \sum_i \mathcal{N}_i) + \beta(E - \sum_i \mathcal{N}_i E_i) \tag{4.30}$$

α and β are the undetermined multipliers.

Next, we use Stirling's approximation and differentiate F

$$\left(\frac{\partial F}{\partial \mathcal{N}_j}\right)_{\mathcal{N}_{k \neq j}} = -\ln \mathcal{N}_j - \alpha - \beta E_j = 0 \tag{4.31}$$

Resulting in

$$\mathcal{N}_j^* = e^{-\alpha} e^{-\beta E_j} \tag{4.32}$$

How do we determine α and β? We must use our constraint relations. First, since $\mathcal{N} = \sum_j \mathcal{N}_j$ applies to *all* distributions, it most certainly can be applied to *the most probable* distribution. Thus

$$\mathcal{N} = \sum_j \mathcal{N}_j^* = \sum_j e^{-\alpha} e^{-\beta E_j} \tag{4.33}$$

or

$$e^{-\alpha} = \frac{\mathcal{N}}{\sum_j e^{-\beta E_j}} \tag{4.34}$$

Substituting eqns 4.32 and 4.34 into eqn 4.28 yields

$$\rho_k = \frac{e^{-\beta E_k}}{\sum_j e^{-\beta E_j}} \tag{4.35}$$

This is the probability distribution we want! It can be used to find the expectation value of any mechanical property that depends upon the microscopic state of the system. All we need do now is figure out what β is.

First, we note that the denominator of eqn 4.35 is the normalization term for the distribution of all states. It is an important quantity which will appear in all canonical ensemble averages, and so is given a name.

$$Q(N, V, \beta) = \sum_k e^{-\beta E_k} \tag{4.36}$$

Q is the *canonical ensemble partition function*, so called because it is a sum over all the states partitioned by energy level.

If we knew what β was, we could form ensemble averages. How? For mechanical quantity J

$$\langle J \rangle = \sum_k \rho_k J_k = \sum_k \frac{J_k e^{-\beta E_k}}{Q} \tag{4.37}$$

We will make a physical connection with thermodynamics, and use this to identify β. For example, the thermodynamic internal energy is found by calculating the expectation value of the energy

$$U = \langle E \rangle = \sum_j E_j \rho_j = \sum_j \frac{E_j e^{-\beta E_j}}{Q} \tag{4.38}$$

Similarly for pressure

$$P = \langle P \rangle = \sum_j P_j \rho_j = \sum_j \frac{P_j e^{-\beta E_j}}{Q} \tag{4.39}$$

We postulate that $\langle P \rangle$ corresponds to the thermodynamic pressure and that $\langle E \rangle$ corresponds to the thermodynamic energy. Eqn 4.38 gives E in terms of β, which could in principle be solved for β in terms of E. In practice, it is more desirable to have E as a function of β, rather than the other way around, however.

We will now evaluate β. First, we recognize that when a system is in state j, $dE_j = -P_j dV$ is the work done on the system when its volume is increased by dV, keeping N constant. P_j is the pressure associated with state j. Thus we can write

$$P_j = -\left(\frac{\partial E_j}{\partial V}\right)_N \tag{4.40}$$

We can use this in eqn 4.39 to write

$$\langle P \rangle = \sum_j P_j \rho_j = -\sum_j \frac{\left(\frac{\partial E_j}{\partial V}\right) e^{-\beta E_j}}{Q} \tag{4.41}$$

Next, we differentiate eqn 4.38 with respect to V, keeping β and N constant.

$$\left(\frac{\partial U}{\partial V}\right)_{N,\beta} = \sum_j \frac{\left(\frac{\partial E_j}{\partial V}\right)_{\beta,N} e^{-\beta E_j}}{Q} - \beta \sum_j \frac{E_j \left(\frac{\partial E_j}{\partial V}\right)_{\beta,N} e^{\beta E_j}}{Q} + \beta \sum_j \sum_k \frac{E_j e^{-\beta E_j} \left(\frac{\partial E_k}{\partial V}\right)_{\beta,N} e^{-\beta E_k}}{Q^2} \tag{4.42}$$

This simplifies to

$$\left(\frac{\partial U}{\partial V}\right)_{\beta,N} = -\langle P\rangle + \beta\langle E\cdot P\rangle - \beta\langle E\rangle\langle P\rangle \tag{4.43}$$

Similarly, we differentiate eqn 4.39 with respect to β. The result is

$$\left(\frac{\partial P}{\partial \beta}\right)_{N,V} = \langle P\rangle\langle E\rangle - \langle P\cdot E\rangle \tag{4.44}$$

Combining eqns 4.43 and 4.44, we get that

$$\left(\frac{\partial E}{\partial V}\right)_{N,\beta} + \beta\left(\frac{\partial P}{\partial \beta}\right)_{N,V} = -P \tag{4.45}$$

Note: E (or more exactly, $\langle E\rangle$), is a function of N, V, β. This refers to the population of energy levels. E_j, on the other hand, *is* the energy level itself, and depends only on N and V.

Let's compare eqn 4.45 with another equation which we know from thermodynamics

$$\left(\frac{\partial U}{\partial V}\right)_{T,N} = T\left(\frac{\partial P}{\partial T}\right)_{V,N} = -P \tag{4.46}$$

Rewrite this in terms of $1/T$ instead of T and changing notation ($U = E$)

$$\left(\frac{\partial E}{\partial V}\right)_{N,1/T} + \frac{1}{T}\left(\frac{\partial P}{\partial (1/T)}\right)_{N,V} = -P \tag{4.47}$$

Comparing eqns 4.47 and 4.45, we identify $\beta = c/T$, c being a constant. The value of c is taken as k_B, Boltzmann's constant, by applying the result obtained here to an ideal gas. We will come back to this later. Thus we have the important relation

$$\beta = \frac{1}{k_B T} \tag{4.48}$$

It is conventional to let $\beta = 1/k_B T$, so we will use this symbol throughout this course.

4.3.1 Relationship Between the Canonical Ensemble and Thermodynamics

We now can write down some thermodynamics. Eqn 4.38 can alternately be expressed as

$$U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N} = k_B T^2\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} \tag{4.49}$$

and the expression for P can be written as

$$P = k_B T\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} \tag{4.50}$$

The two equations above are nice; they tell us that we can obtain pressure and energy from knowledge of the partition function. If an expression for entropy can be found, we will be able to determine all the thermodynamics of the canonical ensemble.

We know S is related to U and PV (for fixed N) by

$$dS = \frac{(dU + PdV)}{T} \tag{4.51}$$

But we know that

$$U = \sum_j \rho_j^{NVT} E_j \tag{4.52}$$

where we have been explicit in stating that the probability density of the canonical ensemble is used. Thus

$$\begin{aligned} dU &= \sum_j \left[\rho_j^{NVT} dE_j + E_j d\rho_j^{NVT}\right] \\ &= \sum_j \left[\rho_j^{NVT} \left(\frac{\partial E_j}{\partial V}\right)_N dV + E_j d\rho_j^{NVT}\right] \\ &= -PdV + \sum_j E_j d\rho_j^{NVT} \end{aligned} \tag{4.53}$$

Combining these last two equations, we obtain

$$dS = \frac{(-PdV + \sum_j E_j d\rho_j^{NVT} + PdV)}{T} \tag{4.54}$$

$$dS = \frac{\sum_j E_j d\rho_j^{NVT}}{T} \tag{4.55}$$

Recall that $\rho_j = \frac{e^{-\beta E_j}}{\sum_k e^{-\beta E_k}}$, which we can solve for E_j in terms of ρ_j, and use this in eqn 4.55. The result is

$$dS = -\frac{\sum_j (\ln \rho_j^{NVT} d\rho_j^{NVT} + \ln Q d\rho_j^{NVT})}{\beta T} \tag{4.56}$$

Since $\sum_j \rho_j^{NVT} = 1$, the second term in the numerator is zero. We thus obtain what we sought

$$dS = -k_B \sum_j \ln \rho_j^{NVT} d\rho_j^{NVT} \tag{4.57}$$

Eqn 4.57 is an important equation, in that it establishes the link between entropy and the microscopic state of a system. It can be integrated (the integration constant set so as $S(T=0) = 0$ for a perfect crystal) and the resulting equivalent equations obtained

$$S = \frac{U}{T} + k_B \ln Q = k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k_B \ln Q \tag{4.58}$$

$$S = -k_B \sum_j \rho_j^{NVT} \ln \rho_j^{NVT} \tag{4.59}$$

$$S = -k_B \langle \ln \rho_j^{NVT} \rangle \tag{4.60}$$

All of the above equations tells us that, if we know Q, we know everything about the thermodynamics of the system. As we will see, this means that a primary challenge of ours is to evaluate Q. (Is this possible? That means we have to obtain the E_j's of an N–body system! It turns out that we will approximate the problem by only considering one- ,two- , and perhaps three–body problems as an approximation of the actual systems).

To continue, we now wish to derive an expression for the Helmholtz free energy, A, in terms of Q. A is the natural thermodynamic potential of the canonical ensemble. We know that

$$A = U - TS \tag{4.61}$$

so

$$A = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} - k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} - k_B T \ln Q \tag{4.62}$$

or

$$A = -k_B T \ln Q \tag{4.63}$$

We can derive all other thermodynamic quantities easily from eqn 4.63 using standard thermodynamic manipulations.

In the above development, we have implicitly considered a single component system. In a multicomponent system, the formulation proceeds identically to that here (starting at eqn 4.26), except that we use the sum of particles $N_1 + N_2 + \cdots$ in place of N, and the product $N_1!N_2!\cdots$ in place of $N!$.

4.3.2 Using the Canonical Ensemble

Equipartition of Energy

Many physical systems have Hamiltonians of the form

$$\mathcal{H} = \sum_i A_i q_i^2 + \sum_i B_i p_i^2 \tag{4.64}$$

where q_i and p_i are generalized coordinates and momentum. In an ideal gas of spherical particles, for example, $B_i = 1/2m$, with p_i a component of momentum in each of three coordinate directions. $A_i = 0$. In general, if f of the constants A_i and B_i are non-vanishing, then it is easy to show that within the classical limit of the canonical ensemble

$$U = \langle \mathcal{H} \rangle = 1/2 f k_B T \tag{4.65}$$

This says that each independent harmonic term in the Hamiltonian contributes $1/2 k_B T$ to the total energy of the system. This is the *theorem of equipartition of energy*. This theorem only holds for degrees of freedom which can be treated classically; it breaks down when quantum effects are important.

Fluctuations

What is the magnitude of energy fluctuations in the canonical ensemble? The variance of energy is

$$\langle (\delta E)^2 \rangle \equiv \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 - 2E\langle E \rangle + \langle E \rangle^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 \tag{4.66}$$

What is each term here?

$$\langle E^2 \rangle = \frac{\sum_j E_j^2 e^{-\beta E_j}}{Q} = -\frac{1}{Q}\frac{\partial}{\partial \beta}\sum_j E_j e^{-\beta E_j}$$

But this can be simplified

$$\langle E^2 \rangle = -\frac{1}{Q}\frac{\partial}{\partial \beta}(\langle E \rangle Q)$$

$$\langle E^2 \rangle = -\frac{\partial \langle E \rangle}{\partial \beta} - \langle E \rangle \frac{\partial \ln Q}{\partial \beta}$$

Finally, we get with a little more algebra

$$\langle E^2 \rangle = k_B T^2 \frac{\partial \langle E \rangle}{\partial T} + \langle E \rangle^2$$

Thus, eqn 4.66 becomes

$$\langle (\delta E)^2 \rangle = k_B T^2 \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V} = k_B T^2 \left(\frac{\partial U}{\partial T}\right)_{N,V} \tag{4.67}$$

Our usual thermodynamic definition of heat capacity is

$$C_v = \left(\frac{\partial U}{\partial T}\right)_{N,V} \tag{4.68}$$

Thus we see that

$$\langle (\delta E)^2 \rangle = k_B T^2 C_v \tag{4.69}$$

Look at what eqn 4.69 says: the size of spontaneous fluctuations in energy at equilibrium is related to the rate at which the energy of the system will change with changes in temperature. Eqn 4.69 serves as the basis for estimating the heat capacity through simulations carried out at a single temperature in the canonical ensemble.

To appreciate the order of magnitude of energy fluctuations in a macroscopic system, let's compare the standard deviation of energy to its average value

$$\frac{\langle (\delta E)^2 \rangle^{1/2}}{\langle E \rangle} = \frac{(k_B T^2 C_v)^{1/2}}{\langle E \rangle}$$

For an ideal gas, $\langle E \rangle$ is of order $(N k_B T)$ and C_v is of order $(N k_B)$. Thus,

$$\frac{\langle (\delta E)^2 \rangle^{1/2}}{\langle E \rangle} \approx (N^{-1/2})$$

If N is on the order of 10^{20} or so, this is an extremely small number. Note that this argument can be applied in the "thermodynamic limit", far from critical points. (Fluctuations become large near critical points...)

This tells us that the probability distribution for energy is a sharp Gaussian, that for all practical purposes is a delta function. Also, it says that $C_v \geq 0$ always. This result, which falls naturally out of the statistical mechanical formulation, constitutes a criterion for thermodynamic stability.

4.4 Elementary Statistical Mechanics of Fluids

We will eventually introduce other ensembles, but at this point it is worthwhile to stop for a moment and see how we can use what we have learned. Since the canonical ensemble is the most commonly used ensemble, now is a good time to digress and show some elementary statistical mechanical calculations as applied to fluids.

As we saw with the heat capacity, the canonical ensemble provides a powerful framework for calculating thermodynamic properties of gases and liquids from molecular–level information. Consider a fluid of N particles in volume V at temperature T. To specify a microstate in configuration space, we must determine the position, orientation and shape of all molecules. For a molecule of s atoms, this means there are $3s$ degrees of freedom. Recall that either Cartesian or generalized coordinates can be used. As we touched on earlier, there is an advantage to specifying a molecular configuration with the more conceptually difficult generalized coordinates than with simple Cartesian coordinates. Let us again show how generalized coordinates are used in an example.

Consider a linear molecule, such as the one shown in Figure 4.4. This could be a representation of chlorine, for example. To uniquely determine the conformation of this molecule in space, we could specify the three Cartesian coordinates of both atoms, which would give a total of six degrees of freedom for this molecule. Alternatively, we could specify the three Cartesian coordinates of the molecular center of mass, two "Eulerian" angles (Ψ_1 and Ψ_2) which give the overall orientation (we will refer to these as "rotational" degrees of freedom), and 3s-5 internal bond lengths and/or angles ("vibrational" degrees of freedom), ℓ. For this particular molecule, $s = 2$ so there is one bond length which must be specified, ℓ_1. Thus we must specify six generalized coordinates to describe the configuration of this molecule - the same number as the Cartesian coordinate specification.

We could also have a nonlinear, flexible molecule, such as the one shown in Figure 4.5. We could again specify Cartesian coordinates for each atom, or we could define the configuration in terms of generalized coordinates. For

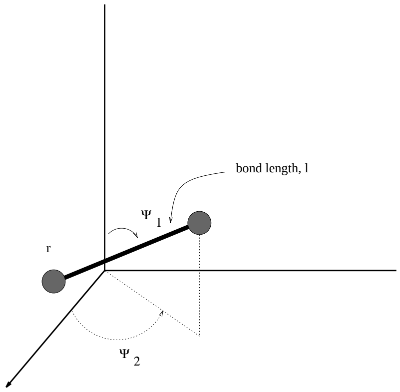

Figure 4.4: Degrees of freedom for a linear molecule (such as N_2).

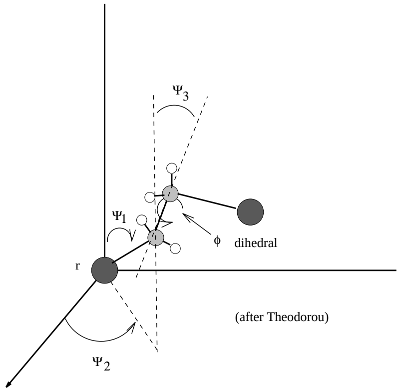

Figure 4.5: Degrees of freedom for a flexible, non–linear molecule (such as 1,2-dichloroethane).

this case, three translational and three rotational degrees of freedom ($\boldsymbol{\Psi}$ are required to specify the position of the center of mass and the overall orientation. If the molecule can isomerize conformationally, it also has b torsional (dihedral) degrees of freedom. In addition, there are $3s$ - b - 6 vibrational degrees of freedom for a nonlinear molecule. In the representation of 1,2-dichloroethane shown in Figure 4.5, there is one torsional and 17 vibrational degrees of freedom (7 bond lengths and 10 bond angles).

We now wish to classify the different degrees of freedom. This can be done on a number of ways:

1. Internal/external degrees of freedom
    - "Internal" degrees of freedom: vibrational and torsional.
    - "External" degrees of freedom: translational and rotational
2. Hard/soft degrees of freedom
    - "Hard" degrees of freedom: vibrational
    - "Soft" degrees of freedom: all others
3. inter–/intra–molecular degrees of freedom
    - *Intramolecular* contributions: nuclear, electronic, vibrational, and torsional

   - *Intermolecular* contributions: potential energy of interaction between molecules. This is a function of position and orientation of constituent parts of different molecules.

4. internal/external degrees of freedom

   - "internal" part: nuclear, electronic, vibrational, and rotational degrees of freedom.
     Note that these degrees of freedom are *not* affected by other molecules.
   - "external" part: all other degrees of freedom.

Based on the separation of energy into an *internal* part and an *external* part, we make the following assumptions: 1) Fast, vibrational degrees of freedom of a polyatomic molecule are not greatly affected by the environment of the molecule. Thus we can lump vibrational energy into the internal part; 2) The kinetic energy associated with the tumbling of molecules in a fluid is also independent of fluid configuration. We therefore add this to the internal part of the potential. This is acceptable if the molecules have no internal torsional degrees of freedom that can cause changes in their shape; 3) The kinetic energy associated with *translation* is always included in the "external" part of the energy, since this will depend on the environment.

With this separation of energy, we can factor the partition function in the following way

$$\begin{aligned} Q(N,V,T) &= \sum_{microstates} e^{-\beta E} \\ &= \sum_{microstates} \exp[-\beta \sum_{i}^{N} E_i^{int} - \beta E^{ext}] \\ &= \left(\sum_{internal} \exp[-\beta \sum_{i}^{N} E_i^{int}] \right) \left(\sum_{external} \exp[-\beta E^{ext}] \right) \\ &= \prod_{i=1}^{N} \left(\sum_{internal} \exp[-\beta E_i^{int}] \right) \left(\sum_{external} \exp[-\beta E^{ext}] \right) \end{aligned}$$

where the sums over "internal" and "external" refer to all possible combinations of internal and external degrees of freedom, respectively.

Finally we get

$$Q(N,V,T) = [q^{int}(T)]^N Q_{ext}(N,V,T) \tag{4.70}$$

The Hamiltonian for Q_{ext} consists of contributions from all kinetic energy modes *not* included in q_{int}, and from the potential energy of the system, $\mathcal{V}$, which depends on the system configuration. That is

$$\mathcal{V} = \mathcal{V}(\mathbf{q})$$

A comment on notation: we will use the vector $\mathbf{q}$ to represent all the generalized coordinates of a molecule of collection of molecules under discussion.

As a simple case, consider a system of inflexible molecules, in which the total potential energy can be expressed solely as a function of the center of mass coordinates. That is

$$\mathcal{V} = \mathcal{V}(\mathbf{r}_1)$$

where $\mathbf{r}_1$ is the vector of Cartesian coordinates describing the position of the molecules.

Such a representation is a good approximation for molecules that "look" like spheres (such as xenon or methane). Long, flexible molecules, such as polymers, are poorly approximated in this way. Likewise, molecules with strong orientationally–dependent dipolar interactions (such as water) are not well–represented in this way. In these cases, we need to treat the potential as a function of the full configuration space ($\mathcal{V} = \mathcal{V}(\mathbf{q})$).

However, under the condition that $\mathcal{V} = \mathcal{V}(\mathbf{r}_1)$, we can derive Q_{ext} from the following Hamiltonian

$$\mathcal{H}_{ext}(\mathbf{r}^N, \mathbf{p}^N) = \mathcal{K}(\mathbf{p}^N) + \mathcal{V}(\mathbf{r}^N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \mathcal{V}(\mathbf{r}_1, \cdots, \mathbf{r}_N) \tag{4.71}$$

Notice in eqn 4.71 that the potential energy is an *intermolecular* potential energy. The kinetic energy depends exclusively on momenta, while the potential energy term depends exclusively on position. Thus, in forming the partition function for this Hamiltonian, we may *separate* the two contributions

$$Q_{ext}(N,V,T) = \frac{1}{h^{3N}N!} \int \exp\left[-\beta \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}\right] d\mathbf{p}^N \times \int \exp[-\beta\mathcal{V}(\mathbf{r}_1, \cdots, \mathbf{r}_N)]\, d\mathbf{r}^N \tag{4.72}$$

Recall that the factor $\frac{1}{h^{3N}N!}$ arises when going from a discrete representation to the classical (continuous) representation of Q. (We can also do a separation of this type for more complicated molecules, as long as all the configurational degrees of freedom can be treated classically. More on this later.)

The integral in momentum space is easy to evaluate; it is a product of $3N$ independent Gaussian integrals. Recall that

$$\int_0^{+\infty} e^{-\alpha^2 k^2}\, dk = \frac{\sqrt{\pi}}{2\alpha}$$

so we have $3N$ independent Gaussian integrals of the form

$$\int_{-\infty}^{+\infty} \exp\left(-\beta \frac{p^2}{2m}\right) dp_i = (2\pi m k_B T)^{1/2} \tag{4.73}$$

This indicates that the center-of-mass momentum vectors obey a Maxwell–Boltzmann distribution of the form

$$\rho^{MB}(\mathbf{p}) = \frac{1}{(2\pi m k_B T)^{3/2}} \exp\left[\frac{-\mathbf{p}^2}{2\pi m k_B T}\right] \tag{4.74}$$

We can then combine eqns 4.70, 4.72, and 4.74 to get the *semi–classical partition function*

$$Q_{cl}(N,V,T) = [q^{int}]^N \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} \times \tag{4.75}$$

$$\int \exp[-\beta\mathcal{V}(\mathbf{r}_1, \cdots, \mathbf{r}_N)]\, d\mathbf{r}_1, \cdots, d\mathbf{r}_N$$

or

$$Q(N,V,T) = \frac{[q^{int}(T)]^N}{N!\Lambda^{3N}} \int \exp[-\beta\mathcal{V}(\mathbf{r}_1, \cdots, \mathbf{r}_N)]\, d\mathbf{r}_1, \cdots, d\mathbf{r}_N \tag{4.76}$$

where Λ is the "thermal wavelength" of the molecules

$$\Lambda = \Lambda(T) = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2} \tag{4.77}$$

Λ is of the order of the de Broglie wavelength for a molecule of mass m and thermal energy $k_B T$. Physical significance: when intermolecular separations become commensurate with Λ, a classical treatment of the translational motion is no longer satisfactory. (Can you think of why this is the case?).

Notice in eqn 4.76 that we have dropped the explicit reference to a classical partition function, although only for convenience. We should always keep the distinction clear between the classical and quantum mechanical definitions of Q.

Eqn 4.76 is often written as

$$Q(N,V,T) = \frac{[q^{int}(T)]^N}{N![\Lambda(T)]^{3N}} \, Z(N,V,T) \tag{4.78}$$

where

$$Z(N,V,T) \equiv \int \exp[-\beta \mathcal{V}(\mathbf{r}_1, \cdots, \mathbf{r_N})] \, d\mathbf{r}^N \tag{4.79}$$

$Z(N,V,T)$ is a very important quantity, and is referred to as the *configurational integral*. The reason Z is so important is that all the dependence of the partition function (hence, thermodynamics) on spatial extent (density) of the system is incorporated in Z. For example, pressure is independent of internal modes.

Recall, for example, that a pressure–explicit equation of state was derived as

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

So that now

$$P = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = k_B T \left(\frac{\partial \ln Z}{\partial V}\right)_{N,T} \tag{4.80}$$

Look what this means: If we can separate a system into internal and external degrees of freedom, and if those external degrees of freedom can be treated classically, then the equation of state can be obtained from the *configurational* part of the partition function only! This is why Z is so important!

More on separation of energy

The *total energy* is a function of the degrees of freedom (generalized coordinates, $\mathbf{q}$) and generalized momentum conjugate to these degrees of freedom ($\mathbf{p}$). In addition, nuclear and electronic degrees of freedom can be excited in some systems at ordinary temperatures, and thus need to be considered in the total energy. If ΔE_i, the successive energy level separation associated with a degree of freedom, is large compared to the thermal energy, we must treat the contribution quantum mechanically. *For Example:* $k_B T = 4.1 \times 10^{-21} J/dof$ at room temperature. Nuclear spin separations are typically $10^{-11} J/dof$, electronic contributions ($10^{-17} J/dof$) and vibrational ($10^{-20} J/dof$) must be treated quantum mechanically. A classical treatment is acceptable for most cases of rotational, internal torsional, and translational contributions.

A complete and rigorous calculation of q^{int} is complicated by the coupling of various internal modes. We simplify the problem in a reasonable way by assuming an independence between various modes. The main approximations are the following:

- Born–Oppenheimer Approximation: electron movement is rapid relative to the motion of massive nuclei. Consequence: the electronic partition function is *independent* of other internal modes.
- Other time scale arguments can be made to separate the other modes.
- Poorest assumption: independence of coupling between rotational and vibrational modes (“rigid rotator”). Turns out to be a good approximation for many systems. Coupling *can* be treated rigorously.

The result of the separation is that internal partition function can be factored

$$q^{int} = q^r q^v q^e q^n$$

4.4.1 Thermophysical Properties of Ideal Gases

For a simple application of the principles we've discussed, consider an ideal gas of molecules. Before you grumble about looking at an ideal gas, stop for a minute. The ideal gas plays a central role as a *reference substance* in statistical thermodynamic formulations. Thus, it is important that we can handle at least this simplest of all systems. We will tackle more complex systems in due time!

For an ideal gas of *atomic species*, there are no interactions between molecules, thus we can write

$$\mathcal{V}(\mathbf{q}) = 0 \tag{4.81}$$

This would not be the case is we had a molecular species with internal energetics; we ignore this case for now. We can see immediately that the configurational integral, eqn 4.79 reduces to

$$Z^{ig}(N,V,T) = \int d\mathbf{r}^N = V^N \tag{4.82}$$

The canonical partition function can be written

$$Q^{ig}(N,V,T) = \frac{[q^{int}]^N}{N!}\left(\frac{V}{\Lambda^3}\right)^N \tag{4.83}$$

We can calculate a number of properties from eqn 4.83.

- *Pressure*:

  Using the equation of state derived earlier (eqn 4.80):

$$P^{ig} = k_BT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = k_BT\left(\frac{\partial V^N}{\partial V}\right)_{N,T} \tag{4.84}$$

$$P^{ig} = \frac{Nk_BT}{V}$$

  or

$$P^{ig}V = Nk_BT = nRT$$

  We have once again derived the ideal gas law!

- Helmholtz free energy:

$$A^{ig}(N,V,T) = -\frac{1}{\beta}\ln\left[\frac{1}{N!}\left(\frac{q^{int}V}{\Lambda^3}\right)^N\right]$$

$$= -\frac{1}{\beta}\left[-(N\ln N - N) + N\ln\left(\frac{q^{int}V}{\Lambda^3}\right)\right]$$

$$Nk_BT\left[-1 + \ln\left(\frac{N\Lambda^3}{Vq^{int}}\right)\right] = NK_BT\left[-1 + \ln\left(\frac{\rho\Lambda^3}{q^{int}}\right)\right]$$

  where $\rho = N/V$ is the *molecular density*.

- chemical potential:

  You can easily show that

$$\mu^{ig}(\rho, T) = -k_B T \left(\frac{\partial \ln Q}{\partial N}\right) = k_B T \ln\left(\frac{\rho \Lambda^3}{q^{int}}\right) \tag{4.85}$$

  where we have used Stirling's approximation. For a monatomic ideal gas, this simplifies to

$$\mu^{ig}(\rho, T) = k_B T \ln(\rho \Lambda^3) \tag{4.86}$$

  This equation defines an absolute scale for chemical potential.

- heat capacity

$$\begin{aligned} C_v^{ig} &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= \frac{\partial}{\partial T}\left[\frac{3}{2} N k_B T + N k_B T^2 \frac{\partial \ln [q^{int}]^N}{\partial T}\right] \end{aligned}$$

  Simplifying,

$$\begin{aligned} C_v^{ig} &= \frac{3}{2} N k_B T + 2 N k_B T \frac{\partial \ln [q^{int}]^N}{\partial T} + N k_B T^2 \frac{\partial^2 \ln [q^{int}]^N}{\partial T^2} \\ &= \frac{3}{2} R + R\left[2T \frac{\partial \ln [q^{int}]}{\partial T} + T^2 \frac{\partial^2 \ln [q^{int}]}{\partial T^2}\right] \end{aligned}$$

  For an ideal, monatomic gas (such as argon), we see the familiar equation

$$C_v^{ig} = 3/2R$$

  The temperature–dependency of the heat capacity arises from molecular structure. Rotational, vibrational (and even electronic and nuclear) degrees of freedom get incorporated in $q^{int}(T)$. It is easy to see now why correlations for heat capacity have the form

$$C_p = C_v + R = a + bT + cT^2 + \cdots$$

- entropy:

  Finally, we can compute the entropy of an ideal gas

$$\begin{aligned} S^{ig} &= \frac{U^{ig} - A^{ig}}{T} \\ &= \frac{N k_B T\left[\frac{3}{2} + T \frac{\partial \ln [q^{int}]^N}{\partial T}\right] - N k_B T\left[-1 + \ln \frac{\rho \Lambda^3}{[q^{int}]^N}\right]}{T} \end{aligned}$$

$$S^{ig} = N k_B \left[\frac{5}{2} - \ln(\rho \Lambda^3) + \ln [q^{int}]^N + T \frac{\partial \ln([q^{int}]^N)}{\partial T}\right]$$

$$S^{ig} = R\left[\frac{5}{2} - \ln(\rho \Lambda^3) + \ln [q^{int}]^N + T \frac{\partial \ln([q^{int}]^N)}{\partial T}\right]$$

  We see for an ideal, monatomic gas

$$S^{ig} = R\left[\frac{5}{2} - \ln(\rho \Lambda^3)\right]$$

  This last equation is a form of the Sakur-Tetrode equation. The assumption of an ideal, monatomic gas enables rapid and fairly accurate evaluation of absolute entropies (see Table 4.1).

Gas	exp. (e.u.)	calc. (e.u.)
He	30.13	30.11
Ne	34.95	34.94
Ar	36.98	36.97
Kr	39.19	39.18
Xe	40.53	40.52
C	37.76	37.76
Na	36.72	36.70
Al	39.30	39.36
Ag	41.32	41.31
Hg	41.8	41.78

Table 4.1: Calculated and measured entropies at 1 atm and 298 ^{o} K. Calculated values were obtained from the Sakur–Tetrode equation, assuming an ideal, monatomic gas. From McQuarrie, *Statistical Mechanics*.

4.4.2 Thermodynamic Properties from Ensemble Averages

So far, we have seen that we can calculate thermodynamic properties, if we know the configurational integral (or the partition function). Our goal is to formulate the statistical mechanical problem in such a way that we can calculate properties from molecular simulations. One might be tempted to think that molecular simulations are simply a way of calculating Z. As we shall see, however, computing Z for non-trivial systems is extremely difficult (but not impossible). As a result, rarely do we compute configurational integrals directly from molecular simulations, but it turns out that this is unnecessary for obtaining many properties of interest!

Simulations are generally designed to compute *ensemble averages* (or, equivalently, time averages). What we would like to do now then is to derive expressions for thermodynamic properties written as *ensemble averages*. We will begin by deriving an expression for the pressure of a system.

Virial Theorem: Pressure as an Ensemble Average

There are many ways to derive the virial theorem. We will follow a mechanical derivation, much along the lines of Clausius' original derivation. The form given here is after that given by D. N. Theodorou.

Consider an isotropic fluid of N molecules in a volume V at temperature T (see Fig. 4.6). For simplicity, we consider a fluid of structureless molecules, subject to central forces. This derivation can be extended to molecular fluids by considering molecules as collections of atoms, some of which interact through bond forces. Newton's second law, applied to molecule i yields

$$m_i \frac{d^2 x_i}{dt^2} = F_{x_i} \tag{4.87}$$

Analogous formulae apply for y and z. $\mathbf{F}_i$ is the total force experienced by molecule i at a given time. Multiplying eqn 4.87 by x_i yields

$$x_i F_{x_i} = m_i x_i \frac{d^2 x_i}{dt^2} = \frac{d}{dt}\left(m_i x_i \frac{dx_x}{dt}\right) - m_i \left(\frac{dx_i}{dt}\right)^2 \tag{4.88}$$

Summing over all molecules and taking time averages under equilibrium conditions

$$\langle \sum_{i=1}^{N} x_i F_{x_i} \rangle_t = \langle \sum_{i=1}^{N} \frac{d}{dt}\left(x_i p_{i,x}\right) \rangle_t - \langle \sum_{i=1}^{N} \frac{p_{i,x}^2}{m_i} \rangle_t \tag{4.89}$$

Recall the definition of a time average:

$$\langle \mathcal{A} \rangle_t = \lim_{\tau \to \infty} \int_0^\tau \mathcal{A}\, dt$$

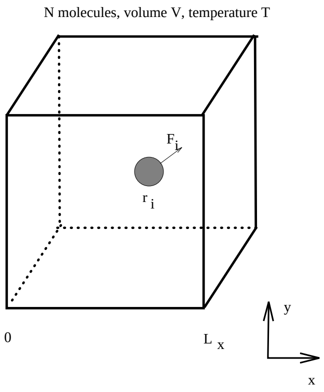

Figure 4.6: Schematic of the construct used in deriving the virial theorem. The grey sphere represents the position of molecule i in a fluid of N particles at temperature T in volume V. $\mathbf{F}_i$ is the total force on the molecule.

In eqn 4.89, we have used the fact that $\mathbf{p}_i = m_i \frac{d\mathbf{r}_i}{dt}$.

Let us examine the first term after the equal sign in eqn 4.89. By definition,

$$\langle \sum_{i=1}^{N} \frac{d}{dt}(x_i p_{i,x}) \rangle_t = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} \left[\sum_{i=1}^{N} \frac{d}{dt}(x_i p_{i,x}) \right] dt$$

$$= \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} \frac{d}{dt} \left[\sum_{i=1}^{N} (x_i p_{i,x}) \right] dt$$

$$= \lim_{\tau \to \infty} \frac{1}{\tau} \left(\left[\sum_{i=1}^{N} x_i p_{i,x} \right]_{\tau} - \left[\sum_{i=1}^{N} x_i p_{i,x} \right]_0 \right) \tag{4.90}$$

The momentum must be bounded (that is, $p_{i,x}$ cannot be infinite). Also, the position x_i is bounded, because molecule i cannot leave the box. As a consequence, the limit on the right hand side of eqn 4.90 must be zero. Therefore, we have

$$\langle \sum_{i=1}^{N} \frac{d}{dt}(x_i p_{i,x}) \rangle_t = 0 \tag{4.91}$$

Consider the second term in eqn 4.89. Motion in the system is isotropic, so

$$\langle \sum_{i=1}^{N} \frac{p_{i,x}^2}{m_i} \rangle_t = \frac{1}{3} \langle \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} \rangle_t = \frac{2}{3} \langle \mathcal{K} \rangle_t \tag{4.92}$$

where $\mathcal{K}$ is the kinetic energy.

We now invoke the ergodic hypothesis. As we have seen, the kinetic energy is related to the temperature and the number of degrees of freedom through the equipartition theorem. Thus

$$\langle \sum_{i=1}^{N} \frac{p_{i,x}^2}{m_i} \rangle_t = \left(\frac{2}{3} \right) \left(\frac{3N}{2} \right) k_B T = N k_B T \tag{4.93}$$

Combining eqns 4.89, 4.91, and 4.93

$$\langle \sum_{i=1}^{N} x_i F_{x_i} \rangle_t = -N k_B T \tag{4.94}$$

Similar relationships exist for y and z, thus

$$\frac{1}{3}\langle\sum_{i=1}^{N}\mathbf{r}_i\cdot\mathbf{F}_i\rangle = -Nk_BT \tag{4.95}$$

We have dropped the subscript t in eqn 4.95 to denote averaging in any ensemble. The quantity $\sum_{i=1}^{N}\mathbf{r}_i\cdot\mathbf{F}_i$ is called the *(total) virial*.

Consider the nature of the force on atom i, $\mathbf{F}_i$. There are two sources

1. Forces arising due to interactions with the box walls. We give these forces the symbol $\mathbf{F}_i^w$.
2. Forces due to interactions with other fluid molecules. We give this component the symbol $\mathbf{F}_i^{int}$.

Thus,

$$\mathbf{F}_i = \mathbf{F}_i^{int} + \mathbf{F}_i^w \tag{4.96}$$

Eqn 4.95 can equivalently be written as

$$\frac{1}{3}\left(\langle\sum_{i=1}^{N}\mathbf{r}_i\cdot\mathbf{F}_i^w\rangle + \langle\sum_{i=1}^{N}\mathbf{r}_i\cdot\mathbf{F}_i^{int}\rangle\right) = -Nk_BT \tag{4.97}$$

The quantities $(1/3)\sum_{i=1}^{N}\mathbf{r}_i\cdot\mathbf{F}_i^w$ and $(1/3)\sum_{i=1}^{N}\mathbf{r}_i\cdot\mathbf{F}_i^{int}$ are referred to as the wall virial and internal virial, respectively.

Focus on the wall virial term in eqn 4.97, and consider the x component. For most physical systems, "wall" forces are short ranged. Molecules will only experience wall forces if they are within a few molecular diameters of the wall. As a consequence, all the molecule–wall contributions that contribute to the virial term will have $x_i \approx L_x$ or $x_i \approx 0$. Thus

$$\langle\sum_{i=1}^{N}x_iF_{x_i}^w\rangle = L_x\langle\sum_{i=1}^{N}F_{x_i}^w\rangle_{x=L_x} \tag{4.98}$$

where $\langle\sum_{i=1}^{N}F_{x_i}^w\rangle_{x=L_x}$ is the average force exerted from the wall at L_x on the gas. It is minus the average force exerted by the gas on the wall. Thus, it is *related to the pressure*

$$\langle\sum_{i=1}^{N}F_{x_i}^w\rangle_{x=L_x} = -PL_yL_z \tag{4.99}$$

Combining eqns 4.98–4.99

$$\langle\sum_{i=1}^{N}x_iF_{x_i}^w\rangle = -PV \tag{4.100}$$

We then see immediately from eqn 4.97 that

$$PV = Nk_BT + \frac{1}{3}\langle\sum_{i=1}^{N}\mathbf{r}_i\cdot\mathbf{F}_i^{int}\rangle = Nk_BT + \langle\mathcal{W}^{int}\rangle \tag{4.101}$$

where $\langle\mathcal{W}^{int}\rangle$ is called the *internal virial*.

Eqn 4.101 is the *virial theorem* and expresses pressure directly in terms of density, temperature, and intermolecular forces. It is perfectly general, and valid for any intermolecular potential. Clearly, it gives the proper behavior for ideal gases and shows where the source of non-ideality comes from. This equation is in a form amenable for use in molecular simulations, since the pressure can be calculated from an ensemble average. We have succeeded in deriving our first general expression for a thermodynamic quantity in terms of an ensemble average! We don't need to compute the complete configurational integral to get the pressure - we must "only" compute the internal virial. How do we do this?

If the intermolecular forces can be represented in a *pairwise* fashion (i.e. $\mathbf{F}_i^{int} = \sum_{j \neq i} \mathbf{F}_{ij}$, $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$, where $\mathbf{F}_{ij}$ symbolizes the force on i due to j), then eqn 4.101 assumes the form

$$PV = Nk_BT + \frac{1}{3}\langle \sum_{i=1}^{N} \sum_{j=i+1}^{N} (\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_{ij} \rangle \tag{4.102}$$

Eqn 4.102 will be very useful in conducting simulations of the PVT behavior of fluids.

Chemical Potential as an Ensemble Average

In general, "statistical" properties such as entropy, chemical potential, and free energies are more difficult to calculate from a simulation in the canonical, microcanonical, or isothermal–isobaric ensembles than "mechanical" thermodynamic properties such as pressure and internal energy. Because of this, we often would prefer to work in a different ensemble than the canonical ensemble when trying to get these quantities. For example, we could utilize a direct approach by conducting the simulations in the grand canonical ensemble, where μ, or a related quantity, is specified directly. This has its own difficulties, as we shall see, but there are times when an ensemble other than the canonical ensemble is useful. We will discuss other ensembles shortly, but for now, let's restrict ourselves to the canonical ensemble.

The most common way of computing chemical potentials in the canonical ensemble is to utilize Widom's "test particle" method. This elegant technique was proposed by B. Widom [Widom, B. *J. Chem. Phys.*, *39*, 2808, (1963); *86*, 869, (1982)]. This method is also referred to as "ghost particle" insertion. The derivation goes as follows. Consider a fluid of N molecules in a volume V at temperature T (see Fig. 4.7). We know that the free energy is found from eqn 4.63

$$A(N, V, T) = -\frac{1}{\beta} \ln Q(N, V, T)$$

If we consider the same fluid in the same volume and at the same temperature, but at a density corresponding to $N+1$ molecules, then

$$A(N+1, V, T) = -\frac{1}{\beta} \ln Q(N+1, V, T)$$

Subtracting the two yields

$$A(N+1, V, T) - A(N, V, T) = -\frac{1}{\beta} \ln \frac{Q(N+1, V, T)}{Q(N, V, T)} \tag{4.103}$$

But if we then use the definition of the classical partition function (eqn 4.78) we get

$$A(N+1, V, T) - A(N, V, T) = -\frac{1}{\beta} \ln \left(\frac{[q^{int}]^{N+1}}{(N+1)!\Lambda^{3(N+1)}} \frac{N!\Lambda^{3N}}{(q^{int})^N} \frac{Z(N+1, V, T)}{Z(N, V, T)} \right) =$$

$$k_BT \ln \left(\frac{[N+1]\Lambda^3}{Vq^{int}} \right) - \frac{1}{\beta} \ln \left(\frac{Z(N+1, V, T)}{VZ(N, V, T)} \right) \tag{4.104}$$

Focusing on the ratio of configurational integrals, and using the definition of Z

$$\frac{Z(N+1, V, T)}{VZ(N, V, T)} = \frac{\int \exp[-\beta \mathcal{V}_{N+1}(\mathbf{r}_1, \cdots \mathbf{r}_{N+1})] d\mathbf{r}_1 \cdots \mathbf{r}_{N+1}}{V \int \exp[-\beta \mathcal{V}_N(\mathbf{r}_1, \cdots \mathbf{r}_N)] d\mathbf{r}_1 \cdots \mathbf{r}_N} \tag{4.105}$$

where

$$\mathcal{V}_{N+1}(\mathbf{r}_1, \cdots, \mathbf{r}_{N+1}) = \mathcal{V}_N(\mathbf{r}_1, \cdots, \mathbf{r}_N) + \mathcal{V}_{test}(\mathbf{r}_{N+1}; \mathbf{r}_1, \cdots, \mathbf{r}_N)$$

$\mathcal{V}_{test}(\mathbf{r}_{N+1};\mathbf{r}_1,\cdots,\mathbf{r}_N)$ is the total potential energy *felt* by a molecule at $\mathbf{r}$ due to the N molecules of the fluid at $(\mathbf{r}_1,\cdots,\mathbf{r}_N)$. We can therefore write eqn 4.105 as

$$\frac{Z(N+1,V,T)}{VZ(N,V,T)} =$$

$$\frac{\int d\mathbf{r}_{N+1}\int d\mathbf{r}_1,\cdots,d\mathbf{r}_N \exp[-\beta\mathcal{V}_N(\mathbf{r}_1,\cdots,\mathbf{r}_N)]\exp[-\beta\mathcal{V}_{test}(\mathbf{r}_{N+1};\mathbf{r}_1,\cdots,\mathbf{r}_N)]}{\int d\mathbf{r}_{N+1}\int d\mathbf{r}_1,\cdots,d\mathbf{r}_N \exp[-\beta\mathcal{V}_N(\mathbf{r}_1,\cdots,\mathbf{r}_N)]} \tag{4.106}$$

Look at the form of eqn 4.106. The right hand side is an ensemble average over all configurations of the N molecules, and is also an average over all possible positions of the “ghost” particle.

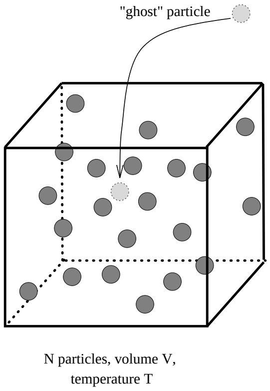

Figure 4.7: Representation of “ghost particle” insertion in Widom’s technique for computing chemical potentials.

The Widom insertion procedure goes as follows. First, take a random configuration of N interacting molecules in volume V and temperature T, weighted according to the canonical ensemble. To this configuration, add a test particle $(N+1)$ at a random point. This test particle “feels” all N particles, but it is not felt by the other particles. Thus, it does not perturb the system. Next, average the Boltzmann factor of the test energy, $\mathcal{V}_{test}$ over all configurations of the “real” N molecules and over all positions of the test molecule. This involves sampling many different canonical conformations and many different “ghost particle” positions/conformations. (It turns out that generating enough of these conformations to get reliable averages is tricky and difficult, which is why it is sometimes desirable to use other methods. Nonetheless, the procedure is relatively straightforward). The result of such a process is that

$$\frac{Z(N+1,V,T)}{VZ(N,V,T)} = \langle\exp(-\beta\mathcal{V}_{test})\rangle \tag{4.107}$$

where the brackets denote a canonical ensemble average over all N–molecule configurations and spatial averaging over all ghost molecule positions.

Now, consider eqn 4.104. In the thermodynamic limit, $N\to\infty$, $V\to\infty$, $N/V=\rho=$ a constant. *In this limit* we therefore have

$$\left(\frac{A(N+1,V,T)-A(N,V,T)}{(N+1)-N}\right) = \left(\frac{\partial A}{\partial N}\right) = \mu(\rho,T) \tag{4.108}$$

where $\mu(\rho,T)$ is the chemical potential at the prevailing molecular density and temperature.

The first term on the right hand side of eqn 4.104 is,

$$k_BT\ln\left[\frac{(N+1)\Lambda^3}{Vq^{int}}\right] = k_BT\ln\left(\frac{\rho\Lambda^3}{q^{int}}\right) \tag{4.109}$$

where again everything is in the thermodynamic limit. But this is just the definition of the ideal gas chemical potential, given the same density and temperature (i.e. all intermolecular interactions turned off)!

$$k_B T \ln\left(\frac{\rho\Lambda^3}{q^{int}}\right) = \mu^{ig}(\rho, T)$$

Thus, in the thermodynamic limit

$$\mu(\rho, T) - \mu^{ig}(\rho, T) \equiv \mu^{ex}(\rho, T) = -k_B T \ln\left[\langle \exp(-\beta \mathcal{V}_{test})\rangle\right] \tag{4.110}$$

The difference $\mu - \mu^{ig}$, taken at the same temperature and *density*, is referred to as the *excess chemical potential*. This is *not* the same as the residual molar Gibbs energy, which is a difference taken under the same temperature and pressure! The ensemble average on the right refers to a molecule in a fluid at density ρ and temperature T. Widom's method can also be implemented in the microcanonical and isothermal–isobaric ensembles, but we won't give the formulas here.

4.5 Other Ensembles

Having given some examples of the use of the canonical ensemble, we now turn to other important ensembles.

4.5.1 Grand Canonical Ensemble

Recall that the canonical ensemble was envisioned in which each system was enclosed in a container with heat conducting walls that are impermeable to the passage of molecules. Thus, each system was specified by N, V, T. In the grand canonical ensemble, each system is enclosed in a container whose walls are both heat conducting *and* permeable to the passage of molecules. Thus thermal of chemical potential gradients between systems results in heat/mass transfer between systems. We can envision this as in Figure 4.8.

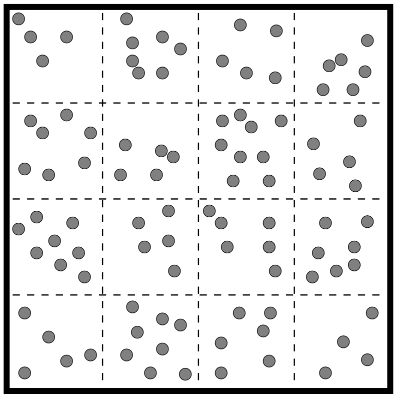

Figure 4.8: Representation of the grand canonical ensemble, with constant μ, V, T.

In this figure, all boxes have the same volume, chemical potential, and temperature at equilibrium. Thus, the energy and number of particles within a box fluctuates. The number of molecules in each system, therefore, can range over all possible values.

We construct a grand canonical ensemble by placing a collection of such systems in a large heat bath at temperature T and a large reservoir of molecules. After equilibrium is reached, the entire system is isolated from the surroundings. Since the entire ensemble is at equilibrium with respect to the transport of heat and molecules, each system is specified by V, T, μ. (If there is more than one component, the chemical potential of each component is the same from system to system).

In deriving an expression of the (μ, V, T) ensemble, we will follow the basic method as that used for the canonical ensemble. However, we must specify a system not only by quantum state (energy level), but also by the number of molecules in that system. For each value of N, there is a set of energy states $\{E_{Nj}(V)\}$. We will use a bit different nomenclature from our previous discussion: Let a_{Nj} be the number of systems in the ensemble that contain N molecules in quantum state j. Note that each value of N has a particular set of levels associated with it, so we specify N then j. The set of occupation numbers, $\{a_{Nj}\}$ forms a distribution. Each possible distribution must satisfy the following conditions:

1. $$\sum_N \sum_j a_{Nj} = \mathcal{A} \tag{4.111}$$

2. $$\sum_N \sum_j a_{Nj} E_{Nj} = \mathcal{E} \tag{4.112}$$

3. $$\sum_N \sum_j a_{Nj} N = \mathcal{N} \tag{4.113}$$

In the above equations, $\mathcal{A}$ is the number of systems in the ensemble, $\mathcal{E}$ is the total energy of the ensemble (remember: the ensemble is isolated!), and $\mathcal{N}$ is the total number of molecules in the ensemble.

For any possible distribution, the number of states is given by a multinomial distribution

$$W(\{a_{Nj}\}) = \frac{\mathcal{A}!}{\prod_N \prod_j a_{Nj}!} \tag{4.114}$$

As in the treatment of the canonical ensemble, the distribution that maximizes W subject to the constraints of eqns 4.111-4.113 completely dominates all the others. You can show that when we maximize eqn 4.114, you obtain

$$a_{Nj}^* = e^{-\alpha} e^{-\beta E_{Nj}(V)} e^{-\gamma N} \tag{4.115}$$

Notice that we have 3 undetermined multipliers, as we should since we have 3 constraints. We determine α in terms of the two other multipliers. If we sum both sides of eqn 4.115 and use eqn 4.111, we obtain

$$e^{-\alpha} = \frac{\mathcal{A}}{\sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}} \tag{4.116}$$

The probability that a randomly chosen system contains N molecules and is in the jth energy state with energy $E_{Nj}(V)$ is

$$P_{Nj}(V, \beta, \gamma) = \frac{e^{-\beta E_{Nj}(V)} e^{-\gamma N}}{\sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}} = \frac{e^{-\beta E_{Nj}(V)} e^{-\gamma N}}{\Xi} \tag{4.117}$$

We use the probability in eqn 4.117 to form averages.

- Energy:

  $$\langle E(V, \beta, \gamma) \rangle = \frac{1}{\Xi} \sum_N \sum_j E_{Nj}(V) e^{-\beta E_{Nj}(V)} e^{-\gamma N} \tag{4.118}$$

  or

  $$\langle E(V, \beta, \gamma) \rangle = -\left(\frac{\partial \ln \Xi}{\partial \beta} \right) \tag{4.119}$$

- Pressure:

  Recall that $P = -\left(\frac{\partial E}{\partial V}\right)$. Let's keep nomenclature straight: P here represents pressure, while P_{Nj} is a probability. So we can write for the average pressure

$$\langle P(V,\beta,\gamma)\rangle = \frac{1}{\Xi}\sum_N\sum_j\left(-\frac{\partial E_{Nj}}{\partial V}\right)_{\beta,\gamma} e^{-\beta E_{Nj}(V)}e^{-\gamma N} \tag{4.120}$$

  or

$$\langle P(V,\beta,\gamma)\rangle = \frac{1}{\beta}\left(\frac{\partial \ln\Xi}{\partial V}\right)_{\beta,\gamma} \tag{4.121}$$

- Number of molecules (density since V is fixed)

$$\langle N(V,\beta,\gamma)\rangle = \frac{1}{\Xi}\sum_N\sum_j N e^{-\beta E_{Nj}(V)}e^{-\gamma N} \tag{4.122}$$

  or

$$\langle N(V,\beta,\gamma)\rangle = -\left(\frac{\partial \ln\Xi}{\partial \gamma}\right)_{V,\beta} \tag{4.123}$$

Now, the question remains: what is β and γ? Remember what we did to get the multipliers for the canonical ensemble: we derived equations that relate $\left(\frac{\partial <E>}{\partial V}\right)_{N,\beta}$ to $\left(\frac{\partial <P>}{\partial \beta}\right)_{N,V}$ and compared this with the corresponding thermodynamic quantities $\left(\frac{\partial E}{\partial V}\right)_{N,T}$ and $\left(\frac{\partial P}{\partial T}\right)_{N,V}$. We saw that $\beta \propto 1/T$

We follow a slightly different approach here. It is straightforward to show that β here has the same value as in the canonical ensemble. That is, $\beta = 1/k_bT$. The mathematical derivation follows that used for the canonical ensemble. *Physically,* you can see why from the following (hand waving) argument.

A grand canonical ensemble can be considered to be a collection of canonical ensembles in thermal equilibrium with each other, but with all possible values of N. Now imagine that each cell is instantly made impermeable, but heat can still flow between cells. This would give a *collection* of canonical ensembles with (N,V,T) fixed. If we use the same analysis on this system as we did with the canonical system, we get that $\beta = 1/(k_BT)$. The result is that each system must have the same value of β, regardless of N.

If you accept this, then the question still remains: What about γ? To see how we can assign meaning to γ, let's consider a function

$$f(\beta,\gamma,\{E_{Nj}(V)\}) = \ln\Xi = \ln\sum_N\sum_j e^{-\beta E_{Nj}(V)}e^{-\gamma N} \tag{4.124}$$

Taking the total derivative of f

$$df = \left(\frac{\partial f}{\partial \beta}\right)_{\gamma,\{E_{NJ}\}} d\beta + \left(\frac{\partial f}{\partial \gamma}\right)_{\beta,\{E_{NJ}\}} d\gamma + \sum_N\sum_j\left(\frac{\partial f}{\partial E_{Nj}}\right)_{\beta,\gamma,E_{Ni\neq j}} dE_{Nj} \tag{4.125}$$

But we have already shown that

$$\frac{\partial f}{\partial \beta} = -\langle E\rangle$$

$$\frac{\partial f}{\partial \gamma} = -\langle N\rangle$$

Differentiating eqn 4.124 yields

$$\frac{\partial f}{\partial E_{Nj}} = -\beta\frac{e^{-\beta E_{Nj}}e^{-\gamma N}}{\sum_N\sum_j e^{-\beta E_{Nj}}e^{-\gamma N}}$$

So

$$df = - < E > d\beta - < N > d\gamma - \beta \sum_N \sum_j P_{Nj} dE_{Nj} \tag{4.126}$$

The last term in eqn 4.126 represents the differential change in energy for moving between states. As we have already stated, this is the reversible work done *by* the systems. It is assumed that this is only P-V work, so that

$$df = - < E > d\beta - < N > d\gamma + \beta < P > dV \tag{4.127}$$

Now, we add $d(\beta < E >) + d(\gamma < N >)$ to both sides of eqn 4.127. The result

$$d(f + \beta < E > + \gamma < N >) = \beta d < E > + \gamma d < N > + \beta < P > dV \tag{4.128}$$

We can compare this to the thermodynamic relation

$$TdS = dE + pdV - \mu dN$$

and use the fact that $\beta = 1/k_B T$ to get that

$$\gamma = \frac{-\mu}{k_B T} \tag{4.129}$$

This provides the meaning for the last undetermined multiplier.

$$S = \frac{< E >}{T} - \frac{< N > \mu}{T} + k_B \ln \Xi \tag{4.130}$$

In eqn 4.130, the integration constant has been set to zero for consistency with the 3rd law.

Now that we have brought in the statistical quantity (entropy) along with the mechanical quantities E, P and N, we may calculate all of the thermodynamics of a system in the grand canonical ensemble. The relevant quantity here is $\Xi(\mu, V, T)$, which is called the grand (canonical ensemble) partition function. As we saw, it is defined as

$$\Xi(\mu, V, T) = \sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{\beta \mu N} \tag{4.131}$$

Here's an important point to get clear: *The canonical ensemble partition function, Q, provides the connection between thermodynamics and statistical mechanics for a closed, isothermal (N,V,T constant) system. The grand canonical ensemble partition function, Ξ, provides the link for an open, isothermal system (μ, V, T) constant.*

Summing over j for fixed N in eqn 4.131 allows us to express a relationship between Q and Ξ

$$\Xi(\mu, V, T) = \sum_N Q(N, V, T) e^{\beta \mu N} \tag{4.132}$$

The term $e^{\beta \mu}$ is often denoted λ. Thus, we see that $\mu = k_B T \ln \lambda$, and we associate λ with an absolute activity, since the difference in chemical potentials between two states is given by

$$\Delta \mu = k_B T \ln(a_2/a_1)$$

The number of systems in an ensemble is arbitrarily large, so N is arbitrarily large, and hence we can take the number of particles to approach infinity.

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} Q(N, V, T) \lambda^N \tag{4.133}$$

The summation to infinity enables us to eliminate the fixed N in the summation, which has certain mathematical advantages. Finally, let us show that pV is the thermodynamic characteristic function of $\ln \Xi$. Compare eqn 4.130

$$S = \frac{< E >}{T} - \frac{< N > \mu}{T} + k_B \ln \Xi$$

with the thermodynamic equation

$$G = \mu N = E + pV - TS$$

We see immediately that

$$pV = k_B T \ln \Xi(V, T, \mu) \tag{4.134}$$

This completes our initial discussion of the grand canonical ensemble.

4.5.2 Isothermal–Isobaric (NPT) Ensemble

The isothermal–isobaric ensemble describes the equilibrium distribution in phase space under the constraint of constant *number of particles*, *temperature*, and *pressure*. Thus, the *volume will fluctuate*. Therefore, volume must join the list of microscopic quantities that comprise phase space. That is, a point in phase space is given by specifying V, $\mathbf{q}^N$, and $\mathbf{p}^N$. The probability density is derived in the manner used for the canonical ensemble. The result is

$$\rho^{NPT}(\mathbf{q}^N, \mathbf{p}^N, V) = \frac{\exp\left(-\beta[\mathcal{H}(\mathbf{q}^N, \mathbf{p}^N; V) + PV]\right)}{Q_{NPT}(N, P, T)} \tag{4.135}$$

where Q_{NPT} is the isothermal–isobaric partition function in the semi-classical form

$$Q_{NPT} = \frac{1}{N! h^{3N} V_0} \int dV \int d\mathbf{q}^N d\mathbf{p}^N \exp\left(-\beta[\mathcal{H}(\mathbf{q}^N, \mathbf{p}^N; V) + PV]\right) \tag{4.136}$$

The factor V_0 is some basic unit of volume chosen to render Q_{NPT} dimensionless. This choice is not fundamentally important.[2]

Notice that

$$Q_{NPT} = \frac{1}{V_0} \int dV \exp(-\beta PV) Q_{NVT}(\mathbf{q}^N, \mathbf{p}^N; V) \tag{4.137}$$

where Q_{NVT} is the canonical ensemble partition function of the system at volume V.

The connection with thermodynamics is via the Gibbs function

$$G(N, P, T) = -\frac{1}{\beta} \ln Q_{NPT}(N, P, T) \tag{4.138}$$

If we are to generate state points in the NPT ensemble, we must clearly provide for changes in the sample volume as well as energy.

As before, it is possible to separate configurational properties from kinetic properties. Thus, we can obtain thermodynamic properties from the configurational integral, which has the form

$$Z_{NPT} = \int dV \exp(-\beta PV) \int d\mathbf{q}^N \exp(-\beta \mathcal{V}(\mathbf{q}) \tag{4.139}$$

(Some definitions of Z_{NPT} include the terms $1/N!$ and $1/V_0$ as normalizing factors).

4.6 Equivalence of Ensembles - Preliminaries

Ensembles are artificial constructs; they should produce average properties that are consistent with one another. What we would like to show next is that, regardless of which ensemble you choose, the results obtained should be the same. Therefore, the choice of which ensemble to work in boils down to a matter of convenience.

In the thermodynamic limit, (i.e. infinite system size) and as long as we avoid the neighborhood of phase transitions, all commonly–used ensembles do indeed give the same average properties. The equivalence of ensembles can

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[2] W. W. Wood, in *Physics of Simple Liquids*, Temperley, H.; Rowlinson, J.; Rushbrooke, G. (eds.), North Holland, Amsterdam, 1968

be shown formally (See Allen and Tildesley). Here, we will show the equivalence for a particular case, and simply state that one can show the same for other cases. To do this, we must once again consider *fluctuations*. We saw that fluctuations about mean values are so small that they can be ignored under most conditions (i.e. away from critical points). Recall that the energy in the NVT ensemble varied like

$$\frac{\sigma_E}{< E >} \approx N^{-1/2}$$

We need to determine the fluctuations in N in an open system represented by the grand canonical ensemble.

Recall that

$$\Xi(\mu, V, T) = \sum_N \sum_j e^{-\beta E_{N_j}} e^{\beta N \mu} = \sum_N Q(N, V, T) e^{\beta N \mu} \tag{4.140}$$

We start with the equality

$$\langle N \rangle \sum_N Q(N, V, T) e^{\beta N \mu} = \sum_N N Q(N, V, T) e^{\beta N \mu} \tag{4.141}$$

Differentiate eqn 4.141 with respect to μ, and divide both sides by Ξ

$$\frac{1}{\Xi} \frac{\partial}{\partial \mu} \left[\langle N \rangle \sum_N Q(N, V, T) e^{\beta N \mu} \right] = \frac{1}{\Xi} \frac{\partial}{\partial \mu} \left[\sum_N N Q(N, V, T) e^{\beta N \mu} \right] \tag{4.142}$$

This leads to

$$\frac{1}{\Xi} \left[\frac{\partial < N >}{\partial \mu} \sum_N Q e^{\beta N \mu} + < N > \sum_N \beta N Q e^{\beta N \mu} \right]$$

$$= \frac{1}{\Xi} \sum_N \beta N^2 Q e^{\beta N \mu}$$

Simplifying this expression,

$$\frac{\partial < N >}{\partial \mu} + \frac{< N > \beta}{\Xi} \sum_N N Q e^{\beta N \mu} = \frac{\beta}{\Xi} \sum_N N^2 Q e^{\beta N \mu}$$

$$\frac{\partial < N >}{\partial \mu} + \beta < N >^2 = \beta < N^2 >$$

or finally

$$< N^2 > - < N >^2 = k_B T \left(\frac{\partial < N >}{\partial \mu} \right)_{V,T} \tag{4.143}$$

Typically, μ is of the same order as $k_B T$. Thus, $\sigma_N^2 \approx < N >$ and

$$\frac{\sigma_N}{< N >} \approx < N >^{-1/2} \tag{4.144}$$

We see from eqn 4.144 that the relative fluctuation in the number of particles goes as $1/\sqrt{< N >}$, (a very small number). This is the standard result for statistical mechanical fluctuations. Therefore, even an open system contains essentially the same number of molecules $< N >$ for fixed μ, V, T. This is an important result, that will help us show why ensembles are equivalent. Eqn 4.143 can be put into a form that has more physical meaning. Starting with the familiar thermodynamic equality

$$d\mu = v dP$$

where T is assumed constant, we obtain

$$\left(\frac{\partial \mu}{\partial \rho} \right)_T = v \left(\frac{\partial P}{\partial \rho} \right)_T$$

where $v = V/N$ and $\rho = N/V$. Then

$$\left(\frac{\partial \mu}{\partial N}\right)_{V,T} V = -\frac{V^3}{N^2}\left(\frac{\partial P}{\partial V}\right)_{N,T}$$

Combining this last equation with eqn 4.143 we find

$$\left(\frac{\sigma_N}{< N >}\right)^2 = \frac{k_B T \kappa}{V} \tag{4.145}$$

where κ, the isothermal compressibility, is defined by

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{N,T}$$

For an ideal gas, we know that $\kappa = 1/\rho$ and $k_B T \kappa / V = 1/ < N >$, consistent with our earlier analysis.

When are fluctuations not negligible? Consider eqn 4.145. At a critical point, or when two phases exist together in the same system, $(\partial P/\partial V)_{N,T}$ is essentially zero, and so κ is infinite. Thus, fluctuations are *large* in these regions. As an example, in a two–phase system having number densities ρ_1 and ρ_2, ρ in the expression

$$< (\rho - < \rho >)^2 >$$

can range from ρ_1 to ρ_2, rather than being narrowly centered on $< \rho >$. Thus, $< (\rho - < \rho >)^2$ is now on the order of $(< \rho >)^2$ itself. For a constant volume system, $\sigma_N / < N >$ is thus on the order of 1, rather that $(< N >)^{-1/2}$. The standard deviation is on the same order as the mean value. Fluctuations in density at the critical point are responsible for critical opalescence phenomenon, in which a pure substance becomes turbid at its critical point.

4.6.1 Equivalence of Ensembles - An Example

Consider the grand canonical ensemble. The partition function for a 1–component system is

$$\Xi = \sum_N Q_{NVT}(N, V, T) e^{\beta N \mu}$$

As we have seen, the only values of N which would be observed are those that only deviate negligibly from $< N >$. We can therefore replace $\ln \Xi$ with the log of the largest term. Let

$$b_N(V, T, \mu) = Q(N, V, T) e^{\beta N \mu}$$

Then

$$\left(\frac{\partial \ln b_N}{\partial N}\right)_{V,T,\mu} = 0$$

$$= \left(\frac{\partial \ln Q}{\partial N}\right)_{V,T} + \beta \mu$$

Let N^* be the value of N satisfying the last equation, and b_{N^*} be the maximum term in Ξ. Then

$$\ln \Xi = \frac{PV}{k_B T} = \ln b_{N^*} = \ln Q(N^*, V, T) + \frac{N^* \mu}{k_B T}$$

or

$$N^* \mu - PV = A(N^*, V, T) = -k_B T \ln Q(N^*, V, T) \tag{4.146}$$

Look at what eqn 4.146 says. It specifies N^* (which equals $< N >$) as a function of V, T, μ. But we could also look at it as specifying μ as a function of the independent variables N^*, V, T. In other words, application of the maximum term procedure, which is legitimate because of the small fluctuations in N, causes the grand canonical ensemble to degenerate into the canonical ensemble. Everything we know indicates that this is a general statement between all valid ensembles: they all give the same thermodynamic results. Thus, *for practical thermodynamic purposes*, there is no distinction between a canonical and grand canonical ensemble. We choose between them simply on the basis of mathematical convenience.

Chapter 5

Application of Ensemble Theory: Mean Field Theories

5.1 Introduction and Motivation

Equilibrium ensembles provide us with a powerful, general formalism for deriving thermodynamic properties from molecular–level information. In practice, however, *exact, analytical* solution of this formalism is impossible for all but the simplest microscopic models. We therefore must invoke approximations to arrive at closed–form solutions. Soon we will show how to do this for a simple case of a low density gas. The approach follows closely from our derivation of the virial for computing pressure. In fact, what we will show is how to derive the *virial equation of state* for low density gases. It turns out that the virial expansion does not converge for higher density gases and liquids, so that more clever techniques are required.

As an alternative, we could think about taking our equilibrium ensembles and solving for the properties of interest *numerically*. This would enable us to use a more detailed model without resorting to simplifying assumptions. The second part of the course will focus on these methods. Before we do this, however, we should first ask the question: Can we make much progress on calculating liquid state thermodynamics with analytical theories? The answer is most definitely yes, but there is a major difficulty. We need to sum over a very large number of system microstates (configurations). That is, we need to know what the configurational integral is

$$Z_{NVT} = \sum_{all\ configs} \exp[-\beta \mathcal{V}(config)]$$

This chapter will focus on various ways we can do this through judicious approximations.

5.2 Mean Field Approximations

One of the most common assumptions used in analytic theories is the *mean field* approximation. The basic idea is to neglect correlations between different parts of the system at some level, and thus avoid the need to consider a multitude of configurations. There are two common strategies.

1. Define a parameter (“order parameter”) that provides a collective description of the configuration (e.g. density, magnetization, concentration). Derive an approximate expression for the Helmholtz or Gibbs energy in terms of the order parameter. Then minimize this free energy to impose equilibrium.

2. Approximate the system of interacting particles by a system of noninteracting particles, subject to an external field. The field represents the effects of other particles on a given particle (hence the term, “mean field”). Derive the thermodynamics by imposing self–consistency. That is, the response that the mean field elicits from a particle must be consistent with the average state of surrounding particles that shape its value.

We will give a couple of examples, but first a word of caution. The term "mean field" is used very loosely to describe a wide range of methods. This can result in tremendous confusion, and so you should use the term with care. It is better to avoid use of the term altogether, and instead refer to the approximation by its name (Bragg–Williams, Debye–Hückel, etc.) Having said this, you will notice that I have used the term for this section! I do this mainly because other people will use the term, so you might as well know what it entails.

We will provide a few examples which demonstrate the use of "mean field" approximations. The approach in the first of these methods is based on modeling the structure of the fluid as a lattice; we assume structural similarity with crystalline solids. Although liquid molecules exhibit random motion, experimentally it is known that the molecules generally spend most of their time trapped in cages created by the proximity of the other molecules. This suggests that such a model, where molecules move locally about a particular site, is not as bad an approximation as it seems at first glance.

5.3 Regular Solution Theory

We wish to construct a simple model which will help us understand, describe, and predict thermodynamic properties of materials. We will use the statistical mechanical formalism derived earlier to link the models with thermodynamics. The **Regular Solution** model (J. Hildebrand) was developed to examine the phase behavior of binary metallic alloys. It can also be applied to liquids!

Lattice Model:

1. Atoms are distributed on the sites of a lattice with coordination number z (nearest neighbors).
2. Sites can be occupied by atoms of substance A or B.
3. No multiple occupancy of sites, and no vacancies allowed.
4. Energy of the mixture made up only of pairwise, nearest neighbor interactions. These interaction energies are designated u_{AA}, u_{BB}, u_{AB} for AA,BB, and AB interactions, respectively.

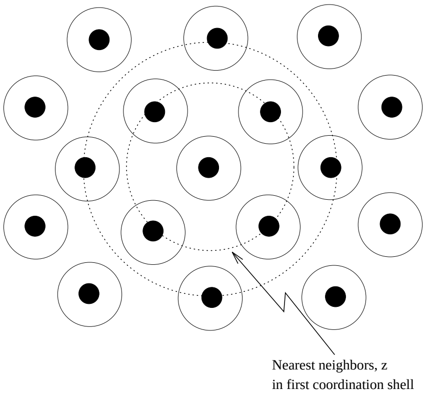

Figure 5.1: Physical picture of a lattice used in Regular Solution Theory

Consider a binary mixture having N_A atoms of A and N_B atoms of B (see Figure 5.1).

$$N_A + N_B = N$$

Mole fractions

$$X_A = N_A/N; \; X_B = N_B/N$$

N_{AA}, N_{BB}, N_{AB}, are the number of pairs AA, BB, AB associated with atoms that are nearest neighbors to one another. Our objective is to derive the thermodynamics of mixing. For example, we would like to know what is the phase diagram and activity coefficients. That is, we want to know what is $g^E(X_A, T)$, the excess molar Gibbs energy.

Note that our lattice model is *incompressible*. We allow no volume change upon mixing.

$$\Delta V_{mix} = 0$$

Thus, the thermodynamics will be pressure independent at given X_A and T:

$$a^E \equiv g^E$$

The molar excess Helmholtz energy will equal the molar Gibbs energy.

We start by defining *counting relations*. Each atom A generates z pairs of the AA or AB type. Sum over all A and we get zN_A pairs distributed over 2 N_{AA} and 1 N_{AB} pairs:

$$zN_A = 2N_{AA} + N_{AB} \tag{5.1}$$

The factor 2 for N_{AA} arises from the fact that each pair N_{AA} is counted twice in the summation, once for each A. Similarly,

$$zN_B = 2N_{BB} + N_{AB} \tag{5.2}$$

As a check, add eqns 5.1 and 5.2:

$$\frac{1}{2}z(N_A + N_B) = N_{AA} + N_{BB} + N_{AB} \tag{5.3}$$

Thus, the total number of pairs ($\frac{1}{2}zN$) is equal to the sum of all pairs. The potential energy of a given configuration is given by

$$E = N_{AA}u_{AA} + N_{BB}u_{BB} + N_{AB}u_{AB} \tag{5.4}$$

Replace N_{AA} and N_{BB} with the expressions in eqns 5.1 and 5.2

$$E = \left(\frac{zN_A - N_{AB}}{2}\right)u_{AA} + \left(\frac{zN_B - N_{AB}}{2}\right)u_{BB} + N_{AB}u_{AB}$$

$$E = \frac{zN_A}{2}u_{AA} + \frac{zN_B}{2}u_{BB} + N_{AB}\left[u_{AB} - \frac{1}{2}(u_{AA} + u_{BB})\right] \tag{5.5}$$

or

$$E = E_A + E_B + \frac{1}{z}N_{AB}\omega \tag{5.6}$$

Note that $E_A \equiv \frac{zN_A}{2}u_{AA}$ is the total potential energy of a lattice of pure A atoms, and $E_B \equiv \frac{zN_B}{2}u_{BB}$ is the total potential energy of a lattice of pure B atoms.

We have defined an *interchange energy* as

$$\omega = z[u_{AB} - 1/2(u_{AA} + u_{BB})] \tag{5.7}$$

The total energy change per exchanged atom is

$$\omega = \frac{2zu_{AB} - zu_{AA} - zu_{BB}}{2} \tag{5.8}$$

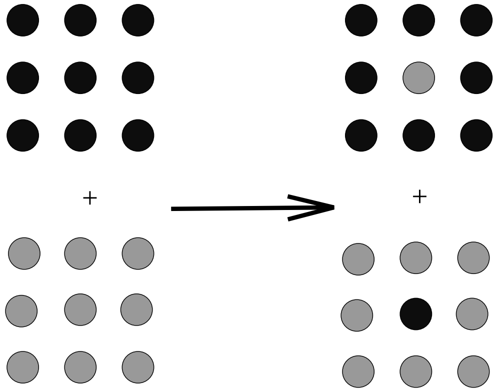

Figure 5.2: Representation of the exchange of two unlike atoms, representing the interchange energy

Negative deviations from ideality mean $\omega < 0$. That is, unlike interactions are *more favorable* than like interactions. On the other hand, positive deviations from ideality mean $\omega > o$. That is, unlike interactions are *less favorable* than like interactions.

Typically for systems acting through van der Waals forces, cross–terms are approximated by the Lorentz–Berthelot combining rule

$$|u_{AB}| \approx (|u_{AA}||u_{BB}|)^{1/2}$$

So,

$$\begin{aligned}\omega &= \frac{z}{2}(|u_{AA}|^{1/2} - |u_{BB}|^{1/2})^2 \\ &= v^* \left[\left(\frac{z}{2v^*}|u_{AA}|^{1/2} - \frac{z}{2v^*}|u_{BB}|^{1/2}\right)\right] \\ &= v^* \left[\left(\frac{|E_A|}{N_A v^*}\right)^{1/2} - \left(\frac{|E_B|}{N_B v^*}\right)^{1/2}\right] \\ &= v^* \left[\left(\frac{|E_A|}{V_A}\right)^{1/2} - \left(\frac{|E_B|}{V_B}\right)^{1/2}\right]\end{aligned}$$

or

$$\omega = v^*(\delta_A - \delta_B)^2$$

where v^* is the volume associated with an atom; V_A and V_B are the volumes occupied by atoms A and B, respectively, $|E|/V$ is the cohesive energy density, and δ is the Hildebrand solubility parameter.

We can write the partition function as

$$Q(N_A, N_B, T) = \sum_{all\ configs} \exp[-\beta E_{config}] \tag{5.9}$$

$$Q(N_A, N_B, T) = \sum_{all\ configs} \exp[-\beta(E_A + E_B + \frac{N_{AB}}{z}\omega)]$$

$$Q = \sum_{N_{AB}} g(N_A, N_B, N_{AB}) \exp[-\beta(E_A + E_B + \frac{N_{AB}}{z}\omega)] \tag{5.10}$$

where $g(N_A, N_B, N_{AB})$ is the number of configurations containing N_{AB} unlike pairs.

At this point, our formulation is exact. To proceed, we need to evaluate the partition function. We could attempt to sum over the very many configurations *numerically*. That is, we could computationally do a simulation of the lattice model. We will discuss this method later. For now, we make a somewhat drastic assumption that will enable us to develop an analytical solution. The approximation is an example of a **mean field approximation**. We assume that, at equilibrium and far from critical points, N_{AB} for a macroscopic system will be strongly peaked about $< N_{AB} >$, the average value.

$$Q_{MF} = \sum_{N_{AB}} g(N_A, N_B, N_{AB}) \exp[-\beta(E_A + E_B + \frac{< N_{AB} >}{z}\omega)] \tag{5.11}$$

Note that this assumption *eliminates fluctuations* in N_{AB}. Now, $\sum_{N_{AB}} g(N_A, N_B, N_{AB})$ equals the total number of lattice configurations of N_A A molecules and N_B B molecules on a lattice of N sites

$$\sum_{N_{AB}} g(N_A, N_B, N_{AB}) = \frac{N!}{N_A! N_B!}$$

thus

$$Q_{MF} = \frac{N!}{N_A! N_B!} \exp[-\beta(E_A + E_B + \frac{< N_{AB} >}{z}\omega)] \tag{5.12}$$

The question we must answer is: What is $< N_{AB} >$???

To proceed, we invoke the Bragg–Williams approximation of *random mixing*. This is another mean field approximation. “There is no short–ranged order apart from that which follows long–ranged order.” This gives

$$< N_{AB} >= N_{AB}^* \equiv N_A z \left(\frac{N_B}{N}\right) \tag{5.13}$$

Eqn 5.13 says that the average number of AB nearest neighbor interaction pairs (indicative of short–ranged order) equals that from a random mixture (denoted by the *). This equals the number of A molecules times the number of lattice sites around an A molecule times the fraction of lattice sites occupied by B (indicative of long–ranged order).

The Bragg–Williams approximation ignores local composition effects.

In reality, for $\omega < 0, < N_{AB} >> N_{AB}^*$. For $\omega > 0, < N_{AB} >< N_{AB}^*$. Now we have

$$Q_{MF} = \frac{N!}{N_A! N_B!} \exp[-\beta(E_A + E_B + \frac{N_A N_B}{N}\omega)] \tag{5.14}$$

We can now derive the thermodynamics of the system from eqn 5.14.

$$A(N_A, N_B, T) = -\frac{1}{\beta} \ln Q_{MF}$$

$$= -k_B T[N \ln N - N - N_A \ln N_A + N_A - N_B \ln N_B + N_B]$$

$$+(E_A + E_B + \frac{N_A N_B}{N}\omega)$$

Helmholtz free energy of mixing is given by

$$\Delta A_{mix}(N_A, N_B, T) =$$

$$A(N_A, N_B, T) - A_A(N_A, T) - A_B(N_B, T)$$

or

$$\Delta A_{mix}(N_A, N_B, T) = A(N_A, N_B, T) - E_A - E_B$$

where the last two terms arise because A and B molecules are indistinguishable, so there are no entropic terms in the pure materials. Divide by N to get the molar Helmholtz energy of mixing, Δa_{mix}:

$$\Delta a_{mix}(X_A, T) = RT(X_A \ln X_A + X_B \ln X_B) + N_{av}\omega X_A X_B$$

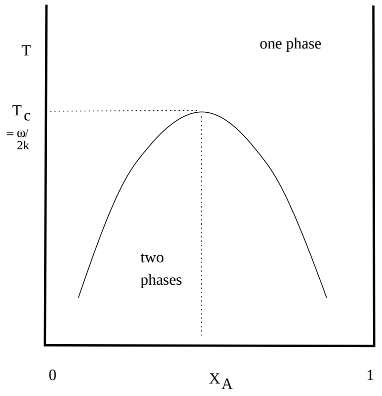

Figure 5.3: regular Solution Theory phase diagram

$$= \Delta a^{id}_{mix} + \omega' X_A X_B$$

Defining the excess free energy, we finally obtain

$$a^E(X_A, T) = g^E(X_A, T) = \omega' X_A X_B \tag{5.15}$$

Let's emphasize a few points. First, the excess Gibbs energy is purely enthalpic. That is,

$$h^E(X_A, T) = \frac{\partial(g^E/T)}{\partial(1/T)} = \omega' X_A X_B$$

thus

$$s^E = \frac{h^E - g^E}{T} = 0$$

Physically, this means there is no deviation from a random organization of molecules allowed, which follows from the assumptions of the model. Second, the solution is regular (hence the name of the theory): $s^E = 0$, $v^E = 0$. The activity coefficients can be represented by the two–suffix Margules model

$$\ln \gamma_A = \frac{\omega}{k_B T} X_B^2$$

$$\ln \gamma_B = \frac{\omega}{k_B T} X_A^2$$

Thus the phase diagram for the case when ($\omega > 0$ will look qualitatively like that shown in Figure 5.3 The phase diagram is symmetric with UCST at $\omega/(k_B T) = 2$

The activity coefficients at infinite dilution are given by

$$\ln \gamma_B^\infty = \frac{\omega}{k_B T}$$

$$\left(\frac{\partial \ln \gamma_B}{\partial x_B}\right)_{X_B \to 0} = -\frac{2\omega}{k_B T}$$

or for this model we have

$$\left(\frac{\partial \ln \gamma_B}{\partial x_B}\right)_{X_B \to 0} = -2 \ln \gamma_B^\infty = \epsilon_B^B$$

where ϵ_B^B is the self–interaction coefficient. It is a measure of how the increase in the concentration of B effects the activity coefficient of B. We can test the model by seeing how well this last expression holds up for real alloys (see Lupis, *Chemical Thermodynamics of Materials*). The results are surprisingly good.

5.4 Quasi–Chemical Approximation

Can we do better than the regular solution model? The Quasi–Chemical Approximation was introduced by Guggenheim [1] to provide a more realistic representation of the degeneracy factor, g. The random distribution of atoms in the Regular Solution theory is termed the *zeroth approximation* by Guggenheim. Guggenheim termed his new estimate of g the *first approximation*. The method is commonly known as the Quasi–Chemical Approximation (QCA) because it implies an equation which corresponds to a chemical reaction. The goal is to *take into account local composition effects*.

5.4.1 QCA Assumptions

1. Again, atoms are assumed to reside on a lattice. As we mentioned before, this is questionable for liquids, although far from critical points, the short–range order of liquids supports this assumption to some extent.
2. In calculating energy, only the chemical contribution is taken into account. Thus, the only source of excess entropy is of a configurational nature. Since this represents a deviation from complete randomness, the sign of excess entropy must always be negative. (This is contrary to experiment).
3. Only the influence of nearest neighbors is taken into account, and pairwise interactions are assumed.
4. Atoms A and B are of similar size and occupy the same kind of sites.

5.4.2 Outline of QCA Derivation

In the following, we sketch out an outline of the QCA approach. The goal is to develop a better expression for g that doesn't assume a random mixture of A and B. Using the expression for g, we would then like to determine the maximal value of the term

$$g \exp[-\beta(E_A + E_B + \frac{N_{AB}}{z}\omega)]$$

and the corresponding value of N_{AB} Having done this, we can substitute the maximum term for the partition function; again, this is the maximum term approximation, valid in the thermodynamic limit far from critical points.

To begin, we start with the exact partition function from Regular Solution theory:

$$Q = \sum_{N_{AB}} g \exp[-\beta(E_A + E_B + \frac{N_{AB}}{z}\omega)]$$

We now seek a better approximation for g. Instead of assuming a random distribution of atoms, we now assume a random distribution of *pairs* AA, AB, BA, and BB. This cuts off correlations at a higher level than the Regular Solution model.

$$\begin{aligned} g_1 &= \frac{(N_{AA} + N_{BB} + N_{AB})!}{N_{AA}! + N_{BB}! + \left(\frac{N_{AB}}{2}\right)! \left(\frac{N_{AB}}{2}\right)!} \\ &= \frac{(1/2)z(N_A + N_B)!}{N_{AA}! N_{BB}! [(N_{AB}/2)!]^2} \end{aligned} \tag{5.16}$$

The numerator in eqn 5.16 is the total number of pairs, while the denominator is the different types of pairs. $[(N_{AB}/2)!]^2$ results from N_{AB}, N_{BA} pairs, and the 2 comes from need to avoid double counting. A completely random distribution of AA, AB, BA, and BB pairs *overestimates* the degeneracy factor, because different pairs cannot truly be distributed at random (see Figure 5.4). To account for this overestimation, we write

$$g = h(N_A, N_B) g_1 \tag{5.17}$$

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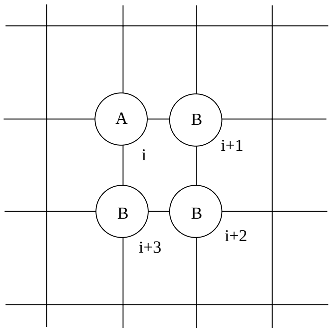
[1] Guggenheim, E.; *Mixtures*, Oxford, 1952



(i,i+1) = AB (i+1,i+2) = BB
(i+2,i+3) = BB (i,i+3) is necessarily AB

Figure 5.4: Schematic of why pairs cannot be truly placed randomly on the lattice for the Quasi-Chemical Approximation

where h is a correction factor for the over counting. We assume h is independent of N_{AA}, N_{AB}, and N_{BB}, but dependent on N_A and N_B. The question now is: How do we find h? We know g in the case of a random distribution

$$g^* = \frac{(N_A + N_B)!}{N_A!N_B!} \tag{5.18}$$

where the $*$ signifies a random distribution of atoms. Eqn 5.17 should still hold in the case of a random distribution of atoms, so we write

$$g^* = h\frac{(1/2)z(N_A + N_B)!}{N^*_{AA}!N^*_{BB}![(N^*_{AB}/2)!]^2} \tag{5.19}$$

We then immediately solve for h:

$$h = \frac{(N_A + N_B)!}{N_A!N_B!}\frac{N^*_{AA}!N^*_{BB}![(N^*_{AB}/2)!]^2}{(1/2)z(N_A + N_B)!} \tag{5.20}$$

But recall that

$$N^*_{AB} \; \frac{zN_AN_B}{N}$$

and that

$$zN_A = 2N_{AA} + N_{AB}$$

$$N^*_{AA} = (1/2)zN_A - (1/2)N^*_{AB}$$

Similarly,

$$N^*_{BB} = (1/2)zN_B - (1/2)N^*_{AB}$$

Thus we get the full expression for g from

$$g = \frac{(N_A + N_B)!}{N_A!N_B!}\frac{(1/2zN_A - 1/2N^*_{AB})!(1/2zN_B - 1/2N^*_{AB})![(N^*_{AB}/2)!]^2}{(1/2zN_A - 1/2N_{AB})!(1/2zN_B - 1/2N_{AB})![(N_{AB}/2)!]^2} \tag{5.21}$$

Note that g is now expressed solely in terms of constants and N_{AB}. To proceed, we search for the value $< N_{AB} >$ that maximizes the partition function term

$$g\exp[-\beta(E_A + E_B + \frac{N_AB}{z}\omega)]$$

and for the associated values of $< N_{AA} >$ and $< N_{BB} >$. The result, after some mathematical manipulation, is

$$\frac{(1/2 < N_{AB} >)^2}{< N_{AA} >< N_{BB} >} = \exp\left(-\frac{2\beta\omega}{z}\right) \tag{5.22}$$

Look at the form of eqn 5.22: It can be viewed as the condition for chemical equilibrium for the reaction

$$AA + BB \rightleftharpoons AB + BA$$

$$K = e^{-\Delta G^o/RT}$$

where "ΔG^o" is given by

$$\Delta G^o = N_{Avo}(2\omega - u_{AA} - u_{BB}) = \frac{2}{z}\omega N_{Avo}$$

This is the origin of the name "Quasi–Chemical" Approximation.

One can derive an expression for the mixture thermodynamics

$$G^E = \left(\frac{N^*_{AB}\omega}{z}\right) +$$

$$RT\left(N^*_{AA}\ln\frac{< N_{AA} >}{N^*_{AA}} + N^*_{BB}\ln\frac{< N_{BB} >}{N^*_{BB}} + N^*_{AB}\ln\frac{< N_{AB} >}{N^*_{AB}}\right) \tag{5.23}$$

where the first term is the Regular Solution Theory result, and the second term is a "correction" factor that accounts for local composition effects. It turns out that a closed, analytical form for G^E in terms of X_B is not obtainable. However, we can write a series expansion to get an approximate expression for G^E and $\ln\gamma_A$ in terms of X_B [2].

$$G^E/RT = \frac{1}{2}zX_B\ln(1+\lambda) - \frac{1}{2}z\lambda X_B^2 +$$

$$\frac{1}{2}z\lambda^2X_B^3 - z\lambda^2(\frac{1}{4}+\frac{5}{3}\lambda)X_B^4 + O(X_B^5) \tag{5.24}$$

$$\ln\gamma_A = \frac{1}{2}z\lambda X_B^2 - z\lambda^2X_B^3 + \frac{3}{4}z\lambda^2(1+\frac{20}{3}\lambda)X_B^4 + O(X_B^5) \tag{5.25}$$

where

$$\lambda = e^{2\beta\omega/z} - 1$$

How well does the model work? For a nearly ideal solution, QCA and RST give identical results. In the RST, z and ω are grouped to form a single parameter that is typically adjusted to fit experimental data. z ranges for most liquids from 8 to 12. In the QCA, the parameters z and ω are specified separately; the additional parameter helps fit a wider range of data! (This is not surprising: if you want a better model, one way to do it is to add more parameters!)

5.5 van der Waals Equation of State

We will now demonstrate another "mean field" theory that most of you are familiar with: the van der Waals equation of state. We will follow closely the original derivation given by van der Waals[3].

We start with the thermodynamic relation

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = k_BT\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N} \tag{5.26}$$

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[2] See Lupis and Elliot, *Acta Met.*, **14**, *1019* (1966)

[3] Johannes Diderik van der Waals; PhD thesis, Leiden, 1873. Nobel Prize, 1910.

where

$$Z(N,V,T) = \int \exp[-\beta\mathcal{V}(\mathbf{r}_1,\cdots,\mathbf{r}_N)]d\mathbf{r}_1\cdots\mathbf{r}_N \tag{5.27}$$

Now, make the pairwise additivity approximation for potentials

$$\mathcal{V}(\mathbf{r}_1,\cdots,\mathbf{r}_N) = \sum_{i=1}^{N}\sum_{j=i+1}^{N}\mathcal{V}_{pair}(|\mathbf{r}_i-\mathbf{r}_j|) \equiv \sum_{i<j}\mathcal{V}_{pair}(r_{ij}) \tag{5.28}$$

At this point, van der Waals assumed something about intermolecular interactions that turned out to be extremely insightful. Namely, he assumed that pair potentials consist of a harshly repulsive and a smooth attractive part (see Figure 5.5). He then assumed that *fluid structure governed mainly by harsh repulsive forces*. This is a good approximation! The form of the potential considered for the derivation of van der Waals equation of state has the following form

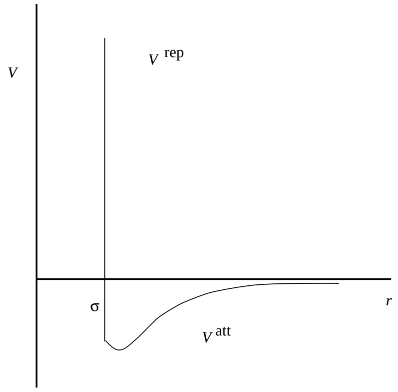

Figure 5.5: Representation of the type of potential envisioned by van der Waals

$$\mathcal{V}_{pair} = \begin{cases} \mathcal{V}^{rep}_{pair}(r) = \infty, & \text{if } r \le \sigma \\ \mathcal{V}^{att}_{pair}(r), & r > \sigma. \end{cases} \tag{5.29}$$

which is shown schematically in Figure 5.5. A physical picture of how molecules interact in this way is shown in Figure 5.6. The "excluded volume" is shown as the dashed line; it represents the region inaccessible to the centers of other molecules, and is a sphere of radius σ centered on the center of each molecule.

We now write for the configurational integral

$$Z(N,V,T) = \int \exp[-\beta\mathcal{V}^{rep}(\mathbf{r}_1,\cdots,\mathbf{r}_N)]\exp[-\beta\mathcal{V}^{att}(\mathbf{r}_1,\cdots,\mathbf{r}_N)]d\mathbf{r}_1\cdots\mathbf{r}_N \tag{5.30}$$

where we have used shorthand notation for $\mathcal{V}^{rep}$ and $\mathcal{V}^{att}$; these are still given by pairwise sums as in eqn 5.28. We need to eliminate the need to sum over all pairs and all configurations in eqn 5.30. Here, we make an approximation that can again be termed a *mean field approximation*. We substitute for the configurational dependent term $\mathcal{V}^{att}(\mathbf{r}_1,\cdots,\mathbf{r}_N)$ an average term

$$\mathcal{V}^{att}(\mathbf{r}_1,\cdots,\mathbf{r}_N) = \mathcal{V}^{att}_{MF} = \frac{1}{2}\sum_{i=1}^{N}\mathcal{V}^{att}_{MF,i} \tag{5.31}$$

where the $1/2$ corrects for double counting of pairwise attractive interactions, and $\mathcal{V}^{att}_{MF,i}$ is the attractive mean potential energy felt by molecule i due to its interactions with all other molecules in the system.

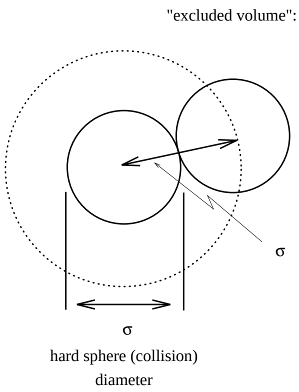

Figure 5.6: Schematic of a hard sphere with excluded volume

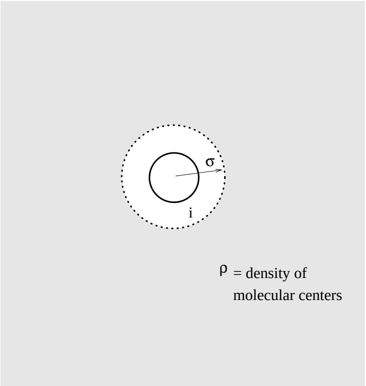

Figure 5.7: Representation of a mean field used in the van der Waals equation. The fluctuating environment is "smeared out", as represented by the gray background

How does one go about calculating $\mathcal{V}_{MF,i}^{att}$? We consider centers of all other molecules as constituting a "smeared" background of uniform density ρ at all distances $\sigma \leq r < \infty$. This *ignores* any two body correlations at distances $r \geq \sigma$. Physically, we can envision the system as looking something like Figure 5.7.

Using this approximation, we can now write

$$\mathcal{V}_{MF,i}^{att} = \int_{\sigma}^{\infty} 4\pi r^2 \, dr \rho \mathcal{V}_{pair}^{att}(r) \tag{5.32}$$

where $4\pi r^2 \, dr\rho$ is the number of molecules in a spherical shell between r and dr from the center of molecule i. From this, we can write a mean field expression for the configurational integral

$$Z(N,V,T) = \exp[-\frac{\beta N}{2} \int_{\sigma}^{\infty} 4\pi r^2 dr \rho \mathcal{V}_{pair}^{att}(r)] \int \exp[-\beta \mathcal{V}^{rep}(\mathbf{r}_1, \cdots, \mathbf{r}_N)] d\mathbf{r}_1 \cdots \mathbf{r}_N \tag{5.33}$$

or

$$Z(N,V,T) = Z^{att}(N,V,T) + Z^{rep}(N,V) \tag{5.34}$$

where

$$Z^{att}(N,V,T) = \exp\left[-\beta \frac{N^2}{V} 2\pi \int_{\sigma}^{\infty} \mathcal{V}_{pair}^{att}(r) r^2 dr\right] \tag{5.35}$$

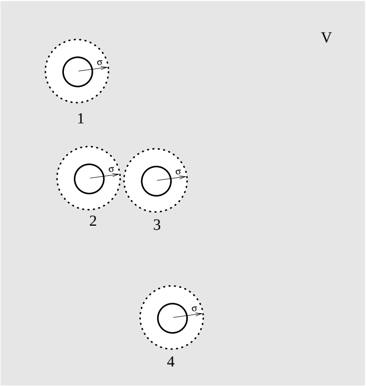

Figure 5.8: Shaded region is the volume accessible for atom 5 to be placed in the volume V

and

$$Z^{rtep}(N,V) = \int \exp[-\beta \mathcal{V}^{rep}(\mathbf{r}_1,\cdots,\mathbf{r}_N)] d\mathbf{r}_1 \cdots \mathbf{r}_N \tag{5.36}$$

But notice in eqn 5.36 that the integrand will always be either zero (for overlapping configurations) or 1 (for non–overlapping configurations. Thus we may write

$$Z^{rep}(N,V) = \int_{non-overlap} d\mathbf{r}_1 \cdots d\mathbf{r}_N \tag{5.37}$$

where the integral over non-overlap means we integrate over all non-overlapping configurations of N hard spheres in volume V. There is no temperature dependence of this integral.

We are now left with a major problem. How do we evaluate the integral in eqn 5.37? We can make an approximation for $Z^{rep}(N,V)$. We assume that Z^{rep} can be written as a product of free volumes, available for the addition of the 1st, 2nd, ..., Nth particle:

$$Z^{rep}(N,V) = \int d\mathbf{r}_1 \frac{\int_{NO} d\mathbf{r}_1 d\mathbf{r}_2}{\int d\mathbf{r}_1} \frac{\int_{NO} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3}{\int_{NO} d\mathbf{r}_1 d\mathbf{r}_2} \frac{\cdots}{\cdots} \frac{\int_{NO} d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N}{\int_{NO} d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_{N-1}} \tag{5.38}$$

where the integrals $\int_{NO}$ represent integrations in which there is no overlap of molecules. Eqn 5.38 can be more compactly written as

$$Z^{rep}(N,V) = V_f^{(1)} \times V_f^{(2)} \times V_f^{(3)} \times \cdots V_f^{(N)} = \prod_{i=1}^{N} V_f^{(i)} \tag{5.39}$$

where $V_f^{(i)}$ is the volume available for adding the center of the ith hard sphere into a non–overlapping configuration of $(i-1)$ hard spheres in a total volume V so that a non–overlapping configuration of i hard spheres is created, averaged over all possible non–overlapping configurations of $(i-1)$ hard spheres.

To demonstrate this idea, consider Figure 5.8. $V_f^{(5)}$ is the volume of the shaded region (inside V, outside all excluded volumes) averaged over all non–overlapping configurations of 1,2,3,4.

Now, let $V_e = \frac{4}{3}\pi\sigma^3$ be the excluded volume of one sphere. We can determine the exact values of $V_f^{(1)}$ and $V_f^{(2)}$:

$$V_f^{(1)} = V$$

$$V_f^{(2)} = V - V_e$$

van der Waals made the following approximation:

$$V_f^{(i)} = V - (i-1)V_e \tag{5.40}$$

The approximation in eqn 5.40 obviously underestimates $V_f^{(i)}$; it fails to recognize that the excluded volume of spheres 1,2,...,i-1 may actually *overlap*. This can be easily seen in Figure 5.9, where for this example the volume available to the third particle is greater than $V - 2V_e$. This approximation also ignores three–body and higher correlations between particles. Despite the limitations, the approximation is a good one at low to moderate densities, where there are few overlaps. This condition can be quantified as

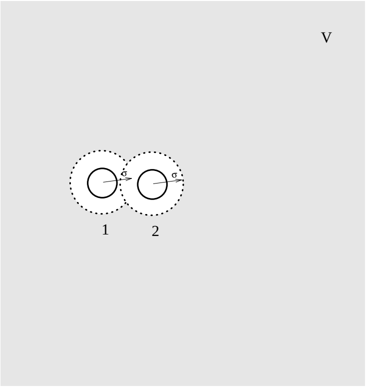

Figure 5.9: Representation of why the van der Waals estimate of accessible volume for atom i is too small. Atoms can have overlap of excluded volume regions if densities are high enough

$$NV_e \ll V \tag{5.41}$$

or equivalently,

$$\rho V_e \ll 1$$

Assuming that the condition in eqn 5.41 is met in our analysis, we then proceed by combining eqns 5.39 and 5.41 to get

$$Z^{rep}(N,V) = \prod_{i=1}^{N}[V - (i-1)V_e] = V^N \prod_{i=1}^{N}[1 - (i-1)\frac{V_e}{V}] \tag{5.42}$$

or

$$\frac{Z^{rep}(N,V)}{V^N} = [1 - \frac{V_e}{V}][1 - 2\frac{V_e}{V}]\cdots[1 - (N-1)\frac{V_e}{V}] \tag{5.43}$$

Using our approximation in eqn 5.41, we can expand the product in the last equation and retain only the first order term in V_e/V:

$$\begin{aligned} \frac{Z^{rep}(N,V)}{V^N} &\approx 1 - [\frac{V_e}{V} + 2\frac{V_e}{V} + \cdots + (N-1)\frac{V_e}{V}] \\ &= 1 - \frac{V_e}{V}[1 + 2 + \cdots + (N-1)] = 1 - \frac{V_e}{V}\frac{(N-1)N}{2} \\ &\approx 1 - \frac{V_e}{V}\frac{N^2}{2} = 1 - \frac{NV_e}{2V}N \approx \left(1 - \frac{NV_e}{2V}\right)^N \end{aligned} \tag{5.44}$$

The last substitution is again justified by eqn 5.41.

Our final result for Z^{rep} an now be written

$$Z^{rep}(N,V) = V^N \left(1 - \frac{NV_e}{2V}\right)^N = V^N \left(1 - \frac{N}{V}\frac{2}{3}\pi\sigma^3\right)^N \tag{5.45}$$

Let us now introduce the following notation.

$$a = -2\pi N_{Avo}^2 \int_\sigma^\infty \mathcal{V}_{pair}^{att}(r) r^2 dr \tag{5.46}$$

$$b = N_{Avo}\frac{2}{3}\pi\sigma^3 = N_{Avo} 4V_{HS} = N_{Avo}\frac{V_e}{2} \tag{5.47}$$

where V_{HS} is the molecular hard sphere volume, N_{Avo} is Avagadro's number and V_e is the molecular excluded volume. Finally, we can write for the configurational integral

$$Z(N,V,T) = \exp\left(+\beta a \frac{N^2}{VN_{Avo}^2}\right) V^N \left(1 - \frac{Nb}{VN_{avo}}\right)^N \tag{5.48}$$

or

$$\ln Z(N,V,T) = \frac{1}{k_BT} a \frac{N^2}{VN_{avo}} + N\ln V + N\ln\left(1 - \frac{Nb}{VN_{Avo}}\right) \tag{5.49}$$

Recall that when we started the derivation, we related the pressure to $\ln Z$:

$$P = k_BT\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N}$$

so

$$P = k_BT\left(\frac{N}{V} + \frac{N^2 b}{V^2 N_{Avo}}\frac{1}{(1 - \frac{Nb}{VN_{Avo}})} - \frac{1}{k_BT} a \frac{N^2}{V^2 N_{Avo}^2}\right) \tag{5.50}$$

Recognizing that the molar volume of the fluid is just $v = \frac{VN_{Avo}}{N}$, we obtain from our last expression

$$P = RT\left(\frac{1}{v} + \frac{b}{v^2}\frac{1}{(1-\frac{b}{v})}\right) - \frac{a}{v^2}$$

$$= \frac{RT}{v} \times \frac{1}{(1-\frac{b}{v})} - \frac{a}{v^2} = \frac{RT}{v-b} - \frac{a}{v^2}$$

or finally

$$(P + \frac{1}{v^2})(v - b) = RT \tag{5.51}$$

This is the result we sought: equation 5.51 is the van der Waals equation of state!

A few comments:

- The van der Waals equation of state is inexact, and we've seen which approximations have made it inexact. Nevertheless, the van der Waals equation unified all experimental knowledge of fluid behavior at the time of its development by
  - accounting for deviations from the ideal gas law
  - predicting gas–liquid equilibrium and the existence of a critical point
  - providing support for the molecular hypothesis

- A major contribution of van der Waals was introducing the concepts of *short–range repulsive* and *long–range attractive* forces between molecules. Also, the idea that the *structure* of a fluid is determined to a large extent by the repulsive forces was very important. In a sense, van der Waals introduced the first perturbation theory, using the hard sphere fluid as a reference fluid.

- Much more accurate equations of state exist today for hard sphere fluids than the one obtained from van der Waals's equation (i.e. $a = 0$). However, this equation forms the basis of most subsequent cubic equations of state. Clearly, van der Waals wrote a very nice PhD thesis!

5.6 Solids: Einstein Model

We can apply lattice models to solids as well as liquids. In the *Einstein model* of a solid, a crystal is considered to consist of a lattice of regularly spaced sites. Each atom in the crystal is confined to a "cage" centered on the lattice site. This confinement is due to repulsive forces between neighbors, which are also kept at their lattice sites. Physically, the crystal can be envisioned as consisting of an array of atoms, all connected to nearest neighbors with stiff springs. We can envision this as is shown in Figure 5.10.

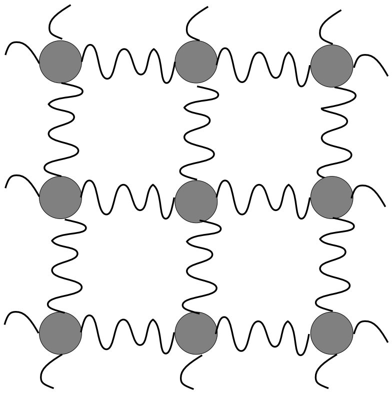

Figure 5.10: Schematic of the Einstein model for a solid. Atoms are fixed about lattice points with harmonic potentials.

Other assumptions of the model include:

1. Vibrations of atoms about their lattice points are independent of neighboring atoms.
2. Potential field for an atom is found by fixing all other atoms to their lattice sites. Thus, each atom feels a *mean field* potential rather than a fluctuating potential. (This is also a "mean field" model!)
3. Vibrations are small.

The mean field potential looks like that shown in Figure 5.11
The resulting partition function can be determined analytically, and is (see Rowley for derivation details):

$$Q = \frac{e^{-\frac{N\beta U_0}{2}} e^{-\frac{3N\Theta}{2T}}}{(1 - e^{-\frac{\Theta}{T}})^{3N}} \tag{5.52}$$

where U_0 is the potential between neighboring atoms and Θ is a characteristic vibrational temperature, $\Theta = \frac{h\nu}{k_B}$. We already know that, given Q, we can calculate all the thermodynamic quantities we wish (A, U, S). Importantly,

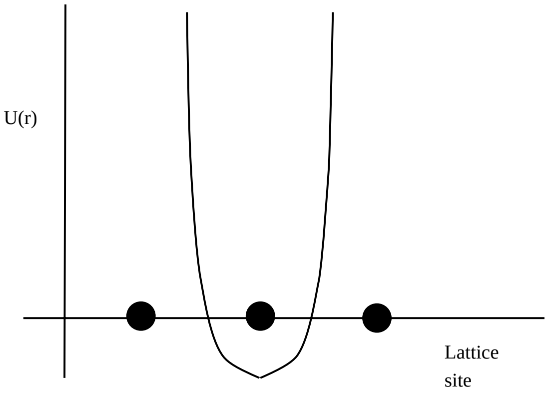

Figure 5.11: Example of what the potential energy of an atom looks like as a function of lateral position in the Einstein model. Neighboring atoms are fixed about their respective lattice sites.

knowledge of the partition function allows us to estimate C_v

$$C_v = 3Nk_B \left(\frac{\Theta}{T}\right)^2 \frac{e^{\Theta/T}}{\left(e^{\Theta/T}-1\right)^2} \tag{5.53}$$

Eqn 5.53 gives good results in the limit of high T, but C_v approaches zero too quickly in the limit of $T \to 0$. The weakness of the Einstein model stems from the mean field treatment we have assumed. In reality, we need to treat coupling of the modes of the solid. There are other more complicated models which attempt to take this into account, but we will not go into the details of these models.

5.7 Adsorption: Lattice Gas Models

Adsorption of gas molecules onto fixed sites on a surface can also be modeled using a lattice approach. The process of adsorption can be envisioned as shown in Figure 5.12. In this section, we will derive the BET adsorption isotherm using the methods we've developed. We will then show how the Langmuir isotherm is a special case of this model. The BET isotherm is named after the authors of a paper describing the isotherm. See: Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.*, **60**, *309*, (1938). The Teller that forms the "T" in BET is the very same Edward

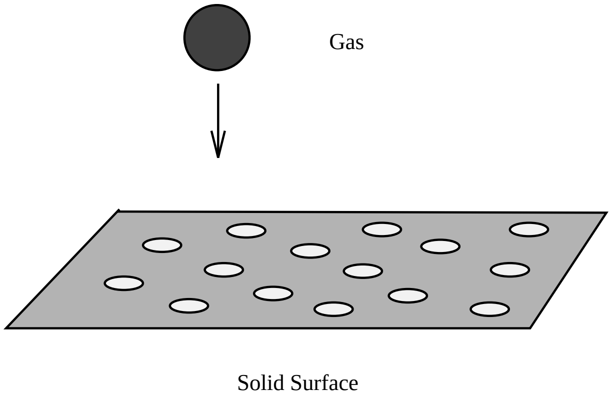

Figure 5.12: Schematic of an atom adsorbing from the gas phase onto well–defined surface sites.

Teller who advocated the development of the hydrogen bomb. We will run across his name again when discussing Metropolis Monte Carlo...

The system we are interested in consists of gas molecules adsorbing on a surface. We want to account for the fact that *multiple layers* can be formed. By definition, an isotherm is simply an expression for the adsorbed amount as a function of ambient gas pressure at a given temperature. Before going it to the derivation, we should point out the usefulness of the BET isotherm model. All practically important adsorbents and heterogeneous catalysts are porous solids. A key parameter in characterizing them is the *specific surface area*. The surface areas of practical materials are huge (several hundred m^2/g is common). How does one measure this?

If the physical adsorption capacity of a material were limited to a closed–packed monolayer, determination of the saturation limit from an experimental isotherm with a molecule of known size would provide a simple, straightforward way of estimating the specific surface area. The problem is that chemisorption sites are widely spaced in most materials, so the saturation limit bears little relation to the surface area. Also, physical adsorption generally involves *multilayer adsorption*. The formation of the second and subsequent layers begins at pressures well below that required for a complete monolayer; it is not obvious how one extracts surface area from an isotherm.

Brunauer, Emmett, and Teller developed a simple model for multilayer adsorption that can be used to extract monolayer capacity and hence surface areas. Thus, we see one of the important roles of theory: it helps us interpret and make sense of experimental data.

The BET isotherm has the following form

$$\frac{c}{c_m} = \frac{b\left(\frac{P}{P_s}\right)}{\left(1-\frac{P}{P_s}\right)\left(1-\frac{P}{P_s}+b\frac{P}{P_s}\right)} \tag{5.54}$$

for $P < P_S$. The symbols have the following meanings:

- c: adsorbed amount per unit mass sorbent, mol/g.
- c_m: adsorbed amount that would correspond to full coverage of the surface by a *monolayer*.
- P: gas phase pressure.
- P_s: vapor pressure of saturated liquid sorbate at the prevailing temperature.

In general, the isotherm looks like that shown in Figure 5.13. Isotherms are assigned to different "types" according to their shape. The BET isotherm is a type II in the Brunauer classification. Measurements are typically performed using a nonpolar gas (N_2, Ar) at liquid nitrogen temperatures, over a range of pressures $0.005 < \frac{P}{P_s} < 0.35$.

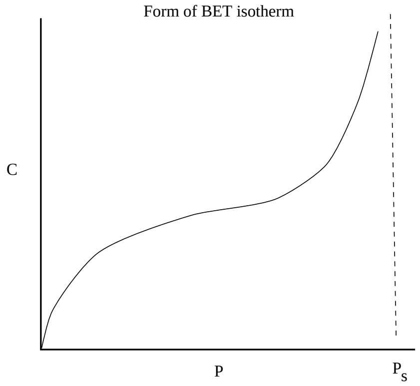

Figure 5.13: Typical shape (type II) of the BET isotherm.

Experimental results are plotted in the form $\frac{P}{c(P_s-P)}$ vs $\frac{P}{P_s}$. According to the BET isotherm, the plot should be linear.

$$\frac{P}{c(P_s-P)} = \frac{1}{c_m b}\left[(b-1)\left(\frac{P}{P_s}\right)+1\right]$$

We obtain c_m and b from the slope and intercept. By knowing the size of the adsorbate (i.e. surface area occupied by it), we can translate c_m (mol sorbate / g sorbent) into a specific surface area (cm^2 internal + external surface / g sorbent). Absolute specific surface areas can be determined to within 20% by this method. The BET method is a rather standard analytical technique these days.

What assumption go into the model?

1. The surface consists of an array of B identical adsorption sites.
2. Gas molecules can adsorb directly on the surface to form the first layer. Gas molecules can also adsorb on top of already adsorbed molecules, to form layers 2, $\cdots$, n. For now, we assume up to n layers can be formed.
3. There are no lateral interaction between molecules in layer 1, apart from the requirement that no two molecules can occupy the same sorption site. In the statistical mechanical formulation, all molecules in the first layer can be modeled as independent entities, each with its own partition function q_1.
4. Molecules in layers 2,. . .,n form a phase which is similar to a saturated liquid at temperature T. They also can be treated in the formulation as independent entities, each with its own partition function q_L. The quantity q_L is the same for all layers 2,$\cdots$,n.
5. The pressure is sufficiently low that the gas phase can be treated as ideal. If the sorbate molecules have internal structure, they are characterized by an internal partition function q_G^{int}.

Physically, our adsorbing fluid looks like that shown in Figure 5.14.

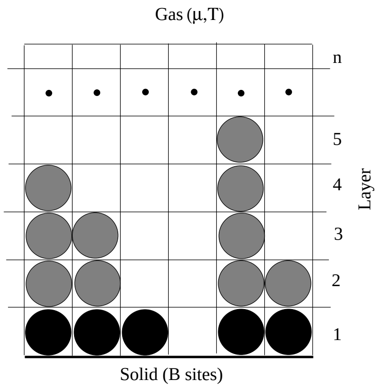

Figure 5.14: Representation of fluid layers in the BET model.

To derive the isotherm, we start from the grand canonical ensemble. It turns out that this ensemble is most convenient for sorption applications, because it naturally allows the number of molecules in a system to fluctuate but fixes chemical potential. This is analogous to a sorption experiment, where pressure is fixed (i.e. chemical potential) and the resulting number of molecules (i.e. loading) is recorded. Let the gas chemical potential be μ. Given this, for a gas that can have internal structure, we can write

$$\mu = k_BT\ln\left(\frac{\rho_G\Lambda^3}{q_G^{int}}\right) = k_BT\ln\left(\frac{P\Lambda^3}{k_BTq_G^{int}}\right)$$

The inclusion of P comes from the ideal gas law, and allows us to connect the chemical potential with the gas pressure. By virtue of phase equilibrium, the chemical potential must be μ throughout the *adsorbed* phase.

Let us now focus on the section of the surface containing B sites. The adsorbed phase is characterized by a given spatial extent (B, n), chemical potential, μ, and temperature T. We can write a partition function for the first adsorbed layer, which we call q_1. Three contributions go into q_1:

1. Potential energy of adsorptive (surface-molecule) interaction.
2. For molecules with internal structure, contributions from vibrational motion of bonds and bond angles, plus torsional and rotational motion. Note that these same basic modes will be active in the gas phase and go into q_G^{int}. However, $q_G^{int} \neq q_1$, since the values of these contributions will in general be quite different in the adsorbed and gas phases.
3. Contributions from center of mass vibration around equilibrium positions of sorption; that is, uninhibited translation along the surface is no longer possible.

For simplicity, let's consider in the following a spherical (i.e. structureless) molecule kept to a site by a solid–molecule potential, $\mathcal{V}_s(\mathbf{r})$, as shown in Figure 5.15. The equilibrium position of the sorbate is (x_0, y_0, z_0); the sorption potential about this point is well approximated by

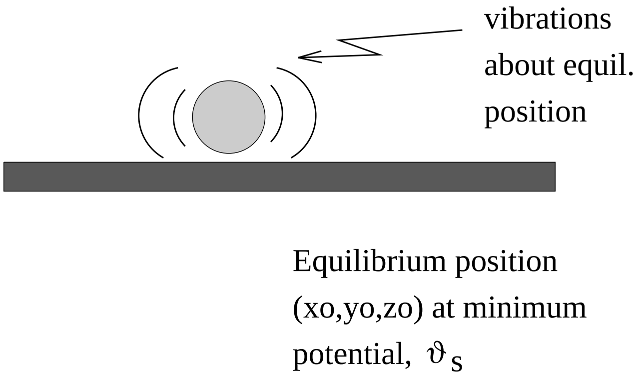

Figure 5.15: Molecules are assumed to be localized around a sorption site (x_0, y_0, z_0), with small local vibrations.

$$\mathcal{V}_s = \mathcal{V}_{s,0} + \left(\frac{\partial \mathcal{V}_s}{\partial \mathbf{r}}\right)_{\mathbf{r}_0} \cdot (\mathbf{r} - \mathbf{r}_0) + \frac{1}{2}\left(\frac{\partial^2 \mathcal{V}_s}{\partial x^2}\right)_{\mathbf{r}_0} (x - x_0)^2 +$$

$$\frac{1}{2}\left(\frac{\partial^2 \mathcal{V}_s}{\partial y^2}\right)_{\mathbf{r}_0} (y - y_0)^2 + \frac{1}{2}\left(\frac{\partial^2 \mathcal{V}_s}{\partial z^2}\right)_{\mathbf{r}_0} (z - z_0)^2$$

The second term on the right is zero (potential is a minimum at $\mathbf{r}_0$). Given this, we can write a Hamiltonian that consists of a potential energy $\mathcal{V}_{s,0} < 0$, plus three independent harmonic oscillator Hamiltonians.

Recall from quantum mechanics that the energy levels of a one–dimensional harmonic oscillator are non–degenerate and given by

$$\epsilon_n = (n + \frac{1}{2})h\nu,\ n = 0, 1, 2, \ldots$$

where ν is the classical frequency. Then

$$q_{ho} = \sum_{n=0}^{\infty} e^{-\frac{\epsilon_n}{k_B T}} = e^{-\frac{h\nu}{2k_B T}} \sum_{n=0}^{\infty} (e^{-\frac{h\nu}{k_B T}})^n$$

$$= \frac{e^{-\frac{h\nu}{2k_BT}}}{1-e^{-\frac{h\nu}{k_BT}}} = \frac{e^{\frac{h\nu}{2k_BT}}}{e^{-\frac{h\nu}{k_BT}}-1}$$

$$= \frac{e^{-\frac{\Theta}{2T}}}{1-e^{-\frac{\Theta}{T}}}$$

For this problem, the three frequencies of the independent harmonic oscillators can be written in a slightly different form as

$$\omega_x = \sqrt{\frac{1}{m}\left(\frac{\partial^2 \mathcal{V}_s}{\partial x^2}\right)_{\mathbf{r}_0}}$$

$$\omega_y = \sqrt{\frac{1}{m}\left(\frac{\partial^2 \mathcal{V}_s}{\partial y^2}\right)_{\mathbf{r}_0}}$$

$$\omega_z = \sqrt{\frac{1}{m}\left(\frac{\partial^2 \mathcal{V}_s}{\partial z^2}\right)_{\mathbf{r}_0}}$$

Thus, we may write the partition function of a molecule sorbed on layer 1 as

$$q_1 = \exp(-\beta\mathcal{V}_{s,0})\frac{\exp(-\beta\hbar\omega_x/2)}{1-\exp(-\beta\hbar\omega_x)} \times \frac{\exp(-\beta\hbar\omega_y/2)}{1-\exp(-\beta\hbar\omega_y)} \times \frac{\exp(-\beta\hbar\omega_z/2)}{1-\exp(-\beta\hbar\omega_z)} \tag{5.55}$$

Note that if vibrations are small enough compared to $(k_BT/\hbar)$, then in the classical limit

$$q_1 = \exp(-\beta\mathcal{V}_{s,0}) \cdot \left(\frac{k_BT}{\hbar}\right)^3 \cdot \frac{1}{\omega_x\omega_y\omega_z}$$

Similarly, we can write a partition function, q_L, that reflects the local environment in one of the adsorbed layers sorbed on top of the first layer.

To proceed, we now consider the grand partition function. We must define some counting relations:

- Let there be N_1, N_2, $\cdots$, N_n molecules on the 1st, 2nd, $\cdots$, nth layers.
- The number of molecules on a layer will *fluctuate* in response to a fixed chemical potential, μ.
- A molecule must sit on either a surface site, B, or another molecule. Thus

$$0 \le N_n \le N_{n-1} \le \cdots \le N_2 \le N_1 \le B$$

We now write the grand partition function

$$\Xi(\mu, B, n, T) = \sum_{N_1=0}^{B}\sum_{N_2=0}^{N_1}\cdots\sum_{N_n=0}^{N_{n-1}}$$

$$\left(\frac{B!}{(B-N_1)!N_1!}\frac{N_1!}{(N_1-N_2)!N_2!}\cdots\frac{N_{n-1}!}{(N_{n-1}-N_n)!N_n!}\right) \times$$

$$\left(q_1^{N_1}(q_L)^{N_2+\cdots+N_n}\exp[(N_1+N_2+\cdots+N_n)\mu]\right) \tag{5.56}$$

In eqn 5.56, the first term represents the number of ways of arranging N_1 non–interacting molecules on a lattice of B sites, times the number of ways of arranging N_2 non–interacting molecules on top of N_1 molecules, etc. The second term is made up of N_1 individual partition functions for molecules in the first layer (q_1) times the individual partition functions for the molecules in subsequent layers 2 through n times the chemical potential term.

Despite the complicated appearance, $\Xi(\mu, B, n, T)$ can be calculated analytically! Define $q_L \exp(\beta\mu) = x$, $\frac{q_1}{q_L} = \lambda$. Then

$$\Xi(\mu, B, m, T) = \sum_{N_1=0}^{B} \sum_{N_2\ 0}^{N_1} \cdots \sum_{N_n=0}^{N_{n-1}} \left(\frac{B!}{(B-N_1)!N_1!} \frac{N_1!}{(N_1-N_2)!N_2!} \cdots \frac{N_{n-1}}{(N_{n-1}-N)!N_n!} \right) \times [(\lambda x)^{N_1} (x)^{N_2+\cdots+N_n}] \tag{5.57}$$

Do the inner summation first

$$\sum_{N_n=0}^{N_{n-1}} \frac{N_{n-1}!}{(N_{n-1}-N_n)!N_n!} x^{N_n} = (1+x)^{N_{n-1}}$$

where the last expression is just the binomial theorem.

Similarly, we can do summations over the N_{n-1} term all the way through N_2. Having done this, we are left with the final summation

$$\Xi(\mu, B, n, T) = \sum_{N_1=0}^{B} \frac{B!}{(B-N_1)!N_1!} (\lambda x)^{N_1} (1 + x + x^2 + \cdots + x^{n-1})^{N_1}$$

We do this last sum to find

$$\Xi(\mu, B, n, T) = \left[1 + \lambda x(1 + x + \cdots + x^{n-1})\right]^B$$

or

$$\Xi(\mu, B, n, T) = \left[1 + \lambda x \left(\frac{1-x^n}{1-x} \right) \right]^B \tag{5.58}$$

Eqn 5.58 enables us to compute the form of the BET isotherm in terms of n, x, and λ. In particular, we can compute the average number of adsorbed molecules at equilibrium

$$< N > \equiv < N_1 + N_2 + \cdots + N_n > = k_B T \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{B,n,T}$$

$$< N > = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\frac{1}{\beta} \frac{\partial x}{x}} \right)_{B,n,T} = x \left(\frac{\partial \ln \Xi}{\partial x} \right)_{B,n,T}$$

or

$$< N > = xB \left[1 + \lambda x \left(\frac{1-x^n}{1-x} \right) \right]^{-1} \times$$

$$\lambda \frac{nx^{n+1} - (n+1)x^n + 1}{(1-x)^2}$$

Which can be simplified to yield

$$\frac{< N >}{B} = \frac{\lambda x \left[1 - (n+1)x^n + nx^{n+1}\right]}{(1-x)\left[1 - x + \lambda x - \lambda x^{n+1}\right]} \tag{5.59}$$

Eqn 5.59 is the equation for an adsorption isotherm! We must now use some physical insight to identify the parameters in this equation. By definition,

$$\frac{< N >}{B} = \frac{c}{c_m}$$

In other words, $< N > /B$ is equal to the amount adsorbed divided by the amount equivalent to a monolayer. What does $x = q_L \exp(\beta\mu)$ represent physically?

Consider the average number of molecules in layer 1 ($< N_1 >$). We can calculate this quantity from the form of Ξ

$$< N_1 >= \lambda \cdot \frac{1}{\Xi}\left(\frac{\partial \ln \Xi}{\partial \lambda}\right)_{x,B}$$

Now if we use eqn 5.58, we get

$$\frac{< N_1 >}{B} = \frac{\lambda^x(1-x^n)}{1-x+\lambda x-\lambda x^{n+1}}$$

Combining this equation with eqn 5.59, we see that

$$\frac{< N >}{< N_1 >} = \frac{1-(n+1)x^n+nx^{n+1}}{(1-x)(1-x^n)}$$

Now, consider what happens to our model system as the gas phase pressure approaches the saturation pressure ($P \rightarrow P_s$). In this limit, all n layers will be filled with saturated liquid. Thus

$$\lim_{P \rightarrow P_s} \frac{< N >}{< N_1 >} = n$$

From the previous expression, we can write this as

$$\frac{1-(n+1)x^n+nx^{n+1}}{(1-x)(1-x^n)} = n$$

valid for $P \rightarrow P_s$. Expanding

$$1-(n+1)x^n+nx^{n+1} = n(1-x-x^n+x^{n+1})$$

$$1-x^n = n(1-x) \rightarrow (1-x)[1+x+\cdots+x^{n-1}-n] = 0$$

The only real solution to this last equation is $x = 1$. We must therefore conclude that as $P \rightarrow P_s$, $x \rightarrow 1$.

Now, recall that $x = q_L \exp(\beta\mu)$ and $\mu = k_B T \ln\left(\frac{P\Lambda^3}{k_B T q_G^{int}}\right)$ Thus,

$$x = q_L \frac{P\Lambda^3}{k_B T q_G^{int}} \tag{5.60}$$

In the limit of $P \rightarrow P_s$, we see

$$1 = q_L \frac{P_s\Lambda^3}{k_B T q_G^{int}} \tag{5.61}$$

or that

$$q_L = \frac{k_B T q_G^{int}}{P_s \lambda^3} \tag{5.62}$$

Eqn 5.62 has given us a concrete meaning for the partition function q_L. We now combine eqn 5.60 with the limiting form, eqn 5.62, to get

$$x = \frac{P}{P_s} < 1 \tag{5.63}$$

Now we use eqn 5.63, along with the fact that $\frac{<N>}{B} = \frac{c}{c_m}$ to re-write the form of our isotherm

$$\frac{c}{c_m} = \frac{\lambda\left(\frac{P}{P_s}\right)\left[1-(n+1)\left(\frac{P}{P_s}\right)^n+n\left(\frac{P}{P_s}\right)^{n+1}\right]}{\left(1-\frac{P}{P_s}\right)\left[1-\frac{P}{P_s}+\lambda\frac{P}{P_s}-\lambda\left(\frac{P}{P_s}\right)^{n+1}\right]} \tag{5.64}$$

where we have made use of the fact that

$$\lambda = \frac{q_1 P_s \Lambda^3}{k_B T q_G^{int}}$$

Eqn 5.64 is the general form of the BET isotherm for a limited number of adsorbed layers, n. If we let $n \to \infty$, we obtain the simpler equation

$$\frac{c}{c_m} \; \frac{b(P/P_s)}{[1-(P/P_s)][1-(P/P_s)+b(P/P_s)]} \tag{5.65}$$

where

$$b \equiv \lambda = \frac{q_1 P_s \Lambda^3}{k_B T q_G^{int}}$$

Eqn 5.65 is the BET isotherm equation we gave at the start of this section!!! Besides deriving the form of the equation, we have found a molecular–level interpretation for the parameter b is the BET isotherm. Recall that

$$q_1 = \exp(-\beta \mathcal{V}_{s,0}) \cdot \left(\frac{k_B T}{\hbar}\right)^3 \cdot \frac{1}{\omega_x \omega_y \omega_z}$$

We see immediately that we expect b to depend on temperature. Furthermore, for structureless (spherical) sorbates that have no internal modes, b is governed by the surface–sorbate energetics and by the mass of the sorbate. For sorbates with internal degrees of freedom, perturbations in these degrees of freedom will affect b as well.

Let us see what happens to eqn 5.64 in the limit of $n = 1$; that is, let's only allow a single layer to adsorb on the surface. Then,

$$\left(\frac{c}{c_m}\right)_{n=1} = \frac{b(P/P_s)}{1+b(P/P_s)} \tag{5.66}$$

Eqn 5.66 is the Langmuir isotherm for monolayer adsorption! Thus, the Langmuir isotherm is merely a specific case of the more general BET isotherm.

The Langmuir and BET isotherms can also be derived (and usually are derived) using kinetic arguments. However, we now see how we can assign molecular–level meaning to the parameters, and understand the behavior and trends of the isotherms. We can also attempt to calculate the isotherms from first principles (if we know something about molecular-surface interactions).

In reality, variations are commonly seen from the BET and Langmuir isotherms, mostly due to the fact that adsorption sites are not all equivalent, and sorbates *do* interact. Various other isotherm models attempt to account for this. For example, the Tempkin isotherm has three constants

$$\frac{c}{c_m} = \xi_1 \ln(\xi_2 K P_A)$$

where the constants ξ_1 and ξ_2 correspond to allowing the enthalpy of adsorption to vary linearly with pressure, and P_A is the partial pressure of species A. Similarly, the Freundlich isotherm corresponds to a logarithmic change in adsorption enthalpy with pressure

$$\frac{c}{c_m} = \xi_1 P_A^{1/\xi_2}$$

5.8 Polymer Chains

Polymer physics is a rich field for statistical mechanics and molecular simulation. The literature is very large; excellent introductory texts are: *Statistical Mechanics of Chain Molecules*, P. J. Flory; *Scaling Concepts in Polymer Physics*, P.-G. de Dennes; *The Theory of Polymer Dynamics*, M. Doi and S. F. Edwards. We won't have time to cover many topics in the statistical physics of polymeric systems. This is a very rich and rapidly evolving field. The best we can do here is to introduce a simple model to give a flavor of what can be done.

The type of information that one can obtain from simple theories is somewhat limited; polymer chains are complicated and the interactions between chains (and within chains) can be strong. The *connectivity* of the chains means that correlations between parts of a chain are important. (This is also what gives polymers their useful properties!).

Molecular simulations of polymers is a rapidly expanding field, because analytic theories are somewhat lacking. Despite the shortcomings, we can learn something about the behavior of chain molecules from some very simple models.

One thing that would be interesting for us to examine is the length of a polymer chain as a function of the number of mers (where a “mer” is a bead or “monomer” unit). We will introduce a mean field treatment to try to answer this question.

5.8.1 Mean Field Polymer Formulation

Consider an idealized polymer chain having M monomer units. The M mers are linked to form a single chain. For example, we could have a very simple chain representative of polyethylene that looked like that shown in Figure 5.16. Notice that the chain is in an all–*trans* conformation. This is the most extended conformation available to a chain (and it is not linear). We will designate the longest possible chain length (with fixed bond angles and lengths) as L_{max}. Chains can rotate about dihedral angles, so conformations will in general be shorter than L_{max}, as shown in Figure 5.17. We wish to address the fundamental question: Given M for a polymer, what is $< L >$?

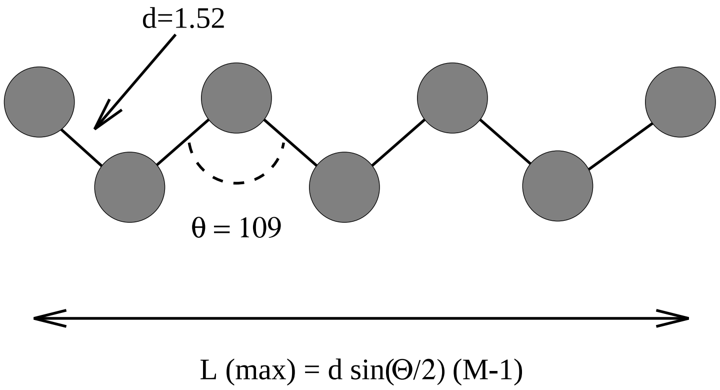

Figure 5.16: Schematic of an all–trans polymer chain. The end–to–end vector is at a maximum length.

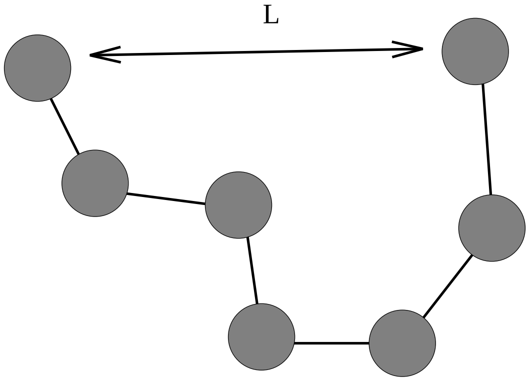

Figure 5.17: An actual chain will in general have a shorter end–to–end length vector.

The possible lengths of the chain are

$$0 \leq L \leq L_{max}$$

Our model of the chain will be *freely jointed*; that is, dihedral angles may take on any value, and all conformations are equally likely, since we do not allow segments to interact with one another. This is a commonly used (and highly unrealistic!) model of a polymer; despite the limitations of the model, we will be able to understand some of the behavior actually observed.

Notice that our assumption allows us to treat the segments of the chain as independent subunits, in line with our earlier models[4]. We also assume that the chain is long (i.e. M is big enough that we can treat the system in a statistical thermodynamic fashion). Given these assumptions, the polymer length, L, is simply the sum of the bond length vectors *projected onto* the end–to–end vector of the chain (designated as **L**. The method for projecting these lengths is illustrated in Figure 5.18 In this figure, we see a 2-dimensional projection of a chain with uniform segment lengths being projected onto the end–to–end vector **L**. The projected segment i has a length ℓ_i, so that the total end-to-end length is

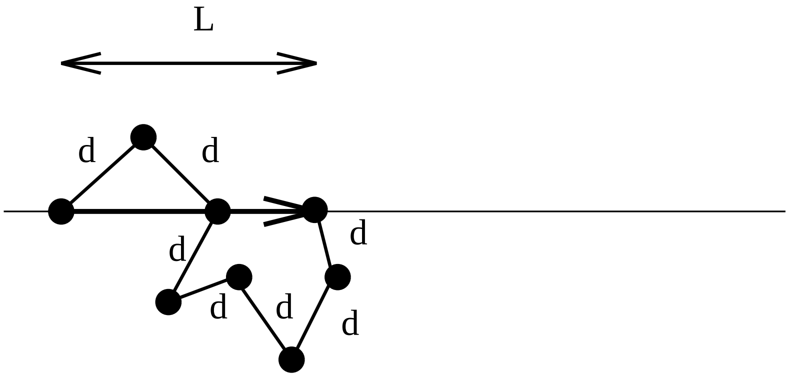

Figure 5.18: Method of projecting segments of the chain onto the end–to–end vector to arrive at the total end–to–end length.

$$L = \sum_{i=1}^{M} \ell_i$$

Now we attempt to add some realism to our model. In reality, individual mers exert intramolecular forces, which give rise to "steric" constraints. Basically, a real chain is not free to take on any shape it desires. The steric interactions serve to extend the chain into a longer length than would arise with a completely freely jointed chain. We model these interactions in a "mean field" sense, by considering a single end–to–end force, τ, which pulls the chain along the end–to–end vector. τ mimics the very many intramolecular interactions present in a real chain, and "stretches" or freely jointed chain. Given the external field τ, we may define the following partition function

$$Q_{mf}(\tau, N, T) = \sum_{\ell} Q_{fj}(L, M, T) e^{\beta \tau \ell} \tag{5.67}$$

where Q_{mf} is our mean field partition function, and Q_{fj} is the partition function for the freely–jointed chain. We see that the Gibbs free energy may be written

$$dG = -SdT - Ld\tau + \mu dM$$

$$G = -k_B T \ln Q_{mf}(\tau, M, T)$$

---

[4] We are going to have another "mean field" model. See the danger of just saying "mean field"?

(Compare these expressions for those obtained in the (N, P, T) ensemble).

We now ask the question, what is Q_{fj} for a given chain length L? Each segment can exist in $i = 1, 2, \cdots, n$ orientations. Since each segment is independent, there is a partition function j_i associated with each orientation. Also, we know that each segment orientation has a length ℓ_i. Q_{fj} is just the number of ways we can arrange the segments of our freely jointed chain times the individual partition function for each segment

$$Q_{fj}(L, M, T) = \sum_{M_i} M! \prod_{i=1}^{n} \frac{j_i^{M_i}}{M_i!} \tag{5.68}$$

Substituting eqn 5.68 into eqn 5.67, we obtain an expression for our mean field partition function

$$Q_{mf}(\tau, M, T) = \sum_{M_i} M! \prod_{i=1}^{n} \frac{(j_i e^{\beta\tau\ell_i})^{M_i}}{M_i!} \tag{5.69}$$

As we have seen before, this partition function can be determined by summing the expression using the multinomial theorem. When this is done, the result is

$$Q_{mf}(\tau, M, T) = \left(\sum_{i=1}^{n} j_i e^{\beta\tau\ell_i} \right)^M = q_{mf}^M \tag{5.70}$$

where q_{mf} is the partition function of an individual segment of the chain. Let us examine the physical meaning of these terms. Clearly, j_i is proportional to the probability of a length ℓ_i being observed when there is no force on the chain $(\tau = 0)$. When there is a force, $j_i e^{\beta\tau\ell_i}$ is proportional to this probability.

We now set out to determine average properties from our partition function. The average end–to–end length is by definition

$$< L >= \frac{\sum_L L Q_{mf}(\tau, M, T)}{\sum_L Q_{mf}(\tau, M, T)} = M \frac{\sum_i \ell_i j_i e^{\beta\tau\ell_i}}{\sum_i j_i e^{\beta\tau\ell_i}} \tag{5.71}$$

or it can be found from the identity

$$< L >= - \left(\frac{\partial G}{\partial \tau} \right)_{M,T} = k_B T \left(\frac{\partial \ln Q_{mf}}{\partial \tau} \right)_{M,T}$$

or more simply

$$< L >= M k_B T \left(\frac{\partial \ln q_{mf}}{\partial \tau} \right)_T \tag{5.72}$$

We are now left with determining what q_{mf} is and solving for $< L >$. This can be done for a general three–dimensional freely jointed chain, but for simplicity we consider here only the simple case of a *one–dimensional polymer chain*. In such a chain, each segment can orient in either the $+x$ or $-x$ direction. In this case, each segment contributes either $+d$ or $-d$ to the end–to–end chain length. Such a chain resembles a folding ruler. In random walk language, this is a random walk along a line with each step of length $+d$ or $-d$.

Question: For $\tau = 0$, what is $< L >$??? What about for finite τ?

There are only two possible states for our one–dimensional polymer ($+$ or $-$), and each state has equal probability. Therefore, the individual partition functions are

$$j_1 = j_2 = j$$

The lengths associated with the states are

$$\ell_1 = +d$$

$$\ell_2 = -d$$

When we sum over these two states, q_{mf} becomes

$$q_{mf} = je^{\beta\tau d} + je^{-\beta\tau d} \tag{5.73}$$

Substituting in eqn 5.71, we get that

$$< L >= Md \tanh(\beta\tau d) \tag{5.74}$$

We can compute the fractional extension from

$$\frac{< L >}{< L_{max} >} = \tanh(\beta\tau d)$$

where we recall that Md is L_{max} for a freely jointed chain.

Plotting these results leads to interesting conclusions, as shown in Figure 5.19. We see that for a fixed force ($\tau = 1 \times 10^{-12} N$), L/L_{max} is 1 at very low temperatures, and then falls to nearly zero at extremely high temperatures. At a fixed temperature, (300 K), the chain is very short for a small τ (as expected, $< L >= 0$ at $\tau = 0$, but quickly rises to a maximum extension for large values of τ (see Figure 5.20). What is the physical explanation for this behavior? At low temperature and finite τ, the system maximizes its free energy by adopting a fully extended state. Entropic penalties are small, since the temperature is low. However, at high T, the thermal energy of the system "randomizes" the conformations, and we see that the average chain length again goes back to the near zero.

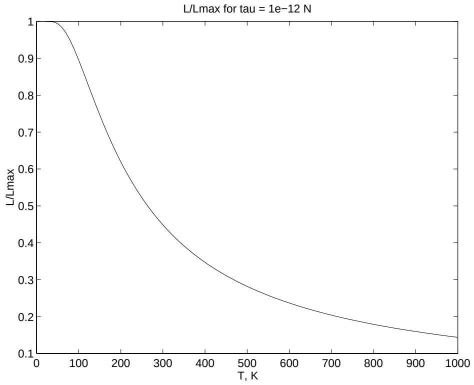

Figure 5.19: Mean field scaling for end–to–end length vs temperature for fixed field strength.

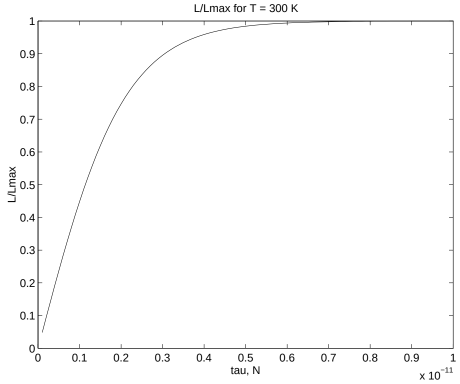

Figure 5.20: Scaling for end–to–end length at 300 K for variable field strength.

Basically, $k_B T$ swamps out τ. For fixed T, we see that in the limit of $\tau \rightarrow 0$, $< L > \rightarrow 0$, and for $\tau \rightarrow \infty$, $< L > \rightarrow < L_{max} >$. This *qualitative* behavior is seen with real polymers, so our very simple model is successful in capturing at least this gross behavior. It is interesting to note that this simple model can also be used to look at the behavior of chain molecules in confining media (such as microporous materials) that exert a “field” that extends the chains.

Chapter 6

Intermolecular Interactions

6.1 Introduction

In previous chapters, we saw that the thermodynamics of an ideal or very dilute gas can be computed quite accurately with the statistical mechanical formalism we have developed. In addition, we have seen that by making judicious approximations, we can calculate properties (or at least trends in properties) of liquids, solids, adsorbed gases, and polymers. However, we were not able to obtain the same degree of accuracy as with ideal gases. The approximations we used all relied upon a *mean field treatment* in which we could decouple individual parts of the system. In general, nonideal fluids and solids exhibit significant intermolecular forces between molecules which do in fact couple separate particles. These forces affect both thermodynamic and transport properties. What we'd like to do in this chapter is see how we can begin to incorporate these forces into our analysis.

Nothing we have developed so far prevents us from accounting for intermolecular interactions in a more or less rigorous way. To obtain thermodynamic properties, we simply must be able to evaluate the configurational integral

$$Z = \int d\mathbf{q}^N \exp[-\beta\mathcal{V}(\mathbf{q}_1, \cdots, \mathbf{q}_N)] \tag{6.1}$$

The word "simply" is perhaps misleading. To evaluate Z we must take a two-step approach. First, we need to know the form of the potential energy, $\mathcal{V}(\mathbf{q}^N)$. That is, we need to know how $\mathcal{V}$ varies with $\mathbf{q}$. Second, we need to be able to evaluate this potential energy *for all possible configurations* if we are to directly compute Z. This is a non-trivial problem, but let's see if we can make some progress.

We start by examining ways of representing the potential energy. After we do this, we will go on to look at techniques which will enable us to either approximate Z or evaluate it directly. A good treatment of potential energy functions and their theory can be found in the classic book by Reed and Gubbins[1]. Here, we will sketch out just enough of the basics to enable us to perform some calculations, while sweeping many of the details under the rug!

The total potential energy $\mathcal{V}$ is typically set at zero when all molecules of the assemblage are separated completely from one another. We now imagine bringing all the molecules into contact to form our system at some density, ρ and temperature, T. Repulsion and attraction between molecules give rise to mutual interaction energies. The value of the potential is determined from three basic characteristics. First, there are *various types* of interactions characteristic of the molecules involved. We need to be able to distinguish between the ways different species are expected to interact. Second, the *distance between molecules and their relative orientation* are important in determining how the species interact. We have already implicitly used this to state that interactions are zero when molecules are very far away from each other. Finally, we must account for the *number of molecules interacting with one another*.

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[1] Reed, T. M.; Gubbins, K. E. *Applied Statistical Mechanics*, 1973

Now lets once again consider our collection of molecules at a specified temperature and density. We will refer to a set of molecular positions and orientations that specify how the molecules of such a system are positioned as a **configuration**. To calculate $\mathcal{V}$ for a given configuration, we will typically make the following assumptions:

1. Intermolecular pair potential energies are those for an isolated pair of molecules.
2. The configurational energy of a system of many molecules is the sum of all possible isolated pair energies. This is known as the *pairwise additivity assumption*.
3. The pair potential depends only on the distance between molecular centers of mass.
4. We can approximate the potential energy with an analytic equation containing one or more molecular constants characteristic of the type of molecule.

The first two assumptions may cause errors at high density, but these errors are usually not all that serious. Assumption three is only valid for monatomic molecules. Polyatomic molecules must be treated differently. (We will discuss this later). The fourth assumption depends on how good the analytic function is; in practice there is a trade off between realism and computational tractability. Such analytic potential energy functions are often referred to as *forcefields*.

Our knowledge of intermolecular forces comes from two main sources. First, we have quantum theory, which addresses the problem of molecular interactions head on. That is, with quantum theory we can compute, with varying levels of accuracy, what the potential energy is of a given configuration as a function of orientation, separation, etc. Quantum calculations enable us to determine molecular geometry and in theory we can also handle reactions. What can we do with this information? Besides being of use in its own right, such information can enable us to fit empirical potential energy functions to the results, and thereby have a means of evaluating energetics for a theoretical or numerical treatment. There are a number of ways of performing quantum calculations, each with strengths and weaknesses. The major methods include Hartree–Fock methods, density functional theory, and semi–empirical approaches. Recently, people have been trying to develop what are known as *ab initio molecular simulations*, where quantum and classical calculations are "mixed" so that energetics are calculated "on the fly" during a simulation. Such techniques would eliminate the need to have a forcefield at all. The biggest weakness of quantum calculations is that they are prohibitive in terms of computational requirements for all but the simplest systems, although every year people are able to study bigger systems in more detail due to computational and methodological advances.

The second way of determining intermolecular forcefields is through the use of experiment. For example, dilute gas properties such as second virial coefficients, viscosities, etc. can be measured. As we will show shortly, these properties give us information on molecular interactions which can be put into a forcefield and used to *predict* properties under conditions other than what the experiments were conducted under. We can also get vital information from spectroscopy and molecular beam experiments. The least elegant (but arguably most effective) method is to postulate a reasonable form of a forcefield, adjust the parameters for a simple system until a good fit with existing experiments are obtained, and then *transfer* this forcefield to other systems for use at other conditions.

6.2 Configurational Energy

Let's discuss some practical issues related to forcefields. We wish to calculate $\mathcal{V}(\mathbf{q}^N)$. We separate $\mathcal{V}$ into a sum of terms involving 1) all possible pairs ij; 2) all possible triplets ijk; 3) all possible quadruplets $ijkl$; $\cdots$; and the final term is the simultaneous interaction of all N molecules. Mathematically, we represent this as

$$\mathcal{V} = \sum_{i<j} \phi_{ij} + \sum_{i<j<k} \Delta\phi_{ijk} + \sum_{i<j<k<l} \Delta\phi_{ijkl} + \cdots + \Delta\phi_{123\ldots N} \tag{6.2}$$

Each term in eqn 6.2 has the following meaning. ϕ_{ij} is the mutual potential energy of the pair located at i and j *isolated* from the influence of all other molecules. $\Delta\phi_{ijk}$ is the *additional* mutual potential energy of the trio at i,

j, and k that arises from the changes in the electron charge distributions of the isolated pair at i and j when a third member is near at position k. The same hold true for the third and higher terms. Finally, $\Delta\phi_{123\ldots N}$ is the potential energy increment characteristic of the whole system that is not included in the previous terms.

As an example, the total potential energy of a system of 4 molecules 1, 2, 3, and 4 is

$$\mathcal{V}_{1234} = \phi_{12} + \phi_{23} + \phi_{34} + \phi_{13} + \phi_{14} + \phi_{24} +$$

$$\Delta\phi_{123} + \Delta\phi_{234} + \Delta\phi_{134} + \Delta\phi_{124} + \Delta\phi_{1234}$$

It is usually assumed (although not proven in general) that the terms in $\mathcal{V}$ decrease in magnitude. That is:

$$\phi_{ij} > \Delta\phi_{ijk} > \Delta\phi_{ijkl} > \cdots > \Delta\phi_{123\ldots N}$$

A potential energy $\mathcal{V}$ of a system of molecules is said to be *additive* when all the terms in the summation except the first sum over pairs are zero. This is the pairwise additivity assumption. The pairwise additivity assumption is perfectly valid for dilute gases, where the probability of three molecules coming into close enough contact to interact is diminishingly small compared to the probability of a two–body encounter. However, pairwise additivity causes some error at higher densities. How important are these errors? It is hard to know, as discrepancies between experiment can be due to neglect of three–body and higher terms, or poor representations of pairwise interactions. Calculations have indicated that the non–additive contribution to the internal energy of liquid argon at the triple point is on the order of 5 to 10%[2].

6.3 Types of Intermolecular Interaction

Figure 6.1 shows the general form of the pair–potential energy for a neutral molecule. When discussing potentials, will use the following definitions. 1) The potential energy is zero at infinite separation (i.e. $\phi = 0$ at $r = \infty$). 2) The separation at which the curve crosses $\phi = 0$ is called σ. 3) The separation at which the potential is at a minimum ($\phi = -\epsilon$) is called r_0. σ and r_0 are variously referred to as the "diameter" of the molecule represented by such a function. More on this latter. As can be seen from Figure 6.1, the potential energy ϕ is the sum of positive contributions representing repulsive forces and negative contributions representing attractive forces. The main contributions to ϕ are

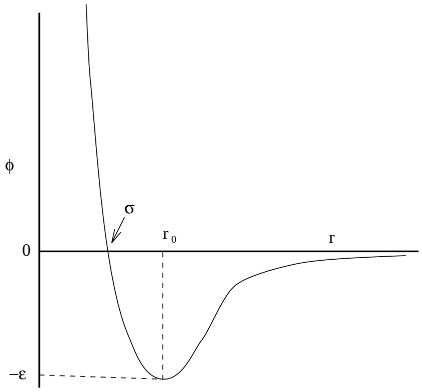

Figure 6.1: Schematic of a pair potential energy function

1. *Short range* ($r \leq \sigma$): Valence or chemical energies, for which chemically saturated molecules contribute a positive term corresponding to a force of repulsion.

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[2] J. S. Rowlinson, *Liquids and Liquid Mixtures*, 2nd ed. Butterworth, 1969

2. *Short and intermediate range* $(\sigma < r \le r_0)$: Residual valence interactions, of which hydrogen bonding is a common example. The magnitudes of "residual chemical" energies are so low compared to usual chemical bonds that they are on the same order as physical interaction energies.

3. *Long–range* $(r \ge r_0)$
   - *Fluctuation or dispersion energies*: The word dispersion is used to designate these energies because they arise from quantum effects that are also associated with the dispersion of light by matter.
   - *Polarization*: Distortion of an electric charge distribution in an electric field.
   - *Direct electrostatic energies*: Classical coulombic energies associated with dipole moments, quadrupole moments, etc.

For non–polar molecules, the centers of negative and positive charges are coincident. Examples include Ar, Cl_2 and CH_4. For polar molecules, centers of negative and positive charge are not coincident. These two centers constitute a dipole and dipole moment. Examples include CH_3COCH_3 (acetone), CH_3Cl, and chlorobenzene. We can also have associating molecules. These are molecules that can form "complexes", such as HF, H_2O, NH_3 and CH_3OH. For all of these types of molecules, the form of the pair potential is not known for the intermediate region. Expressions for the short–ranged and long–ranges interactions are added together, and the intermediate region is derived empirically as a smooth joining of these two extreme regions. Next, we will briefly review how one obtains expressions for these two extreme regions.

6.4 Short–Range Repulsion Interaction

Figure 6.2 shows a schematic of the mutual potential energy for a pair of argon atoms in their lowest energy states as a function of the inter–nuclear separation in the short range region [3]. This curve was determined using quantum calculations, and the essential features have been more or less confirmed with experiment. Note that the (normalized) energy scale is logarithmic, and that beyond very small separations, $\ln\phi$ vs r is essentially linear. The very short–range region, where the curve deviates from linear behavior, is a very high energy region; only thermal energies corresponding to millions of degrees Kelvin can enable molecules to reach this separation. Thus, for practical purposes, the repulsive pair potential can adequately be expressed by

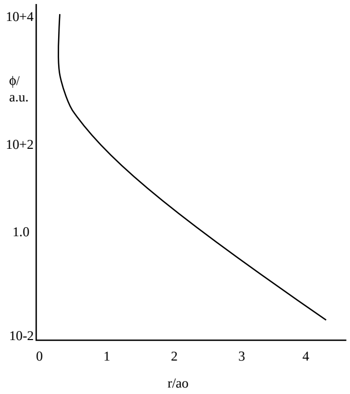

Figure 6.2: Schematic of mutual potential energy for a pair of argon atoms in the lowest energy state as a function of separation in the short–range region. Curve determined from quantum calculations of Abrahamson.

$$\phi^{rep} = Be^{-br} \tag{6.3}$$

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[3] A. A. Abrahamson, *Phys. Rev.*, 130, 693, (1963)

where B and b are constants characteristic of the molecules.

The exponential form of eqn 6.3 has been used to correlate the scattering data of molecules and ions in high–velocity molecular beam experiments. Notice, however, that eqn 6.3 yields a large but finite repulsive energy of B for a separation of $r = 0$. This defect can be remedied in one of two ways. First, we could add a rigid core to our potential for very short ranges. Alternatively, for a small interval in r, we could let

$$(d \ln \phi^{rep})/(d \ln r) = -br$$

and then $br \approx$ constant $= s$. Integrate

$$(d \ln \phi^{rep})/(d \ln r) = -s$$

to obtain

$$\ln \phi^{rep} = -s \ln r + \ln K$$

or

$$\phi^{rep} = K r^{-s} \tag{6.4}$$

Notice that unlike eqn 6.3, this equation shows the proper behavior as separation goes to zero. The main point is that any empirical repulsive potential should have the form of either eqn 6.3, eqn 6.4, or an approximate form of these two that exhibits a steeply increasing potential as intermolecular distance gets smaller. Recall that this was one of the things that van der Waals assumed about the way species interact. The second was that molecules attract one another at larger separations. We need to look at this interaction next.

6.5 Dispersion Interactions

The mutual attraction energy for $r > r_0$ arises from fluctuations or dispersion energies. There are a number of expressions for these energies, and many quantum calculations have been performed to examine these energies for rare gas atoms. The most common way of obtaining dispersion energies is through the London formulas. The basic idea here goes as follows.

- The time–averaged charge distribution of an atom or non–polar molecule is such that the negative and positive centers are coincident.

- *However*, there are rapid fluctuations in the electronic charge distributions, so that *at any instant*, the charge centers are not coincident.

- For $r > r_0$, one can perform a multi–pole expansion for the charge distribution and add this to the Hamiltonian operator in the Schrödinger wave equation for two molecules. The wave equation can then be solved to yield the time averaged value of the pair.

- The *excess* of this energy over that for $r = \infty$ is the *dispersion* energy, ϕ_{ij}^{dis} of pair ij. The result is a series in ascending powers of r^{-1}:

$$\phi_{ij}^{dis} = -\frac{C_{6,ij}}{r^6} - \frac{C_{8,ij}}{r^8} - \frac{C_{10,ij}}{r^{10}} - \cdots \tag{6.5}$$

- By modeling the electronic quantum states as harmonic oscillators, the coefficients are given by the London–Margenau formulas

$$C^{6,ij} = \frac{3}{2} \frac{\alpha_i \alpha_j h \nu_i \nu_j}{\nu_i + \nu_j} \tag{6.6}$$

$$C^{8,ij} = \frac{45h^2\alpha_i\alpha_j}{32\pi^2 m}\left(\frac{\nu_i}{2\nu_i+\nu_j} + \frac{\nu_j}{2\nu_j+\nu_i}\right) \tag{6.7}$$

$$C_{10,ij} = \frac{315h^3}{256\pi^4 m^2}\frac{\alpha_i\alpha_j}{\nu_i+\nu_j} \tag{6.8}$$

where h is Planck's constant, m is electronic mass, and α is polarizability. The frequency ν corresponds to a classical frequency of oscillation for electrons in the molecule ($\Delta E_{level} = h\nu$).

ΔE is approximately the first ionization potential, I, for the molecule, so we can estimate C_6 by replacing $h\nu$ with I to give

$$C_{6,ij} = \frac{3}{2}\frac{\alpha_i\alpha_j I_i I_j}{I_i + I_j}$$

If i and j are the same species,

$$C_{6,ii} = (3/4)\alpha_i^2 I_i$$

and the ratio of C_8 and C_{10} to C_6 can be obtained. Using numerical values for h, π, and m we get

$$\left(\frac{C_8}{C_6}\right)_{ii} = \frac{38.10}{I_i}$$

$$\left(\frac{C_{10}}{C_6}\right)_{ii} = \frac{762.1}{I_i}$$

where I units are in eV and the overall units of the ratios are Å^2 and Å^4, respectively. The dispersion interaction can be written in the form

$$\phi_{ij}^{dis} = -\frac{C_{6,ij}}{r^6}\left[1 + \left(\frac{C_8}{C_6}\right)_{ij}\frac{1}{r^2} + \left(\frac{C_{10}}{C_6}\right)_{ij}\frac{1}{r^4} + \cdots\right] \tag{6.9}$$

The fractional contribution of the C_8 and C_{10} terms are about 20% of the total dispersion energy for argon. Given the distance dependence, this means from a pragmatic point of view we should focus our attention most immediately on the C_6 term.

It turns out that an alternative dispersion formula for C_6 was obtained by Slater and Kirkwood. The form is

$$C_{6,ij} = \frac{3a_0^{(1/2)}e^2\alpha_i\alpha_j}{2[(\alpha_i/n_i)^{1/2} + (\alpha_j/n_j)^{1/2}]} \tag{6.10}$$

There are three–body term expressions that have also been derived. These depend on polarizabilities, ionization potentials, and the relative *orientation* of the three species. The basic point here is that we do have some theoretical justification for the form of the dispersion-type energetic contribution to a forcefield, and the leading term has a $(r^6)^{-1}$ dependence.

6.6 Composite Potential Energy Functions for Non–Polar Molecules

A reasonable form for a composite pair potential function for two atoms i and j is obtained by adding the repulsive and attractive terms

$$\phi_{ij}^B = Be^{-br} - Ar^{-6} \tag{6.11}$$

where the notation has been simplified and A is represented by

$$A = C_6\left(1 + \frac{C_8}{C_6}\frac{1}{r^2} + \frac{C_{10}}{C_6}\frac{1}{r^4} + \cdots\right) = C_6 Y(r) \tag{6.12}$$

The parameters A, B, and b are typically adjusted to fit available experimental data, and then used at a variety of other conditions. However, we see that the *form* of this empirical function is not arbitrary. There are a variety of other potential models, however. For example, the Buckingham potential has the form

$$\phi_{ij}^{B} = \frac{\epsilon}{1 - 6/s_0} \left(\frac{6}{s_0} \exp\left[s_0 \left(1 - \frac{r}{r_0} \right) \right] - \left(\frac{r_0}{r} \right) \right) \tag{6.13}$$

In this model, ϵ and r_0 have the same meaning as before. s_0 is defined to be equal to br_0; it is the value of the repulsion exponent s in the approximate reciprocal–r expression at the point where $r = r_0$.

The Mie m, n potential is a composite function obtained by adding an attractive term $-Ar^{-m}$ to the repulsive term Br^{-n}.

$$\phi_{ij}^{M} = Br^{-n} - Ar^{-m} \tag{6.14}$$

The most commonly used potential of the form in eqn 6.14 is the *Lennard–Jones 6–12 potential,* in which $n = 12$ and $m = 6$

$$\phi_{ij}^{LJ} = Br^{-12}Ar^{-6} \tag{6.15}$$

which can also be written as

$$\phi_{ij}^{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{6.16}$$

where

$$\sigma = r_0(1/2)^{1/6}$$

A crude model that is still quite effective is the *Sutherland* model. This model is often used in obtaining parameters for the van der Waals equation of state.

$$\phi^S = -\epsilon \left(\frac{\sigma}{r} \right)^6, \; r > \sigma$$

$$\phi^S = \infty, \; r \leq \sigma$$

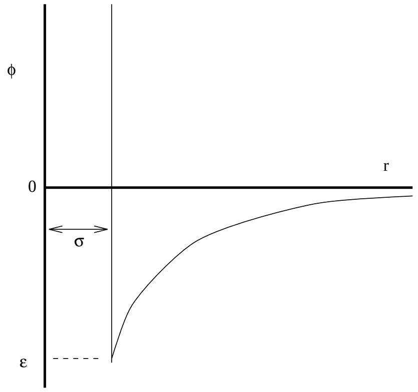

Figure 6.3: Schematic of the Sutherland potential function.

There are a whole host of other potential models, including the Kihara rigid–core, the square well and the hard sphere models. There are also models for structured molecules, which we will not go into at the present time. We will come back to these models when we begin our discussion on simulating fluids.

Up to this point, we have focused on the interactions between two molecules *of the same type.* This enables us to study pure component systems, but we would like to examine mixtures. The question is, then, how does one handle *unlike* pair interactions? Typically, we try to relate the unlike pair potential parameters (i.e. ϵ,σ,m, and n) to the parameters for the two *like* species. Note that since we are usually only concerned with pair interactions, we can do this even for multi–component mixtures. The formulas describing the way we do this are called "combining rules" or "mixing rules". It turns out that if one makes reasonable assumptions, both the attractive and repulsive interaction terms for unlike species are approximately equal to the geometric mean of the respective terms for the two like pairs at the same separation. For example, for the Lennard–Jones 6–12 potential, we usually write

$$\epsilon_{ab} = (\epsilon_{aa}\epsilon_{bb})^{1/2} \tag{6.17}$$

We could write a similar expression for σ_{ab}, but since differences in the diameters of different species are usually small, it is common to use an arithmetic mean

$$\sigma_{ab} = (\sigma_{aa} + \sigma_{bb})/2 \tag{6.18}$$

This last expression is exact for hard spheres. Eqns 6.17 and 6.18 are often referred to as Lorentz-Berthelot combining rules.

In addition to repulsion–dispersion potentials, we also need to account for electrostatic interactions for charged species, as well as dipole moments and quadrupole moments. Often, this just involves attaching a coulombic potential term onto the dispersion–attraction potential function. Other models, which we will discuss later, seek to address orientational effects (such as hydrogen bonding) and "partial" charges. These models can become quite sophisticated, and the evaluation of the long–ranged potentials (which go as $1/r$) is difficult. Special techniques are required to handle these systems.

Chapter 7

Distribution Functions in Classical Monatomic Liquids

7.1 Introduction and Physical Interpretations

So far, we have discussed some basic statistical mechanics and shown how we can compute properties using "mean field" theories. These theories all discount any type of structure that the material may have, or they assume "perfect" structure. By making this assumption, we can "smear out" molecular interactions and come up with the resulting thermodynamics of the system. We know, however, that real materials do have order and structure, particularly on short length scales. What we would like to do now is show how we can account for this structure to compute properties of a relatively simple fluid: a classic, monatomic liquid.

The basic idea behind this chapter is that, elucidation of the structure of fluids is important to understanding fluid behavior. Although liquids often exist at densities comparable to solids, the liquid state lacks the well–defined long–range order of crystalline solids. Dense fluids do not exhibit the dynamic chaos of dilute gases, but the movement of a molecule in a dense fluid is *correlated* with the location of its neighbors. Such correlations lead to *local* and *short–ranged order*. This order is responsible for many of a fluids properties.

Consider Figure 7.1, which represents a snapshot of a collection of spherical molecules, with an arbitrary particle picked as a reference. At a distance r from the reference particle, the density of other particles, $\rho(r)$, will depend on time. However, on average the density will be a quantity dependent *only upon distance*, r.

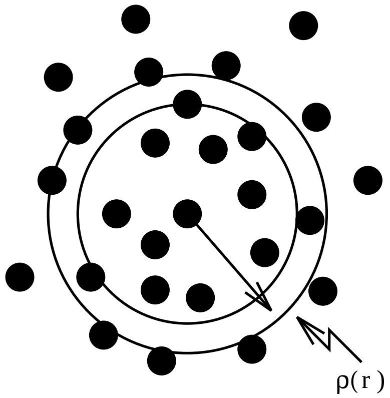

Figure 7.1: Typical arrangement of a fluid of spherical particles. The density at a given radius r with respect to a reference particle is shown.

We can immediately recognize several qualitative features from Figure 7.1. First, $\rho(r)$ must tend toward zero as r goes to zero, since additional particles cannot occupy the same location as the reference particle. Second, at large r, the influence of the reference particle is zero, and $\rho(r)$ must approach ρ, the macroscopic density. Third, at intermediate separations, $\rho(r)$ may be less than or exceed ρ, depending on whether the distance r corresponds to distances of repulsion or attraction between particles. This means that physically, we expect $\rho(r)$ to look like that shown in Figure 7.2, where the horizontal line labeled ρ is the average bulk density.

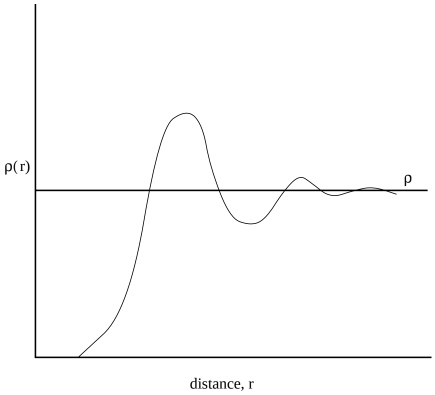

Figure 7.2: Schematic of the function $\rho(r)$ for a fluid.

Now, we define a function $g(r) = \rho(r)/\rho$. The behavior of $g(r)$ is such that

$$g(r) \rightarrow 1 \, as \, r \rightarrow \infty$$

$$g(r) \rightarrow 0 \, as \, r \rightarrow 0$$

$g(r)$ is called the *radial distribution function*. We will develop an expression for $g(r)$ formally, but the above physical picture should always be kept in mind during the development.

It is $g(r)$ that one refers to when we speak of the "structure" of a liquid. $g(r)$ depends not only on r, but also on ρ and T. We will shortly see how macroscopic properties of a fluid can be described in terms of $g(r)$ in conjunction with a pairwise intermolecular potential function, $\mathcal{V}(r)$. For example, we will show how the internal energy of a monatomic fluid can be written as

$$U = \frac{3}{2}Nk_BT + \frac{N\rho}{2}\int_0^\infty \mathcal{V}(r)g(r)4\pi r^2 dr$$

By inspection, we can see where the terms in the proceeding equation come from. The first term is the kinetic energy contribution normally attributed to a monatomic gas. The second term represents a configurational energy; the integrand is simply the intrinsic intermolecular energy at separation r multiplied by the density of particles at that separation. It turns out that many other properties can also be derived in terms of $\mathcal{V}$ and $g(r)$. Evaluation of these expressions is often done using *integral equation theories*, which we will discuss a bit later.

7.2 Development of Equations Describing Distribution Functions

We will now derive the n–particle density and n–particle distribution function in the canonical ensemble. We take as our system a fluid of N molecules in a system volume = V at system temperature = T. The *probability density* in configuration space is

$$\rho(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \frac{\exp\left[-\beta\mathcal{V}(\mathbf{r}_1, \cdots, \mathbf{r}_N)\right]}{\int d\mathbf{r}_1 \cdots d\mathbf{r}_N \exp\left[-\beta\mathcal{V}(\mathbf{r}_1, \cdots, \mathbf{r}_N)\right]} \tag{7.1}$$

or

$$\rho(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \frac{\exp\left[-\beta \mathcal{V}(\mathbf{r}_1, \cdots, \mathbf{r}_N)\right]}{Z(N, V, T)} \tag{7.2}$$

The *probability* of finding particle 1 at position $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$, particle 2 at position $\mathbf{r}_2$ to $\mathbf{r}_2 + d\mathbf{r}_2$, $\cdots$, particle N at position $\mathbf{r}_N$ to $\mathbf{r}_N + d\mathbf{r}_N$ is

$$\mathcal{P}(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \rho(\mathbf{r}_1, \cdots, \mathbf{r}_N) d\mathbf{r}_1 \cdots \mathbf{r}_N \tag{7.3}$$

Now we define a function

$$\rho^{1\cdots n}(\mathbf{r}_1, \cdots, \mathbf{r}_n) = \int \rho(\mathbf{r}_1, \cdots, \mathbf{r}_N) d\mathbf{r}_{n+1} d\mathbf{r}_{n+2} \cdots d\mathbf{r}_N \tag{7.4}$$

Such that the probability of finding particle 1 at position $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$, particle 2 at position $\mathbf{r}_2$ to $\mathbf{r}_2 + d\mathbf{r}_2$, $\cdots$ particle n at position $\mathbf{r}_n$ to $\mathbf{r}_n + d\mathbf{r}_n$ is

$$\rho^{1\cdots n}(\mathbf{r}_1, \cdots, \mathbf{r}_n) d\mathbf{r}_1 \cdots d\mathbf{r}_n \tag{7.5}$$

Note that the above definitions all keep track of the *identity* of the particles. In practice, we are more interested in the probability of finding *any* particle at $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$, *any* particle at $\mathbf{r}_2$ to $\mathbf{r}_2 + d\mathbf{r}_2$, $\cdots$, *any* particle at $\mathbf{r}_n$ to $\mathbf{r}_n + d\mathbf{r}_n$ irrespective of their identities. The probability density for this is

$$(N-1) \cdots (N-n+1) \rho^{1\cdots n}(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \frac{N!}{(N-n)!} \rho^{1\cdots n}(\mathbf{r}_1, \cdots, \mathbf{r}_n) \tag{7.6}$$

where N is the number of ways of choosing the location of the first particle, $N-1$ ways for particle 2, etc., $N-n+1$ ways of choosing particle n. $\rho^{1\cdots n}\mathbf{r}_1, \cdots, \mathbf{r}_n$ is again the probability density of a particular set of n particles at $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$, $\cdots$, $\mathbf{r}_n$ to $\mathbf{r}_n + d\mathbf{r}_n$.

Having defined all these terms, we can now formally define the n–particle density by

$$\rho_N^{(n)}(\mathbf{r}_1, \cdots, \mathbf{r}_n) = \frac{N!}{(N-n)!} \frac{\int d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N \exp[-\beta \mathcal{V}(\mathbf{r}_1, \cdots, \mathbf{r}_N)]}{Z(N, V, T)} \tag{7.7}$$

Notice that $\rho_N^{(n)}$ is a function of n positions in space. The *probability* of finding a configuration with a particle at $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$, $\cdots$, and a particle at $\mathbf{r}_n$ to $\mathbf{r}_n + d\mathbf{r}_n$ is thus

$$\mathcal{P}_N^{(n)}(\mathbf{r}_1, \cdots, \mathbf{r}_n) = \rho_N^{(n)}(\mathbf{r}_1, \cdots, \mathbf{r}_n) d\mathbf{r}_1 \cdots \mathbf{r}_n \tag{7.8}$$

The normalization condition is

$$\int \rho_N^{(n)}(\mathbf{r}_1, \cdots, \mathbf{r}_n) d\mathbf{r}_1 \cdots \mathbf{r}_n = \frac{N!}{(N-n)!} \tag{7.9}$$

To fix concepts, let's consider the special case of an ideal gas. Here, we know that $\mathcal{V}(\mathbf{r}_1, \cdots, \mathbf{r}_N) = 0$ and $Z(N, V, T) = V^N$. So

$$\rho_N^{(n),ig}(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \frac{N!}{(N-n)!} \times \frac{1}{V^N} \tag{7.10}$$

$$\rho^n \frac{N!}{N^n (N-n)!} = \rho^n \left(1 - \mathcal{O}(\frac{n}{N})\right) \tag{7.11}$$

We now define the n–particle distribution function

$$g_N^{(n)} = \frac{\rho_N^{(n)}(\mathbf{r}_1, \cdots, \mathbf{r}_n)}{\rho^n} \tag{7.12}$$

Physically, $g_N^{(n)}$ measures the extent to which the fluid deviates from complete randomness (i.e. from above we see that $g_N^{(n),ig} \approx 1$).

7.3 The Pair Distribution Function

We now consider a special distribution function, the *pair distribution function*. In the NVT ensemble, we define it as

$$g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \frac{\rho_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)}{\rho^2}$$

$$= \frac{N(N-1)}{\rho^2}\frac{\int \exp[-\beta\mathcal{V}(\mathbf{r}_1,\cdots,\mathbf{r}_N)]d\mathbf{r}_3\cdots d\mathbf{r}_N}{Z(N,V,T)} \tag{7.13}$$

The normalization condition is

$$\int \rho_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = \rho^2 \int g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = N(N-1) \tag{7.14}$$

What happens to $g_N^{(2)}$ in the limit of large separations? We expect that structural correlations disappear; the structure becomes indistinguishable from an ideal gas *at the same density*. That is,

$$\lim_{|\mathbf{r}_1-\mathbf{r}_2|\to\infty} g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \frac{\rho_N^{ig(2)}(\mathbf{r}_1,\mathbf{r}_2)}{\rho^2}$$

$$= \frac{\rho^2\frac{N(N-1)}{N^2}}{\rho^2} = 1 - \frac{1}{N} \tag{7.15}$$

As expected, this approaches 1 for a large system.

Now in a homogeneous system, the structure is the same around any point. $g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ only depends on the relative position *vector* $\mathbf{r}_2 - \mathbf{r}_1$ Thus

$$g^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = g^{(2)}(\mathbf{r}_1,\mathbf{r}_1+\mathbf{r}_2-\mathbf{r}_1)$$

$$\equiv g^{(2)}(\mathbf{r}_2-\mathbf{r}_1) \equiv g^{(2)}(\mathbf{r}_{12}) \tag{7.16}$$

Eqn 7.16 is valid *only* for a homogeneous environment.

In a homogeneous and isotropic system, the structure only depends on the magnitude of the intermolecular separation; the direction is unimportant. Thus

$$g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) \equiv g(|\mathbf{r}_2-\mathbf{r}_1|)$$

$$= g(r_{12}) = g(r) \tag{7.17}$$

where eqn 7.17 is again only valid if the medium is homogeneous *and* isotropic.

7.3.1 Physical Interpretation of $g(r)$

Let's provide some physical meaning to the equations we have developed. Let us define the probability of finding a molecule at $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$ *and* a molecule at $\mathbf{r}_2$ to $\mathbf{r}_2 + d\mathbf{r}_2$ as:

$$\rho^2 g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

If we wish to know the probability of finding a *particular* molecule at $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$ and another *particular* molecule at $\mathbf{r}_2$ to $\mathbf{r}_2 + d\mathbf{r}_2$, the probability is:

$$\frac{\rho^2}{N(N-1)} g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

Now, consider the probability of finding a particular molecule at $\mathbf{r}_2$ to $\mathbf{r}_2 + d\mathbf{r}_2$, *provided that a particular molecule has already been placed* at $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$. It is just the last expression divided by $d\mathbf{r}_1 / \int d\mathbf{r}_1$. That is:

$$\frac{\rho^2}{N(N-1)} \frac{g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2}{d\mathbf{r}_1 / \int d\mathbf{r}_1}$$

Given this result, we can write the expected number of molecules in volume element $\mathbf{r}_2$ to $\mathbf{r}_2 + d\mathbf{r}_2$, provided a particular molecule has been placed at $\mathbf{r}_1$. This will simply be equal to the last expression (the probability of such an event as described here) times $(N-1)$, the number of molecules available, given that one molecule has been placed at $\mathbf{r}_1$. Thus, the number of particles is

$$\frac{\rho^2(N-1)}{N(N-1)} \frac{g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2}{d\mathbf{r}_1 / \int d\mathbf{r}_1}$$

Now, we note three things about this.

1. $\int d\mathbf{r}_1 = V$
2. $N/V = \rho$
3. For a given $\mathbf{r}_1$, $d\mathbf{r}_2 = d(\mathbf{r}_2 - \mathbf{r}_1) = d\mathbf{r}_{12}$

Thus, the expected number of molecules in volume element $\mathbf{r}_{12}$ to $\mathbf{r}_{12} + d\mathbf{r}_{12}$ defined relative to position $\mathbf{r}_{12}$ provided we have placed a molecule at $\mathbf{r}_{12}$ is

$$\rho g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_{12}$$

or, we can say that the expected *density* in volume element $\mathbf{r}_{12}$ to $\mathbf{r}_{12} + d\mathbf{r}_{12}$ around position $\mathbf{r}_1$, where we have placed a molecule at $\mathbf{r}_1$ is

$$\rho g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$$

In a homogeneous and isotropic medium, therefore, we may finally write

$$\rho(r) \equiv \rho g(r) \tag{7.18}$$

Eqn 7.18 is shown schematically in Figure 7.3 We see that $\rho(r)$ is the local density of molecules within a spherical shell of radius r to $r + dr$, centered at a given molecule in the fluid, and averaged over all configurations.

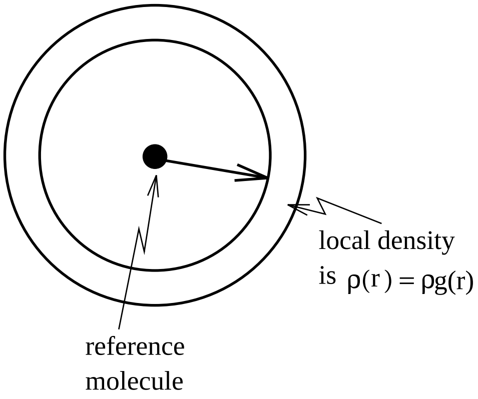

Figure 7.3: Local density for a homogeneous, isotropic fluid.

We can look at this in another way. The probability of finding a given molecule at $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$ and a given molecule at $\mathbf{r}_2$ to $\mathbf{r}_2 + d\mathbf{r}_2$ is again

$$\frac{\rho^2}{N(N-1)} g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

Given a particular molecule at $\mathbf{r}_1$, the probability of finding a given *pair* of molecules at a distance r to $r + dr$ from one another is

$$\frac{\rho^2}{N(N-1)} \int_{r \le |\mathbf{r}_{12}| \le r+dr} g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_{12}$$

where we recall that, given a molecule at $\mathbf{r}_1$, $d\mathbf{r}_{12} = d(\mathbf{r}_2 - d\mathbf{r}_1) = d\mathbf{r}_2$. For a homogeneous and isotropic system, we can write

$$\begin{aligned} \int_{r \le |\mathbf{r}_{12}| \le r+dr} g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_{12} = \\ V \int_{r \le |\mathbf{r}_{12}| \le r+dr} g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_{12} \\ = V \int_{r \le |r_{12}| \le r+dr} 4\pi r_{12}^2 \, g(r_{12}) dr_{12} \end{aligned}$$

Simplifying further

$$= V 4\pi r^2 \, g(r) dr = \frac{N^2}{\rho^2} \frac{1}{V} 4\pi r^2 g(r) dr$$

So we see then that the probability of finding a pair of molecules at a distance r to $r + dr$ from one another is

$$\frac{N}{N-1} \frac{1}{V} \, g(r) 4\pi r^2 dr$$

We now wish to find out what is the typical behavior of $g(r)$. For a Lennard-Jones fluid, the potential looks like that shown in Figure 7.4. Recall that the Lennard-Jones potential energy function is

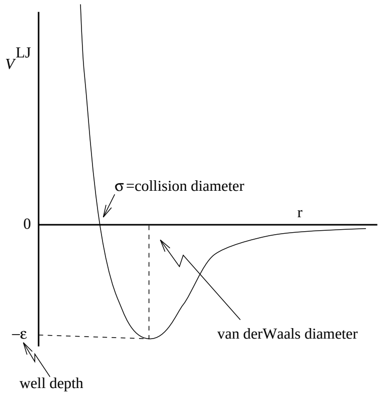

Figure 7.4: Schematic of a Lennard–Jones pair potential.

$$\mathcal{V}_{pair}^{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

Let us now see how $g(r)$ looks as a function of density for Lennard-Jonesium.

For a gas, there is very little structure, as can be seen in Figure 7.5.

For a liquid, there is short–range order (see Figure 7.6).

For a crystal, there is long–range order. For example, an fcc–crystal has peaks at $r/\sigma = 1.12$, $r/\sigma = 1.58$, $r \ \sigma = 2.24$, etc. $g(r)$ for such a crystal would look like that shown in Figure 7.7.

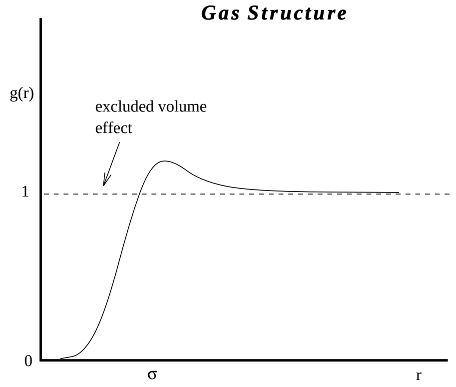

Figure 7.5: Typical form of $g(r)$ for a gas. Note the absence of any real order.

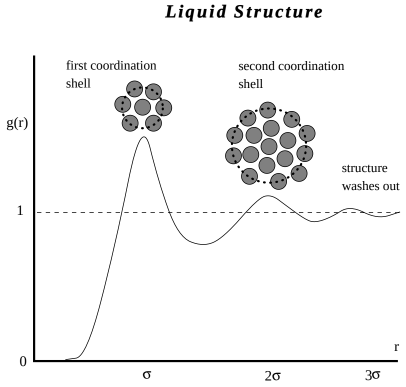

Figure 7.6: Typical form of $g(r)$ for a liquid. We see short–range order out to at least 3σ.

7.4 Experimental Measurement of $g(r)$

The pair distribution function can be measured experimentally using either x–ray or neutron scattering. Schematically, such an experiment looks like that shown in Figure 7.8. One measures a so–called "structure factor", $S(\mathbf{k})$, which equals

$$S(\mathbf{k}) = N\frac{I(\theta)}{I(0)} \tag{7.19}$$

where N is the number of scatterers, $I(\theta)$ is the diffracted intensity at an angle θ, and $I(0)$ is the diffracted intensity in the limit of $\theta \to 0$.

It turns out that one can directly relate $g(r)$ and $S(\mathbf{k})$ through geometric arguments. The final result is

$$S(\mathbf{k}) = 1 + \rho \int g(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \tag{7.20}$$

For an isotropic fluid, $S(\mathbf{k}) = S(k)$, so

$$S(k) = 1 + \rho \int_0^\infty 4\pi r^2 \frac{\sin(kr)}{kr} g(r) dr \tag{7.21}$$

We see that $S(\mathbf{k}) - 1$ is just the Fourier transform of $g(\mathbf{r})$. So to obtain $g(\mathbf{r})$ we simply measure $S(\mathbf{k})$ and take the Fourier transform

$$\rho g(\mathbf{r}) = \frac{1}{(2\pi)^3} \int \exp(i\mathbf{k}\cdot\mathbf{r})[S(\mathbf{k}) - 1] d\mathbf{k}$$

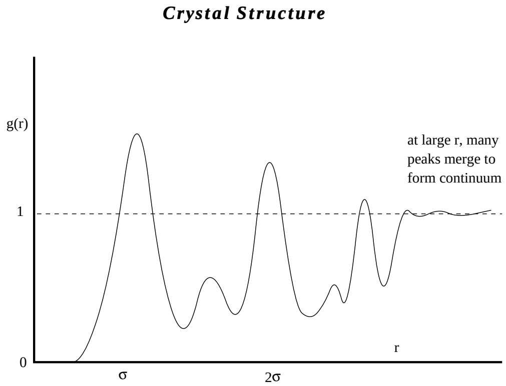

Figure 7.7: Typical form of $g(r)$ for a crystal. Very sharp peaks indicate regular order. At large distances, the very many peaks merge to a continuum.

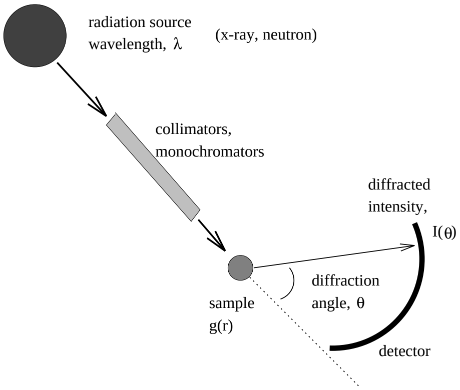

Figure 7.8: The basic idea behind the experiment to measure $g(r)$

For an isotropic fluid, where $g(\mathbf{r}) = g(r)$, we get

$$\rho g(\mathbf{r}) = \frac{1}{(2\pi)^3} \int_0^\infty 4\pi k^2 \frac{\sin(kr)}{kr}[S(k) - 1]dk \tag{7.22}$$

Typical results from liquid and solid measurements of $S(k) - 1$ are shown in Figure 7.9. $S(k)$ will exhibit peaks at $k \approx 2\pi/\Delta r$, where Δr is the distance between successive peaks in $g(r)$. The small–k region of $S(k)$ is called the "small angle" region. It contains information about structural features with *large* characteristic lengths. The large–k ("wide angle") region of $S(k)$ contains information about short–range structure. To get $g(r)$ in liquids, wide–angle experiments must be done using x–ray, neutron, or electron diffraction experiments.

As an example, we may consider the measurements of C. J. Pings on liquid argon at -130 – -110 ^{o} C.[1] Such experiments can be used to test theories, equations of state, and potential energy expressions.

7.5 Thermodynamics From the Radial Distribution Function

We mentioned earlier that if we know the structure and interaction potentials (assumed to be pairwise additive) of a fluid, we could calculate all of its thermodynamic properties. We now proceed to derive expressions for some of

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[1] C. J. Pings, Chem. Eng. Ed.; *4*, 18-23 (1970)

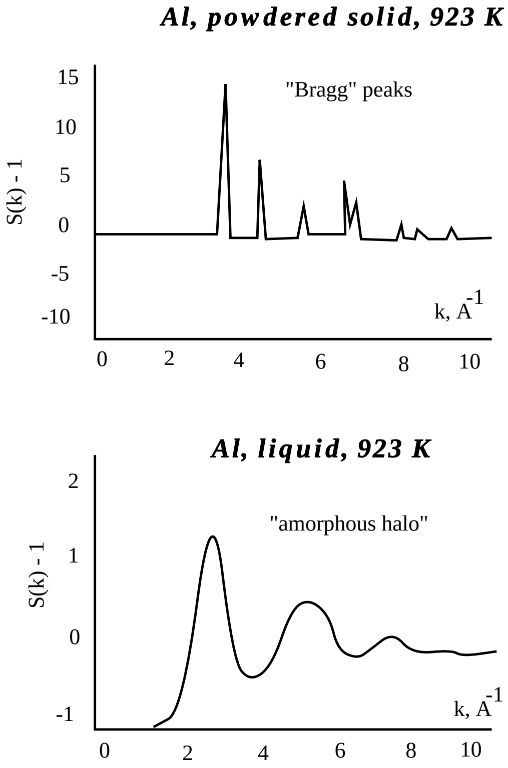

Figure 7.9: Representative structure factors for Al.

these quantities. We will try to use physical arguments whenever possible; more general derivations can be found in the reference books in the library or in standard textbooks.

7.5.1 Internal Energy

Let us start by deriving an expression for the internal energy. The excess internal energy is defined as

$$U^{ex}(N,V,T) = U(N,V,T) - U^{ig}(N,V,T) \tag{7.23}$$

We see that

$$U^{ex}(N,V,T) \equiv < \mathcal{V}(\mathbf{r}_1,\cdots,\mathbf{r}_N) > \tag{7.24}$$

Now, we assume the potential is represented by a pairwise expression, $\mathcal{V}_{pair}(\mathbf{r})$. $g(r)$ gives the probability of finding another molecule in a given volume element at a fixed distance from a particular molecule. The potential energy between this pair is $\mathcal{V}_{pair}(\mathbf{r})$. The differential number of molecules $dN_{\mathbf{r}}$ in an element of spherical volume $d\mathbf{r} = 4\pi r^2 d\mathbf{r}$ at a distance between r and $r + dr$ from the central molecule is

$$dN_{\mathbf{r}} = \rho g(r) 4\pi r^2 dr$$

This is shown schematically in Figure 7.10 The potential energy of this differential system is

$$\mathcal{V}_{pair}(r)\rho g(r) 4\pi r^2 dr$$

For *all* distances from the reference molecule, the total potential energy is

$$\int_0^\infty \mathcal{V}(r)\rho g(r) 4\pi r^2 dr$$

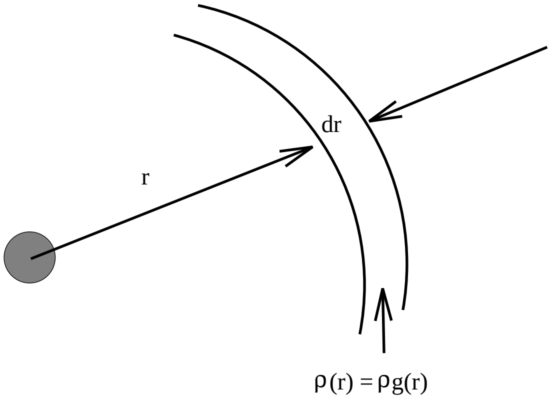

Figure 7.10: Depiction of the number of molecules in a differential element about a reference molecule

where we have dropped the “pair” subscript for convenience.

To obtain the *total* potential energy of the system, we would sum over all molecules, letting each one be the reference. Each integral would be the same as the above expression. Thus, we would expect that the total internal energy would be obtained by multiplying the above expression by N, the total number of molecules. However, this would over count, since each pair interaction would be counted twice. Consequently, U^{ex} is obtained from

$$U^{ex} = 2\pi N\rho \int_0^\infty \mathcal{V}(r)g(r)r^2dr \tag{7.25}$$

The total internal energy, including the ideal gas term and any internal contributions is

$$U = 3/2Nk_BT + U^{int} + U^{ex}$$

Eqn 7.25 is the same result we obtained from physical arguments at the start of our discussion of fluid structure.

7.5.2 Pressure

We can formally derive an expression for the pressure (an equation of state, if you will) starting from the virial theorem, which we derived earlier. Consider the thermodynamic quantity PV. This quantity has units of energy and is extensive; thus we can obtain an expression for the configurational part of PV by adding contributions from successive “shells” as we did with the internal energy.

We know that the total expression for PV is

$$PV = k_BTV \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} = (PV)^{ig} + (PV)^{ex}$$

where $(PV)^{ig} = Nk_BT$. The excess part, $(PV)^{ex}$, is a measure of the effect of intermolecular forces. If the forces are attractive, the product will be negative (reduces PV), whereas repulsive forces increase PV.

The excess part must arise from the force $-d\mathcal{V}/dr$ acting between a particular molecule and all others dN_r in a shell at a distance r from the reference molecule. As before the total force is

$$-\left(\frac{d\mathcal{V}}{dr}\right)\rho g(r)4\pi r^2dr$$

and the total pressure is the total force divided by the areas at r, $4\pi r^2$. We then multiply this total pressure by the volume enclosed by the sphere of radius r $(4/3\pi r^3)$ to get the $(PV)^{ex}$ contribution for the reference molecule interacting with all other molecules in a differential shell at r. We then integrate over all r and multiply by $N/2$ (to avoid double counting) to get the total $(PV)^{ex}$ term:

$$(PV)^{ex} = \frac{N}{2}\int_0^\infty -\frac{d\mathcal{V}}{dr}\rho g(r)\frac{4}{3}\pi r^3 dr \tag{7.26}$$

Finally we can write

$$PV = Nk_BT - \frac{2\pi}{3}N\rho\int_0^\infty \frac{d\mathcal{V}}{dr}g(r)r^3 dr$$

or

$$P = \rho k_BT - \frac{2\pi\rho^2}{3}\int_0^\infty \frac{d\mathcal{V}}{dr}g(r)r^3 dr \tag{7.27}$$

Eqn 7.27 is the so–called “pressure equation”; we see again that a knowledge of $\mathcal{V}$ and $g(r)$ yields the PVT properties of a fluid.

7.5.3 Compressibility Equation

Other properties can also be expressed in this way. A particularly interesting and important expression is the *compressibility equation.* This can be derived starting with the grand canonical ensemble and by defining a lower–order radial distribution function for the μVT ensemble. The result for the isothermal compressibility, κ_T, is

$$\rho k_BT\kappa_T = 1 + \rho\int_0^\infty 4\pi r^2[g^{(2)}(r) - 1]dr \tag{7.28}$$

It is remarkable that the compressibility equation does not presuppose pairwise additivity! In this sense, eqn 7.28 is more fundamental than the pressure equation, eqn 7.27.

The function $g(r)-1$ is often called the *total correlation function*, and is given the symbol $h(r)$. $h(r)$ approaches zero as $r \to \infty$, indicating no correlation of position between a pair of molecules. We will come back to $h(r)$ later.

7.5.4 Potential of Mean Force – The Reversible Work Theorem

The radial distribution function is related to the Helmholtz free energy by a remarkable theorem:

$$g(r) = e^{-\beta w(r)} \tag{7.29}$$

where $w(r)$ is the reversible work for a process in which two tagged particles are moved through the system from infinite separation to a relative separation r. Clearly,

$$w(r) = w(r;\beta,\rho)$$

Since the process of bringing the particles together is done reversibly at constant NVT, $w(r)$ is the change in the Helmholtz free energy for the process. This theorem can be proved directly by formally calculating the average force between the pair of particles and relating this to $g(r)$. Rather than do this, we start out by assuming eqn 7.29 is true.

To be consistent with our earlier nomenclature, we re–write eqn 7.29 as

$$g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) \equiv \exp[-\beta w_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)]$$

From the definition of $g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$,

$$g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \frac{N(N-1)}{\rho^2}\frac{\int \exp[-\beta\mathcal{V}(\mathbf{r}_1,\cdots,\mathbf{r}_N)]d\mathbf{r}_3\cdots\mathbf{r}_N}{Z(N,V,T)}$$

we get that

$$w_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = -\frac{1}{\beta}\ln\left[\frac{N(N-1)}{N^2}\frac{V^2}{Z(N,V,T)}\right] - \frac{1}{\beta}\ln\int \exp\left[-\beta\mathcal{V}(\mathbf{r}_1,\cdots,\mathbf{r}_N)\right] d\mathbf{r}_3\cdots d\mathbf{r}_N \tag{7.30}$$

In a homogeneous system, we can take the position $\mathbf{r}_1$ as our reference point, and then we get

$$w_N^{(2)}(\mathbf{r}_{12}) = -\frac{1}{\beta}\ln\left[\frac{N(N-1)}{N^2}\frac{V^2}{Z(N,V,T)}\right] - \frac{1}{\beta}\ln\int \exp\left[-\beta\mathcal{V}(\mathbf{r}_{12},\cdots,\mathbf{r}_{1N})\right] d\mathbf{r}_{13}\cdots d\mathbf{r}_{1N} \tag{7.31}$$

Taking the gradient with respect to $\mathbf{r}_{12}$ yields

$$\nabla_{\mathbf{r}_{12}} w_N^{(2)} = -\frac{1}{\beta}(-\beta)\times$$

$$\frac{\int\left[\nabla_{\mathbf{r}_{12}}\mathcal{V}(\mathbf{r}_{12},\cdots,\mathbf{r}_{1N})\right]\exp[-\beta\mathcal{V}(\mathbf{r}_{12},\cdots,\mathbf{r}_{1N})]d\mathbf{r}_{13}\cdots d\mathbf{r}_{1N}}{\int \exp[-\beta\mathcal{V}(\mathbf{r}_{12},\cdots,\mathbf{r}_{1N})]d\mathbf{r}_{13}\cdots d\mathbf{r}_{1N}}$$

Schematically, we can see that for a system having pairwise additive forces, $\nabla_{\mathbf{r}_{12}}\mathcal{V}(\mathbf{r}_{12},\cdots,\mathbf{r}_{1N}) = \nabla_{\mathbf{r}_{12}}\mathcal{V}(\mathbf{r}_{12})$ is just the force acting on atom 1 due to the influence of atom 2. We will call this force $\mathbf{F}_{12}$ Given this definition,

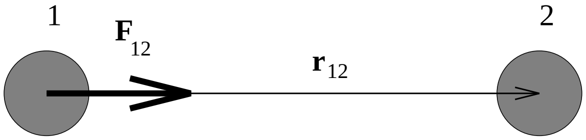

Figure 7.11: Definition of $\mathbf{F}_{12}$

we have

$$\nabla_{\mathbf{r}_{12}} w_N^{(2)}(\mathbf{r}_{12}) = \frac{\int \mathbf{F}_{12}\exp[-\beta\mathcal{V}(\mathbf{r}_{12},\cdots,\mathbf{r}_{1N})]d\mathbf{r}_{13}\cdots d\mathbf{r}_{1N}}{\int \exp[-\beta\mathcal{V}(\mathbf{r}_{12},\cdots,\mathbf{r}_{1N})]d\mathbf{r}_{13}\cdots d\mathbf{r}_{1N}} \tag{7.32}$$

We now clearly see from eqn 7.32 that $w_N^{(2)} \equiv -k_BT\ln g_N^{(2)}(\mathbf{r}_{12})$. $w_N^{(2)}$ can be viewed as a potential that generates the force of interaction between two molecules at a fixed position $\mathbf{r}_{12}$ relative to one another in the fluid, *averaged* over all configurations of the remaining $(N-2)$ molecules. Hence the name *potential of mean force* for $w_N^{(2)}(\mathbf{r}_{12})$.

What is the behavior of $w_N^{(2)}(\mathbf{r}_{12})$? Consider the simple case of a hard sphere fluid. The pair potential of a hard sphere fluid looks like that shown in Figure 7.12. $g(r)$ and $w_N^{(2)}(r)$ are shown schematically in Figure 7.13. It is remarkable that $w_n^{(2)}(\mathbf{r}_{12})$ can be *attractive* over some separation ranges even for a pair potential that is purely repulsive! Why is this? $w_N^{(2)}$ is a free energy, as opposed to an energy. The "pounding" of the rest of the spheres around the pair can create a net effective attraction (see Figure 7.14).

7.6 Getting Thermodynamics From $g(r)$

We have seen that the thermodynamics of a fluid can be obtained from a distribution function and an expression for the potential energy. If we can assume pairwise additivity of potentials, $g(r)$ is the relevant distribution function. If we would like to develop predictive capabilities in our statistical mechanical theories, we need to find a way of getting at $g(r)$. Clearly, *we need a theory for* $g(r)$.

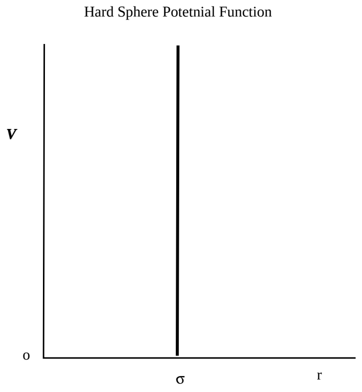

Figure 7.12: Pair potential for hard spheres

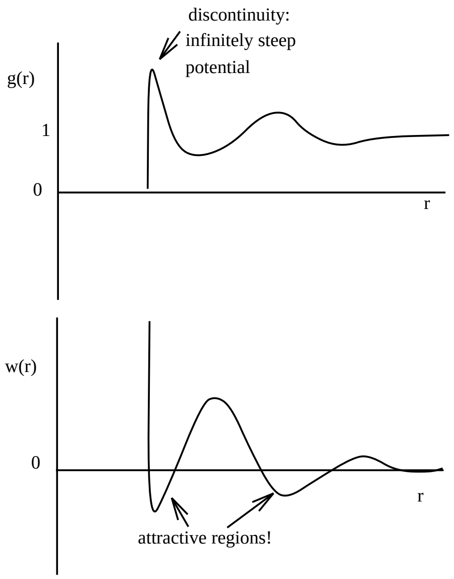

Figure 7.13: Representative plots of $g(r)$ and $w_N^{(2)}(r)$ for a hard sphere fluid

One way to estimate $g(r)$ focuses attention on the potential of mean force, $w(r)$. We separate $w(r)$ into two parts, namely

$$w(r) = \mathcal{V}(r) + \Delta w(r) \tag{7.33}$$

The pair potential, $\mathcal{V}(r)$, describes the reversible work to move the particles in vacuum. Thus, $\Delta w(r)$ is the contribution to $w(r)$ due to the surrounding particles in the system. That is, $\Delta w(r)$ is the change in Helmholtz free energy of the "solvent" due to moving particles 1 and 2 from $|\mathbf{r}_1 - \mathbf{r}_2| = \infty$ to $|\mathbf{r}_1 - \mathbf{r}_2| = r$.

We can think of this in another way. As the density of a fluid becomes small, the interaction between molecules fixed at a distance r apart is not affected by the other $(N-2)$ particles. Thus, the potential of mean force must be equivalent to the pair potential in this limit. That is, in the low density limit

$$\lim_{\rho \to 0} \Delta w(r) = 0 \tag{7.34}$$

As a result

$$g(r) = e^{-\beta \mathcal{V}(r)}[1 + \mathcal{O}(\rho)] \tag{7.35}$$

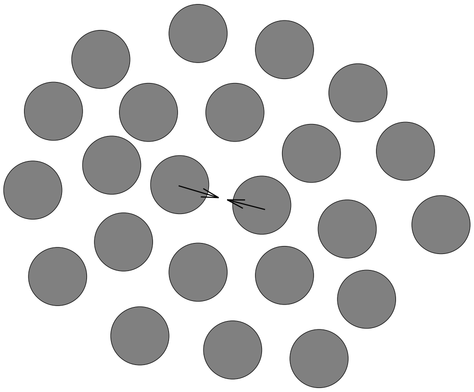

Figure 7.14: Physical reason why the potential of mean force can exhibit "attractive" regions even for a repulsive potential. Neighboring molecules "pound" the pair, forcing them together

For higher densities, we must handle the deviations of $\Delta w(r)$ from zero. To do this, we will estimate $\Delta w(r)$ in terms of $\rho g(r)$ and $\mathcal{V}(r)$. Such an approach yields integral equations for $g(r)$ that are essentially mean field theories! Before tackling this subject, let's examine the low density limit.

7.6.1 Low Density Limit of the Pair Distribution Function

We will begin by writing the second virial coefficient in terms of a pair potential. To do this, we start with the energy equation we derived earlier (eqn 7.25). Writing it in a slightly different form we get

$$U_{ex}/N = (\rho/2)\int g(r)\mathcal{V}(r)d\mathbf{r} = (\rho/2)\int e^{-\beta\mathcal{V}(r)}\mathcal{V}(r)[1+\mathcal{O}(\rho)] \tag{7.36}$$

where we have used the low density limit for $g(r)$, and again U_{ex} is defined as $U - U^{ig}$. Notice that

$$U_{ex}/N = \frac{\partial(\beta A_{ex}/N)}{\partial\beta} \tag{7.37}$$

where A_{ex} is the excess Helmholtz free energy relative to an ideal gas. That is,

$$-\beta A_{ex} = \ln(Q/Q^{ig})$$

Using this, we integrate our expression with respect to β to get

$$-\beta A_{ex}/N = (\rho/2)\int[\exp\{-\beta\mathcal{V}(r)\}-1]+\mathcal{O}(\rho)d\mathbf{r} \tag{7.38}$$

From this expression for the free energy, we can obtain the pressure P via the identity

$$\rho^2\frac{\partial(\beta A_{ex}/N)}{\partial\rho} = \beta P - \rho \tag{7.39}$$

Carrying out the differentiation yields

$$\beta P = \rho + \rho^2 B_2(T) + \mathcal{O}(\rho^3) \tag{7.40}$$

where

$$B_2(T) = -\frac{1}{2}\int[\exp\{-\beta\mathcal{V}(r)\}-1]d\mathbf{r}$$

$B_2(T)$ is called the *second virial coefficient*. Eqn 7.40 should look familiar; it is the first three terms of the virial equation of state. Remarkably, we see that $B_2(T)$ can be determined from knowledge of the pair potential energy. For a homogeneous and isotropic system, we can use scalars for the separation of particles 1 and 2. The result is

$$B_2(T) = -2\pi \int_0^{\infty} [\exp\{-\beta \mathcal{V}(r)\} - 1] r^2 dr \tag{7.41}$$

We can get the same result by starting directly from the pressure equation. The pressure equation, eqn 7.27, was shown to be

$$P = \rho k_B T - \frac{2\pi \rho^2}{3} \int_0^{\infty} \frac{d\mathcal{V}}{dr} g(r) r^3 dr$$

Inserting the low density form of $g(r)$ into this equation yields

$$\frac{\beta P}{\rho} \approx 1 - \frac{2\pi\beta}{3} \rho \int_0^{\infty} \exp[-\beta \mathcal{V}_{pair}(r)] r^3 \frac{\partial \mathcal{V}}{dr} dr \tag{7.42}$$

One can then show that

$$\frac{\beta P}{\rho} = 1 - 2\pi\rho \int_0^{\infty} [\exp\{-\beta \mathcal{V}(r)\} - 1] r^2 dr \tag{7.43}$$

or

$$\frac{\beta P}{\rho} = 1 + B_2(T)\rho \tag{7.44}$$

where

$$B_2(T) = -2\pi \int_0^{\infty} [\exp\{-\beta \mathcal{V}(r)\} - 1] r^2 dr \tag{7.45}$$

We have truncated the virial expansion, eqn 7.44, at the second term. Eqn 7.45 is the same result we obtained earlier.

The equation for the second virial coefficient is often written as

$$B_2(T) = -\frac{1}{2} \int f(\mathbf{r}) d\mathbf{r}$$

where

$$f(r) = \exp[-\beta \mathcal{V}(r)] - 1$$

is the *Mayer f–function*. This function decays rapidly to zero with increasing r for short–ranged potentials. You can see this if you plot $f(r)$ versus reduced temperature, $T^* = k_B T/\epsilon$.

Second virial coefficients can be measured experimentally by noting the deviations of dilute gases from ideal behavior. Such measurements then yield a great deal of information on the nature of intermolecular forces. For example, let's consider a Lennard–Jones pairwise potential. Introducing a reduced length, $r^* = r/\sigma$, the second virial coefficient for a Lennard–Jones fluid is

$$B_2(T^*) = -2\pi\sigma^3 \int_0^{\infty} \left(\exp[-\frac{4}{T^*}(r^{*-12} - r^{*-6})] - 1 \right) r^{*2} dr^* \tag{7.46}$$

Eq 7.46 shows that the dimensionless quantity $B_2^*(T^*) = B_2(T^*)/\sigma^3$ is a *universal function of* T^*; it is independent of the choice of ϵ or σ. This is an example of the *law of corresponding states*. We see that the integrand in eqn 7.46 is negative for $r^* < 1$ and positive for $r^* > 1$. When $T^* \ll 1$, the attractive part of the potential dominates the integrand, with a consequent lowering of the pressure below the ideal gas result. When $T^* \gg 1$, the repulsive part of the integrand is dominant, which raises the pressure above the ideal gas result. It follows that $B_2(T^*)$ is *negative* when the reduced temperature is low, and positive when it is high. The temperature at which $B_2(T)$ passes through zero is called the Boyle temperature.

7.6.2 Integral Equation Approach – BGY Equation

Recall that the pair correlation function, $g(r)$, was written as

$$g(r) = \frac{N!}{\rho^2(N-2)!} \frac{\int \exp[-\beta\mathcal{V}] d\mathbf{r}_3 \cdots d\mathbf{r}_N}{Z(N,V,T)}$$

We cannot solve the integral in this equation analytically, so we must make an approximation or evaluate it numerically. By assuming pairwise additivity, expanding $\mathcal{V}$, and differentiating the last equation with respect to $\mathbf{r}_1$, we can obtain the following expression

$$k_B T \frac{\partial g_{12}}{\partial \mathbf{r}_1} + \frac{\partial \mathcal{V}_{12}}{\partial \mathbf{r}_1} g_{12} + \rho \int \frac{\partial \mathcal{V}_{13}}{\partial \mathbf{r}_1} g^{(3)} d\mathbf{r}_3 = 0 \tag{7.47}$$

The double subscript notation is used to identify interacting particles. Thus, $\mathcal{V}_{12}$ represents the pair potential between particles 1 and 2, and g_{12} is the pair correlation function based on $\mathcal{V}_{12}$. Notice that eqn 7.47 is *recursive*, since it relates the pair correlation function, $g^{(2)}$ to the triplet correlation function, $g^{(3)}$.

Recall that we derived expressions for the general correlation function

$$g^{(n)} = \rho^{(n)}/\rho^3$$

where ρ^3 is the triplet joint probability density function. In general, we can write the recursion formula as

$$k_B T \frac{\partial g^{(n)}}{\partial \mathbf{r}_1} + \sum_{j=2}^{n} \frac{\partial \mathcal{V}_{1j}}{\partial \mathbf{r}_1} g^{(n)} + \rho \int \frac{\partial \mathcal{V}_{1,n+1}}{\partial \mathbf{r}_1} g^{(n+1)} d\mathbf{r}_{n+1} = 0 \tag{7.48}$$

Clearly from eqn 7.48, we can see that lower order correlation functions are given in terms of an integral over the next higher order correlation function. Carried to the limit, we would get $N-1$ such coupled equations for an N–component system. That is, we would have one equation for $g^{(2)}, g^{(3)}, \cdots g^{(N)}$. These recursive formulas are exact for pairwise additive systems, but cannot be solved because we can't calculate the higher order terms.

To solve, we need some way of relating $g^{(n)}$ and $g^{(n+1)}$. Such a relation is called a *closure* relation. Given a closure relation at some level, we could then solve all of the equations for $g^{(n)}$ below the closure level. The simplest closure approximation was proposed by Kirkwood in the 1930s.

$$g^{(3)}_{1,2,3} = g^{(2)}_{12} \times g^{(2)}_{13} \times g^{(2)}_{23} \tag{7.49}$$

The Kirkwood closure relation can be seen to be the product of independent pair–wise "probabilities". That is, if 1,2, and 3 were completely independent of one another, then $g^{(3)}_{123} = g^{(1)}_1 \times g^{(1)}_2 \times g^{(1)}_3$, (i.e. the product of separate "probabilities"). The closure assumed here is that the *pairs* are essentially independent entities. The Kirkwood closure is also equivalent to the assumption that the potential of mean force for a triplet of molecules is pairwise additive. That is,

$$w^{(3)}_{123} = w^{(2)}_{12} + w^{(2)}_{13} + w^{(2)}_{23}$$

When the Kirkwood closure relation is used in eqn 7.47, the result is

$$k_B T \frac{\partial g^{(2)}_{12}}{\partial \mathbf{r}_1} + \frac{\partial \mathcal{V}_{12}}{\partial \mathbf{r}_1} g^{(2)}_{12} + \rho \int \frac{\partial \mathcal{V}_{13}}{\partial \mathbf{r}_1} g^{(2)}_{12} g^{(2)}_{23} g^{(2)}_{13} d\mathbf{r}_3 = 0 \tag{7.50}$$

Eqn 7.50 is called the Born, Green, Yvon (BGY) equation. It is *closed* in that it involves only pair correlation functions and a pair potential. If we have a model for $\mathcal{V}_{ij}$, the pair correlation functions can be solved for, using similar equations for $g^{(2)}_{23}$ and $g^{(2)}_{13}$. Such solutions are done numerically, but they require far less computational power to solve than does the direct evaluation of $Z(N,V,T)$. However, the Kirkwood closure relation is not very exact, and the calculated properties at high densities can be off significantly. Since the function to be obtained in eqn 7.50 is under an integral sign, an equation such as this one is called an *integral equation.*

7.6.3 Another Approach – The Direct Correlation Function

In the late 1950s, a new class of integral equations was developed through use of the *direct* correlation function. To see how these work, we introduce another correlation function

$$h(\mathbf{r}_1, \mathbf{r}_2) = g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - 1 \tag{7.51}$$

For a homogeneous, isotropic fluid, $h(r_{12}) = g(r_{12}) - 1$. $h(r_{12})$ is a measure of the total influence of molecule 1 on molecule 2 at a distance r_{12} (i.e. the *total correlation* between 1 and 2.

In 1914, Ornstein and Zernike proposed a division of $h(r_{12})$ into two parts, a direct part and an indirect part. The direct part is given by a function $c(r_{12})$, and is called the *direct correlation function.* The indirect part is the influence propagated directly from molecule 1 to a third molecule, 3, which in turn exerts an influence on 2, (directly or indirectly) through other particles. This effect is weighted by the density and averaged over all positions of molecules 3. Pictorially, we can think of it as is shown in Figure 7.15. The idea is that 1 is correlated with 2 through a *direct* correlation plus 1 is directly correlated to 3, which is correlated to 2 directly or indirectly through other particles.

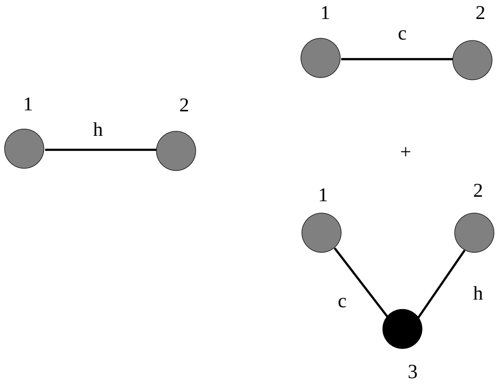

Figure 7.15: Direct and total correlation function

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13}) h(r_{32}) d\mathbf{r}_3 \tag{7.52}$$

Eqn 7.52 is known as the Ornstein–Zernike (OZ) equation. In essence, it is a definition of the direct correlation function, $c(\mathbf{r})$ in terms of the total correlation function, $h(\mathbf{r})$. Just as was done previously, recursive use of the OZ equation leads to

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13}) c(r_{32}) d\mathbf{r}_3 +$$
$$\rho^2 \int \int c(r_{13}) c(r_{34}) c(r_{42}) d\mathbf{r}_3 d\mathbf{r}_4 + \cdots$$

Pictorially, we represent this as in Figure 7.16.

At this point, you might be asking "What is the value of introducing $c(r)$?" It turns out that $c(r)$ has the same range as a pair potential. That is, it decays to zero fairly rapidly, but exhibits non–zero behavior from zero to distances commensurate with the potential range. *$c(r)$ is much shorter–ranged than $h(r)$.* For a Lennard–Jones liquid, Figure 7.17 demonstrates schematically the behavior. We see that the undulations in $h(r)$ are due to *indirect* correlations.

The next question we need to address is: What about molecular liquids? That is, what if we don't just have spheres but structured molecules? In this case, both intramolecular and intermolecular correlations between sites must be considered. An extension of the OZ equation to molecular fluids forms the basis of the Reference Interaction Site Model (RISM) of Chandler and Andersen (1972).

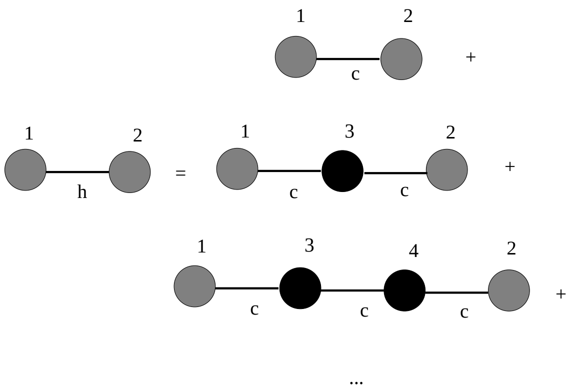

Figure 7.16: Pictorial representation of the OZ equation

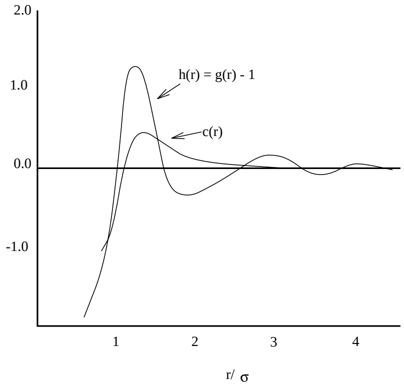

Figure 7.17: $c(r)$ and $h(r)$ for a Lennard–Jones fluid. The undulations in $h(r)$ are due to indirect correlations

7.6.4 Solving the OZ Equation – The Percus–Yevick and Hyper–netted Chain Approximations

The Ornstein–Zernike equation is an integral equation in two unknown functions, $h(r)$ and $c(r)$

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13})h(r_{32})d\mathbf{r}_3$$

If we can come up with a smart way of relating $c(r)$ and $h(r)$, we can convert the OZ equation into an integral equation in one unknown function. By solving that equation, we can obtain the structure of the fluid (i.e. get $h(r)$ and thus $g(r)$) at a given ρ and T. From this, we can get the fluid's thermodynamic properties. Such an additional equation relating $h(r)$ and $c(r)$ provides *closure* to the OZ equation. Together, the closure relation and the OZ equation constitute an integral equation theory for the fluid structure.

Before discussing two of the most useful closure relations, the Percus–Yevick (PY) and hyper–netted chain (HNC) equations, we need to define an additional correlation function. We define the function $y(r)$ as

$$y(r_{ij}) \equiv g(r_{ij})e^{\beta \mathcal{V}_{ij}}$$

We will say more about the utility of $y(r)$ in a minute.

The PY and HNC equations were originally derived using different methods than those used here. The PY equation was originally derived using field theoretic techniques. The HNC equation was derived using graphical techniques (see Rowley for a brief introduction), and by ignoring certain terms. The term "hyper–netted" chain refers to the graphs retained in the final expression. The PY equation can also be obtained graphically; both methods are involved and will not be discussed here. In the 1960s, the PY and HNC equations were derived using the theory of functionals. [2] Functional calculus can also be used to derive most other integral equations. [3] Rather than use these involved techniques, we will derive the PY equation using physical arguments, and just state the HNC equation. The approach follows closely that of McQuarrie. [4]

The direct correlation function was introduced to represent the direct correlation between 2 particles in a system containing $(N-2)$ other particles. It is reasonable to represent the direct correlation function by a difference

$$c(r) = g_{total}(r) - g_{indirect}(r)$$

where $g_{total}(r)$ is just the radial distribution function itself. That is

$$g_{total}(r) = \exp[-\beta w(r)]$$

where $w(r)$ is the potential of mean force.

$g_{indirect}(r)$ is therefore the radial distribution function *without* the direct interaction $\mathcal{V}_{pair}(r)$ included.

$$g_{indirect}(r) = \exp[-\beta(w(r) - \mathcal{V})]$$

Thus, we make the approximation that

$$c(r) \approx \exp[-\beta w(r)] - \exp[-\beta(w(r) - \mathcal{V})]$$

or equivalently

$$c(r) \approx g(r) - \exp[\beta\mathcal{V}(r)]g(r) \tag{7.53}$$

This is the Percus–Yevick closure approximation.

Using our definition of $y(r) = \exp[\beta\mathcal{V}(r)]g(r)$ we can write the PY closure more simply as

$$c(r) = [1 - \exp(\beta\mathcal{V}(r))]g(r)$$

$$= [1 - \exp(\beta\mathcal{V}(r))][h(r) + 1]$$

$$= [\exp(-\beta\mathcal{V}(r)) - 1]y(r)$$

Recalling that the Mayer–f function was defined as

$$f(r) = \exp(-\beta\mathcal{V}(r)) - 1$$

we finally can write

$$c(r) = f(r)y(r) \tag{7.54}$$

Substituting this into the OZ equation we obtain the Percus–Yevick equation:

$$y(r_{12}) = 1 + \rho \int f(r_{12})y(r_{13})h(r_{23})d\mathbf{r}_3 \tag{7.55}$$

Eqn 7.55 only involves $g(r)$ and $\mathcal{V}(r)$. It is a nonlinear, integro–differential equation that can be solved, although with some difficulty, numerically.[5] It can be solved analytically for the hard–sphere potential.

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[2] J. K. Percus, *Phys. Rev. Lett.* 8, 462, (1962)

[3] See, l. Verlet, *Physica*, 30, 95, (1964)

[4] McQuarrie, D. A. *Statistical Mechanics*, (1973)

[5] See, Gillian, M. J. *Mol. Phys.*, 38, 1781, (1979)

7.6.5 The PY Solution For Hard Spheres

Hard spheres are a favorite system to examine, because results can be obtained analytically. Interestingly, many physical systems exhibit behavior that can be explained by analyzing hard sphere behavior, so we will briefly discuss the hard sphere fluid.

There is only one potential parameter to describe a hard sphere fluid, namely d, the hard sphere diameter. The structure of the fluid is determined entirely by the density, ρ, or equivalently by the *packing fraction*, defined as the ratio of the volume of molecules to the volume of the system:

$$\eta = \rho \frac{\pi}{6} d^3$$

Question: What is the upper limit on the packing fraction? Right! An FCC crystal with all molecules in contact:

$$\eta_{max} = \frac{\pi\sqrt{2}}{6} = \frac{\pi}{3\sqrt{2}} = 0.74$$

A hard sphere system exhibits a fluid–solid phase transition (crystallizes) around a packing fraction

$$\eta_{f-s} = 0.49;\ \rho d^3 = 0.95$$

There is no gas–liquid phase transition. Can you see why?

Now, let's use the PY equation to get the structure, and hence thermodynamics, of our hard sphere system. Our discussion follows that of Hansen and McDonald.[6] Recall that the PY closure relation is

$$c(r) = [\exp(-\beta\mathcal{V}_{pair}(r)) - 1]y(r)$$

Thus for a HS system,

$$c(r) = -y(r);\ r < d$$

$$c(r) = 0;\ r > d$$

Remembering our definition of $y(r)$,

$$y(r) = g(r)\exp[\beta\mathcal{V}_{pair}(r)]$$

$$g(r) = y(r)\exp[-\beta\mathcal{V}_{pair}(r)]$$

we see that

$$h(r) = -1;\ r < d$$

$$h(r) = y(r) - 1;\ r > d$$

So let's look at the OZ equation

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13})h(r_{32})d\mathbf{r}_3 \tag{7.56}$$

Applying this to the case when $r_{12} > d$, we can get the combinations for particles 1, 2, and 3 shown in Figure 7.18. Substituting c and h in terms of y, we get the following integrals

$$y(r_{12}) = 0 + \rho \int_A [-y(r_{13})](-1)d\mathbf{r}_3 +$$

$$\rho \int_C [-y(r_{13})][y(r_{32}) - 1]d\mathbf{r}_3 + 0 + 0$$

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[6] J. P. Hansen, I. R. McDonald, "Theory of Simple Liquids", Academics, 1986

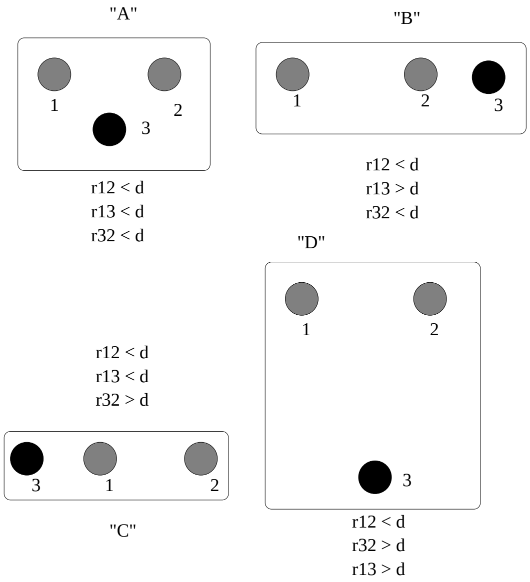

Figure 7.18: Different combinations available for hard spheres 1, 2, and 3

The last two zero terms arise from integrating $c(r_{13})$ when $r_{13} > d$.

Simplifying we get

$$y(r_{12}) - 1 = \rho \int_A y(r_{13}) d\mathbf{r}_3 +$$

$$\rho \int_C y(r_{13}) d\mathbf{r}_3 - \rho \int_C y(r_{13}) y(r_{32}) d\mathbf{r}_3$$

$$= \rho \int_{r_{13}<d} y(r_{13}) d\mathbf{r}_3 - \rho \int_C y(r_{13}) y(r_{32}) d\mathbf{r}_3$$

If we then define $\mathbf{r}_{12} = \mathbf{r}$, $\mathbf{r}_{13} = \mathbf{r}'$, and $\mathbf{r}_{32} = \mathbf{r} - \mathbf{r}'$, the OZ equation can be written

$$y(r) = 1 + \rho \int_{r'<d} y(r') d\mathbf{r}' -$$

$$\rho \int_{r'<d; |\mathbf{r}-\mathbf{r}'|>d} y(r') y(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' \tag{7.57}$$

Eqn 7.57 is an integral equation in terms of the function $y(r)$. It has been solved with Laplace transform methods.[7] The result is

$$c(r) = -y(r) = -\lambda_1 - 6\eta\lambda_2 \left(\frac{r}{d}\right) - \frac{1}{2}\eta\lambda_1 \left(\frac{r}{d}\right)^3;\ r < d$$

$$c(r) = 0;\ r > d$$

where $\lambda_1 = \frac{(1+2\eta)^2}{(1-\eta)^4}$, $\lambda_2 = -\frac{(1+\frac{1}{2}\eta)^2}{(1-\eta)^4}$, $\eta = \frac{\pi}{6}\rho d^3$, the packing fraction.

Now, how do we get the thermodynamics of our system from this? There are two ways.

1. Start with the pressure equation. You can easily show that for hard spheres, the pressure equation

$$P = \rho k_B T - \frac{2\pi\rho^2}{3} \int_0^\infty \frac{d\mathcal{V}}{dr} g(r) r^3 dr$$

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[7] Thiele, E. *J. Chem. Phys.*, 39, 474, 1963

can be written as

$$\frac{\beta P^{HS}}{\rho} = 1 + \frac{2}{3}\pi\rho d^3 \lim_{r \to d^+} g_{HS}(r) \equiv 1 + \frac{2}{3}\pi\rho d^3 g_{HS}(d^+)$$

where $g_{HS}(d^+)$ is the pair distribution function at contact.

Using the PY solution

$$g(d^+) = y(d) = \lambda_1 + 6\eta\lambda_2 + \frac{1}{2}\eta\lambda_1 = \frac{1 + \frac{1}{2}\eta}{(1-\eta)^2}$$

Hence we may write

$$\frac{\beta P^v}{\rho} = 1 + 4\eta g(d^+) = 1 + 4\eta\frac{(1 + \frac{1}{2}\eta)}{(1-\eta)^2}$$

where the superscript v refers to the pressure obtained from the *virial* equation, another name for the pressure equation.

Finally we may write

$$\frac{\beta^v}{\rho} = \frac{1 + 2\eta + 3\eta^2}{(1-\eta)^2} \tag{7.58}$$

We see that indeed the thermodynamics are described solely in terms of the packing fraction.

2. Alternatively, one can start with the compressibility equation, eqn 7.28, and get an expression for the isothermal compressibility. By integrating κ_T from the ideal gas (zero density) state to ρ, one can get the pressure. The result is

$$\frac{\beta P^c}{\rho} = \frac{1 + \eta + \eta^2}{(1-\eta)^3} \tag{7.59}$$

Notice that P^c and P^v are not equivalent! The differences increase with increasing density. Eqns 7.58 and 7.59 give the same values for the second and third virial coefficients, but give incorrect and different values for the higher virial coefficients. Why? The only approximation invoked has been the PY closure relation; this closure relation has introduced some thermodynamic inconsistency into the problem, hence two values which are thermodynamically equivalent (P^c and P^v) are not equal. And so it goes with integral equations – the equations are exact but to solve them we must make approximations which make the results inexact. Even considering this flaw, integral equation theory is still a valuable tool for studying complex systems and has made important contributions.

By examining the virial expansion for hard spheres written in terms of the packing fraction, Carnahan and Starling[8], devised a simple and accurate equation of state for hard spheres. The virial expansion for hard spheres is

$$\frac{\beta P}{\rho} = 1 + \sum_{i=1}^{\infty} \mathcal{B}_i \eta^i \tag{7.60}$$

where

$$\mathcal{B}_i = \left(\frac{6}{\pi d^3}\right)^i B_{i+1}$$

B_i being the ith virial coefficient.

The first seven terms of the expansion are

$$\frac{\beta P}{\rho} = 1 + 4\eta + 10\eta^2 + 18.365\eta^3$$

$$+28.24\eta^4 + 39.5\eta^5 + 56.5\eta^6 + \cdots$$

Because they were good chemical engineers, Carnahan and Starling found a closed form that approximates the infinite series by noting the following:

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[8] N. F. Carnahan, K. E. Starling, *J. Chem. Phys.*, 51, 653, (1969)

- $\mathcal{B}_1$ and $\mathcal{B}_2$ are both integers.
- $\mathcal{B}_3$ is pretty close to 18.
- Suppose that $\mathcal{B}_i$ for all i is given by
$$\mathcal{B}_i = a_1 i^2 + a_2 i + a_3 \tag{7.61}$$
Using $\mathcal{B}_1 = 4$, $\mathcal{B}_2 = 10$ and $\mathcal{B}_3 = 18$, the solution to eqn 7.61 is $a_1 = 1$, $a_2 = 3$ and $a_3 = 0$.
- The formula then predicts $\mathcal{B}_4 = 28$, $\mathcal{B}_5 = 40$ and $\mathcal{B}_6 = 54$, which agrees well with the exact expression.
- The virial expression that results,
$$\frac{\beta P}{\rho} = 1 + \sum_{i=1}^{\infty}(i^2 + 3i)\eta^i$$
may be written as a linear combination of the first and second derivatives of the geometric series $\sum_{i=1}^{\infty} \eta^i$. It can therefore be summed *explicitly*. The result is known as the Carnahan Starling equation of state:
$$\frac{\beta P}{\rho} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} \tag{7.62}$$

"Exact" results for the equation of state of hard spheres have been obtained through computer simulations. Eqn 7.62 provides an excellent fit to these exact results over the entire fluid range. You will notice that it is essentially an average of the results obtained from the PY equation using the pressure and virial equations:

$$\frac{\beta P^{CS}}{\rho} = \frac{\beta}{\rho}(\frac{2}{3}P^c + \frac{1}{3}P^v)$$

.

The Carnahan Starling equation of state is widely used in perturbation theories, which unfortunately we won't have time to go into detail in this class. However, we already saw one perturbation theory: the van der Waals equation of state involved a perturbation theory using the ideal gas as a reference fluid. Most perturbation theories use the hard sphere fluid as the reference.

Chapter 8

Introduction to Molecular Simulation Techniques

We have seen both the power and problems associated with applying statistical mechanical theories to real problems. While the relations are elegant, intellectually pleasing, and fairly easy to solve, they are difficult to formulate in such a way that the solution is tractable. Moreover, the simplifying assumptions which must be made to solve the theoretical expressions often result in a loss of the essential physics of the problem. That is to say, despite the fact that we have a powerful, rigorous formalism for calculating macroscopic properties given a Hamiltonian, an analytical solution to this formalism is impossible for most material systems of practical interest.

An alternative approach is to attempt to solve the full statistical mechanics *numerically*, given a model of molecular geometry and energetics. Such simulations can provide, in principle, *exact* results (subject only to numerical error). In practice, simulations usually invoke approximations. However, these approximations are usually much less drastic than those required in solving analytical theories. There are two main problems in applying simulations to real–life problems.

1. Our knowledge of interaction potentials is limited. Quantum mechanics and empirical fitting to experiment are the ways to overcome this problem.

2. The techniques are extremely demanding of computer time. Fast workstations and supercomputers, coupled with smart algorithms, must be used.

Molecular simulations can be thought of as computer experiments that bridge the gap between theory and experiment. As seen in Figure 8.1, molecular simulations require as input a molecular model consisting of the system geometry and potentials, and a set of thermodynamic constraints that define an ensemble. Results include macroscopic properties (thermodynamics, transport, etc.) and microscopic structure and dynamics (what do the molecules do?). The connection between theory, simulation, and experiment is shown in Figure 8.2.

8.1 Construction of a Molecular Model

Before going into details, we need to discuss some preliminaries. Recall that we've already spent some time discussing molecular potential function or "forcefields". As a reminder, we often assume pairwise additivity, such that

$$\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n) = \sum_{i<j} \mathcal{V}_2^{eff}(\mathbf{r}_1, \mathbf{r}_j)$$

where $\mathcal{V}_2^{eff}$ is an effective two–body potential that attempts to include the effects of three–body and higher terms. We claim that molecules with no pronounced separation of charge can be represented as a set of sites, interacting

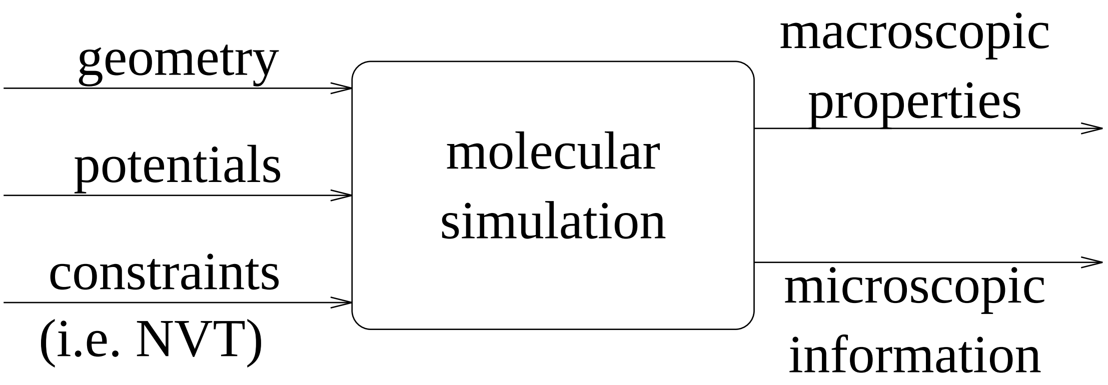

Figure 8.1: Input and output of molecular simulations

via a dispersion energy model (i.e. each site is a Lennard–Jones site). Consider the alkane chain shown Figure 8.3. Such an explicit representation treats each atom as an individual LJ site, and requires interaction parameters for all these interactions.

As an alternative, a simpler "united atom" representation is often used in which each CH_3 and CH_2 group of an alkane is treated as a single interaction site, as shown in Figure 8.4 The advantage of this simpler model is that fewer parameters are required than the model shown in Figure 8.3. This has computational advantages as we shall see, but may not allow as high an accuracy, particularly at high densities.

For molecular fluids, we must also account for bond potentials. Typically, bond length potentials are modeled as a harmonic

$$\mathcal{V}_b(\ell) = 1/2 k_b (\ell - \ell_0)^2 \tag{8.1}$$

where k_b is a force constant and ℓ_0 is the equilibrium bond length. It is usually satisfactory to make the bonds be infinitely stiff ($k_b \to \infty$) unless vibrational spectra are desired.

Bond angles are also typically treated as a harmonic

$$\mathcal{V}_\theta(\theta) = 1/2 k_\theta (\theta - \theta_0)^2 \tag{8.2}$$

where θ_0 is the equilibrium bond angle. It is a little riskier to let $k_\theta \to \infty$, since bond angle variation is thought to play a role in the dynamics of flexible molecules.

It is very important to model torsion (dihedral) angles properly, as these type of conformational motions are very important in determining the properties of a molecular liquid. Recall that we defined a dihedral angle according to Figure 8.5. The potential governing dihedral angle motion is frequently represented as an expansion in the dihedral angle. For example, Ryckaert and Bellemans give the following expression for alkanes[1]

$$\mathcal{V}_\phi = \sum_{i=2}^{N-2} \sum_{j=0}^{5} c_j \, (\cos \ \phi_i)^j \tag{8.3}$$

Such a potential function must capture the fact that *trans/gauche* inter-conversions can take place at room temperature. Schematically, a typical torsion potential looks like that shown in Figure 8.6.

Sometimes, coarser-grained models are used in molecular representations. For example, "freely jointed" chains which resemble pearl necklaces with individual beads connected with a "finite extensible, nonlinear elastic" or FENE potential are often used in polymer simulations. Simple "dumbbell" models can also be used. In these and other models, intermolecular potentials can be represented with Lennard-Jones or other types of potentials.

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[1] Ryckaert, J.P.; Bellemans, A. *Faraday Discuss. Chem. Soc.* **1978**, *66*, 95–106

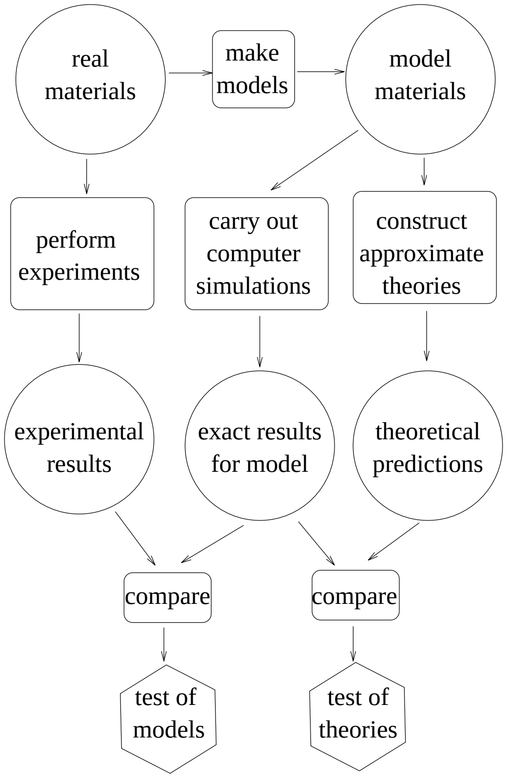

Figure 8.2: Connection between theory, experiment, and molecular simulation. All three approaches are useful in engineering design. (Figure after Allen and Tildesley)

There are various sources of Lennard–Jones parameters that may be used as an initial guess for constructing a model. For example, the Slater-Kirkwood formula (eqn 6.10) can be used with readily available material properties to obtain pure-component parameters. Lorentz–Berthelot combining rules can be used to get interactions between unlike species

$$\sigma_{ij} = 1/2(\sigma_{ii} + \sigma_{jj})$$

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}$$

Typically, potential parameters are refined by comparing results with whatever experimental data is available. For example, second virial coefficients, $B_2(T)$, heats of vaporization, solubility parameter, and critical points have all been used to help refine parameters.

Molecules that have an expressed separation of charge (i.e. polar molecules) are typically described in terms of a combination of LJ parameters and *partial charges*. These partial charges can be obtained in a number of ways

- experimentally measured dipole moments ($\mu = \sum q_i x_i$) or quadrupole moments ($Q = \sum q_i x_i^2$).
- electronic density distributions, available from ab initio quantum calculations

Partial charges interact via Coulomb forces

$$\mathcal{V}_{zz}(r_{ij}) = \frac{z_i z_j}{4\pi\epsilon_0 r_{ij}}$$

An example of a partial charge model is the so–called “TIPS” (transferable intermolecular potentials) model of water.[2] In the TIPS representation (see Figure 8.7), H_2O is represented as a single LJ atom (oxygen) and three

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[2] W. L. Jorgensen, *J. Chem. Phys.*, 77, 4156, (1982)

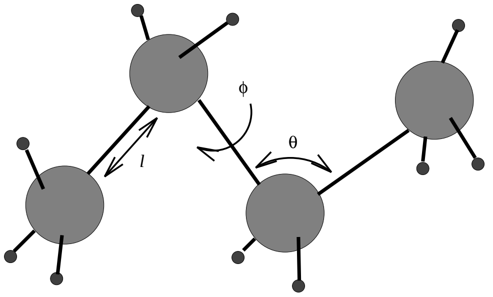

Figure 8.3: All–atom representation of butane. To parameterize the potential, we must include carbon and hydrogen interactions.

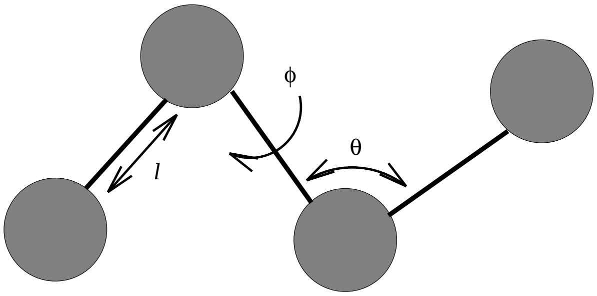

Figure 8.4: United atom representation of butane. This model requires fewer parameters than the one shown in fig 8.3, but is less accurate at high densities

partial charges. The model has a dipole moment of 2.25 D, while experimentally we know water has a dipole moment of 1.85 D. Most of these fixed charge models have dipole moments that are higher than the actual dipole moment because they don't account for the *polarizability* of the molecule. That is, the "charge" on each atomic center will change depending on the environment it is placed in. Thus the fixed dipole moment of the TIPS model is greater than 1.85D to account for polarizability. Newer models account for polarization in a more natural way, but at the expense of greater complexity. This is often the case. More accurate forcefields necessarily introduce added complexity. For example, the Matsuoka–Clementi–Yoshimine water model[3] contains 10 potential parameters!

The total potential energy is the sum of all the various contributions (i.e. $\mathcal{V}_b$, $\mathcal{V}_\theta$, $\mathcal{V}_\phi$, $\mathcal{V}_{pair}$, etc.) Note that we immediately have a problem: the pair potential requires a sum out to an infinite distance! What do we do? Because the LJ potential is short ranged, we can try to get around this problem by truncating the potential at a certain radius, r_c (see Figure 8.8). Typically, $r_c \approx 2.5\sigma$. This causes problems, in that the discontinuity in $\mathcal{V}$ at r_c will cause the total energy of the system to change as pairs of molecules cross r_c. In addition, this places a discontinuity in the force at r_c. There are ways of getting around this problem[4] by shifting the potential so as to avoid discontinuities.

What about the portion of the potential energy that was "cut off"? The contribution to $\mathcal{V}$ from the truncated "tails" of the pair potential function (the so–called "long range correction") is calculated by direct integration, using the energy equation

$$\begin{aligned}\mathcal{V}_{full} &= \mathcal{V}_c + \mathcal{V}_{lrc} \\ &= \mathcal{V}_c + 2\pi N\rho \int_{r_c}^{\infty} r^2 \mathcal{V}(r) g(r) dr\end{aligned}$$

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[3] *J. Chem. Phys.*, 64, 1351, (1976)

[4] Allen and Tildesley, *Computer Simulation of Liquids*, ch 5

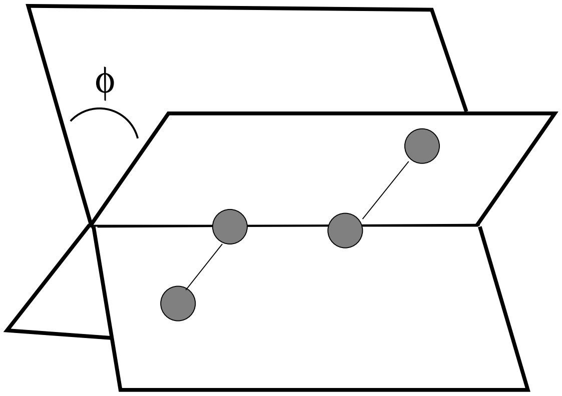

Figure 8.5: Schematic showing how the dihedral (torsion) angle of a chain is defined

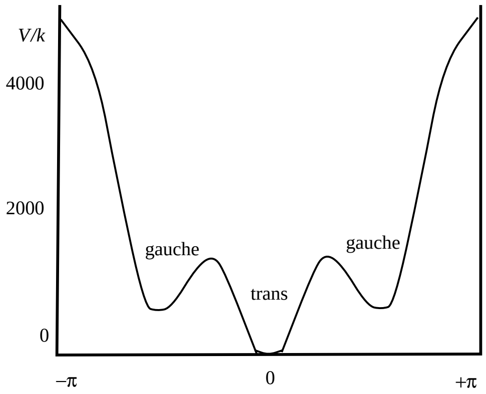

Figure 8.6: Schematic showing the energy distribution for various dihedral angle values. Notice that the *trans*/*gauche* barrier can be overcome at room temperature, although the all–*trans* conformation would be preferred

In isotropic media, we can carry out this integral by assuming in this region $g(r) \approx 1$. it is important to verify that $g(r) \approx 1$ at the cutoff distance. If not, things like the pressure will be incorrect.

Note that potential truncation is a *poor* approximation for long–range potentials, such as Coulombic interactions. Special techniques (Ewald summations) must be used in this case.

8.2 Model System Size and Periodic Boundary Conditions

Typically, a molecular simulation is carried out with anywhere from 10 to 100,000 molecules. Larger systems are generally prohibited due to memory requirements, and (more importantly) speed considerations. Force calculations go as $\mathcal{O}(N^2)$. There have been recent "million particle" simulations using massively parallel computers. For the applications we are interested in, however, there is no need to go to this big of a simulation.

However, because we are using a very small number of particles and trying to determine macroscopic properties, one must be *very careful* that the results are *system size–independent*. It turns out that for low–molecular weight liquids, simulation averages are only weakly dependent on system size for $N \geq 100$.

Unless the actual system being studied is very small (a droplet, microstructure, etc.) a simulation box with ca. 1000 molecules will have a disproportionate number (nearly half) of molecules at the "surface". This would completely skew the behavior of the system. To get around this problem, we employ a trick called *periodic boundary conditions*. The primary simulation box can be envisioned as being surrounded by images of itself; for a "cube",

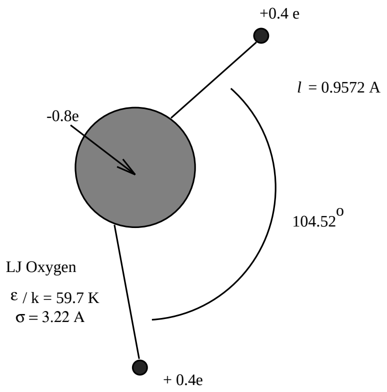

Figure 8.7: "TIPS" model for water (after Jorgensen)

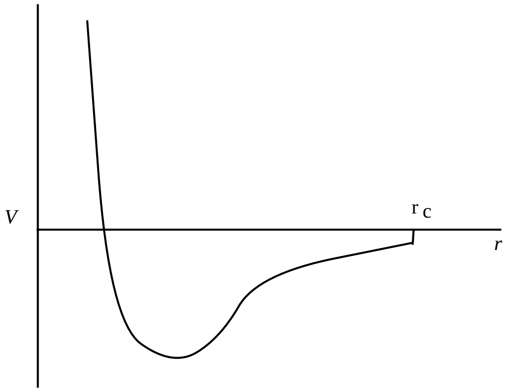

Figure 8.8: Typical potential function, showing the effect of a truncated potential

there would be 26 images around the central box. The central box is the "unit cell". Whenever, during the course of a simulation, a particle exits the box, an identical particle enters through an opposite face, as shown in Figure 8.9[5]. Periodic boundary conditions *cut off long wavelength fluctuations*. Density waves longer than the box length, L are not accounted for. What are the implications of this?

To see how we handle potential calculations using periodic boundary conditions, refer to Figure 8.10. Consider atoms 1 and 2 in the primary (central) box. In three dimensions, there are 27 images of atom 2 in the primary box and the images that can interact with atom 1. If $L/2 \geq r_c$, the potential cutoff radius, then *at most* one of the images of 2 can interact with 1. The image of 2 lying closest to 1 is called the *minimum image*. When $L/2 \geq r_c$, the simulation obeys the *minimum image convention*.

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[5] A good interactive demonstration of this has been developed by Prof. Hammes-Schiffer in the Chemistry department. See it at http://www.nd.edu/chem647/project6/project6.html.

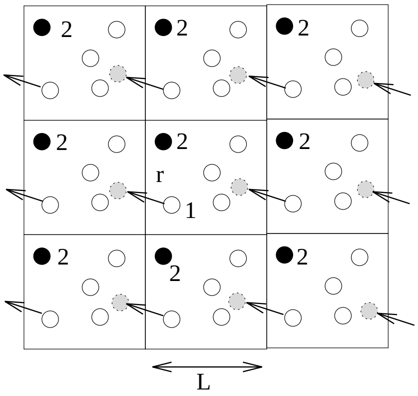

Figure 8.9: Periodic boundary conditions require that an atom leaving a cell be replaced with its image moving in through the opposite cell face

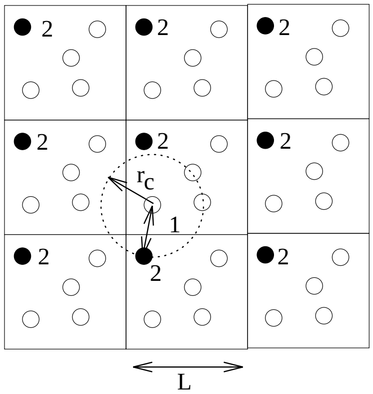

Figure 8.10: Minimum image convention used with periodic boundary conditions

Chapter 9

Monte Carlo Methods

9.1 Historical Background

Monte Carlo simulations are used by scientists in many fields. A number of excellent books have been written on the subject, and the interested student should consult these references.[1]

The name *Monte Carlo* was coined by Metropolis in 1947 to describe a class of numerical techniques developed by von Neuman, Ulam, and Metropolis at Los Alamos near the end of World War II. These techniques were used to simulate the diffusion of neutrons in fissionable material. The name arose because the methods employ random numbers in the calculations, and thus resemble games of chance. (Perhaps today the technique would be called "Las Vegas"...)

Long before this, statisticians used sampling methods to investigate problems. As an example, W. S. Gossett, known as "student", estimated the correlation coefficient in his 't" distribution with the help of a sampling experiment. Joel Hildebrand had his graduate students generate random samplings of spheres in a box to investigate liquid phase properties. The novel contribution of von Neumann and Ulam at Los Alamos was the realization that determinate, mathematical problems could be treated by finding a probabilistic analogue which is then solved by stochastic (i.e. random) sampling.

The sampling experiments involve the generation of random numbers, followed by simple operations. This procedure is ideally suited for computers, and the arrival of the MANIAC computer at Los Alamos enabled Metropolis and co–workers to develop the Metropolis Monte Carlo method in 1953. This method is the subject of this section. At about the same time, Alder and Wainright developed a molecular dynamics procedure, which will be discussed later.

Prior to the arrival of the computer, people attempted to perform such stochastic experiments physically. These techniques are "hit or miss" Monte Carlo. An entertaining example from history: G. Comte de Buffon, a French naturalist, discovered a theorem in mathematical probability in 1777. He found that if a needle of length ℓ is thrown randomly onto a set of equally spaced parallel lines, d apart ($d > \ell$), the probability that the needle will cross a line is $\frac{2\ell}{\pi d}$ (see Figure 9.1). Thus, a simple experiment could be done to estimate π, although no one tried it until 1901. In that year, an Italian mathematician named Lazzerini performed a stochastic experiment by spinning around and dropping a needle 3407 times. He estimated that $\pi = 3.1415929$. You could imagine how much easier this would be on a computer today. This is a remarkably good estimate of π. Do you think Lazzerini was honest or "very lucky"?

One could envision estimating π with another hit or miss experiment. Imagine placing a circular pan inside a square pan, such that the circular pan is inscribed in the square pan. Then, put the pan out in the rain. Of the total number of drops hitting the pans (we will call it N_{trials}), some fraction will land inside the circular pan (N_{hits}). (See Figure 9.2). Thus,

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[1] Allen and Tildesley, 'Computer Simulation of Liquids"; Binder, K "Application of the Monte Carlo Method in Statistical Physics"; Binder has written a number of other good books as well.

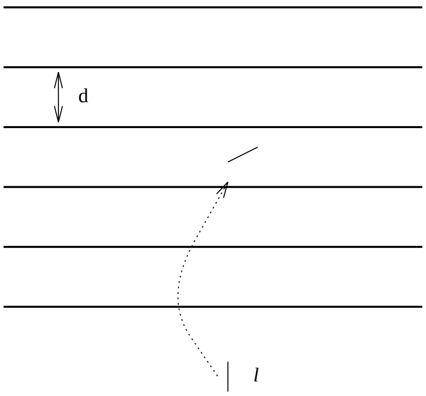

Figure 9.1: Schematic of Buffon's theorem and Lazzarini's experiment

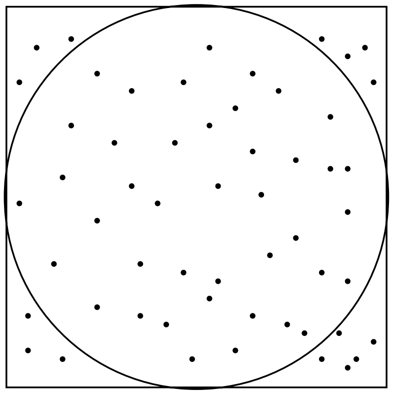

Figure 9.2: Schematic of another hit-or-miss Monte Carlo method for estimating π. The number of raindrops falling in the circular pan relative to the total number falling in the square and circular pans is directly related to π

$$\pi = 4\frac{N_{hits}}{N_{trials}}$$

Today, Monte Carlo simulations are perhaps the most powerful and commonly used technique for analyzing complex problems. In this chapter, we will give an introduction to the method and describe some of the uses.

9.2 Monte Carlo as an Integration Method

To introduce Monte Carlo techniques, let's first consider a way in which stochastic methods can be used to evaluate integrals. The so–called "sample mean method" is a better way of determining integrals from stochastic "experiments". The basic problem is that we wish to evaluate the following integral

$$I = \int_{x_1}^{x_2} f(x)dx \tag{9.1}$$

where $f(x)$ is some arbitrary function, as shown in Figure 9.3. We can re–write the integral as

$$I = \int_{x_1}^{x_2} \left(\frac{f(x)}{\rho(x)}\right) \rho(x)dx \tag{9.2}$$

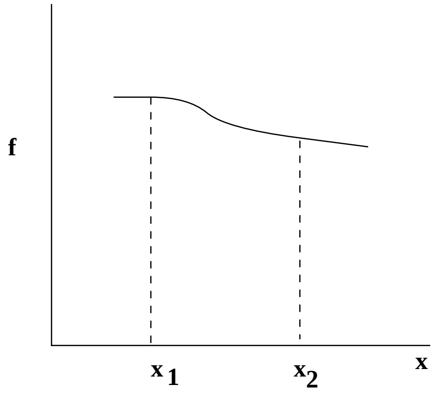

Figure 9.3: A generic 1–dimensional definite integral.

where $\rho(x)$ is an arbitrary probability density function. Then, we perform a number of trials, N_{trials} in which we choose a random number ξ from the distribution $\rho(x)$ in the range (x_1, x_2) and evaluate f at each step. Then,

$$I = \left\langle \frac{f(\xi)}{\rho(\xi)} \right\rangle_{\rho(x)}$$

where the brackets indicate that we have taken an average over the N_{trials} evaluations, and that we used $\rho(x)$ as our (normalized) distribution. Pictorially, this would look like Figure 9.4.

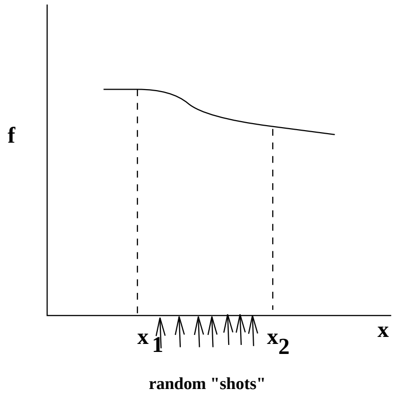

Figure 9.4: Way in which MC integration can be used to estimate an integral.

The simplest application would be to let $\rho(x)$ be a uniform distribution (Figure 9.5)

$$\rho(x) = \frac{1}{(x_2 - x_1)}, \; x_1 \leq x \leq x_2$$

Then, the integral could be estimated from

$$I \approx \frac{(x_2 - x_1)}{N_{trials}} \sum_{i=1}^{N_{trials}} f(\xi_i) \tag{9.3}$$

The justification for eqn 9.3 comes from the Mean Value theorem.

To actually do this, one would carry out the following steps.

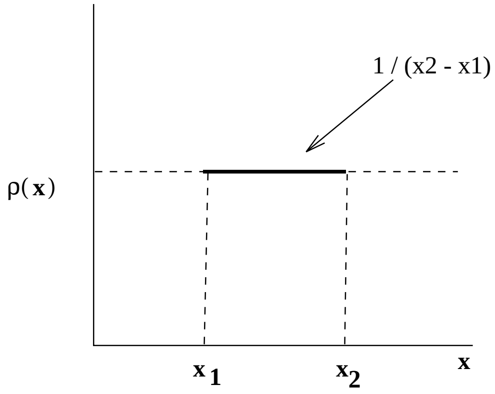

Figure 9.5: Uniform density distribution on the limits of the integral to be evaluated

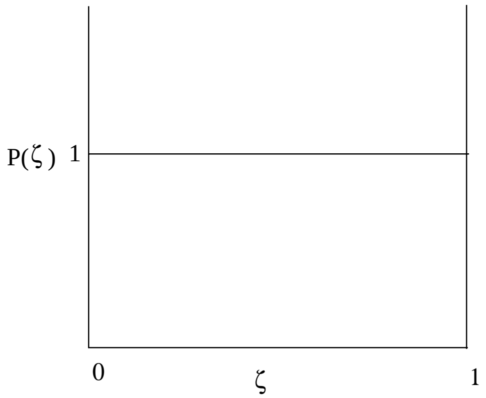

Figure 9.6: Distribution of the random number ζ

1. Generate a random number, ζ, uniformly on the range (0,1), as shown in Figure 9.6.
2. Get a random value in the range (x_1, x_2) by computing $\xi = x_1 + \zeta(x_2 - x_1)$.
3. Calculate $f(\xi)$.
4. Accumulate the sum $S = \sum_i f(\xi_i)$.
5. After N_{trials} such attempts, I is computed from eqn 9.3. Notice that our estimate of I gets better as N_{trials} increases.

This approach can be used to estimate π by considering the equation for a circle in the first quadrant

$$f(x) = (1 - x^2)^{-1/2}$$

with x between $x_1 = 0$ and $x_1 = 1$. If one uses the procedure outlined above, the estimate of π after 10^7 trials is 3.14169.

For simple functions (i.e. one– or two–dimensional) Monte Carlo integration cannot compete with straightforward methods such as Simpson's rule. For example, Simpson's rule obtains $\pi = 3.141593$ after only 10^4 function evaluations. However, for the *multidimensional integrals* encountered in statistical mechanical applications, the sample mean method (with suitable choice of $\rho(x)$) is far superior to standard techniques. Why is this? Consider the evaluation of the configurational integral for a system containing 10 particles, such as shown in Figure 9.7.

$$Z = \int d\mathbf{r}^N \exp[-\beta \mathcal{V}(\mathbf{r}^N)]$$

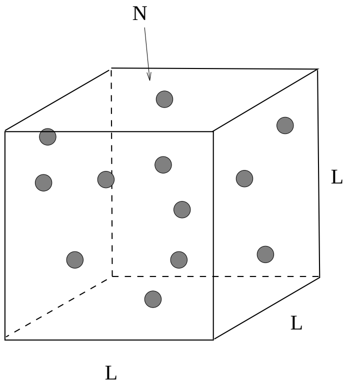

Figure 9.7: A single configuration of 10 particles in a box. This system has 30 configurational degrees of freedom.

Here we can think of

$$f(\mathbf{r}^N) \equiv f(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \exp[-\beta \mathcal{V}(\mathbf{r}^N)]$$

For N molecules in volume $V = L^3$ at temperature T, we have a $3N$–dimensional integral. For $N = \mathcal{O}(10)$, we estimate Z using MC integration as

$$Z \approx \frac{V^N}{N_{trials}} \sum_{i=1}^{N_{trials}} \exp[-\beta \mathcal{V}(\mathbf{r}_1^{(i)}, \cdots, \mathbf{r}_N^{(i)})] \tag{9.4}$$

where $(\mathbf{r}_1^{(i)}, \cdots, \mathbf{r}_N^{(i)})$ is a randomly selected point in the $3N$–dimensional configuration space. That is, it is N triplets of random numbers on $(0, L)$.

A Simpson technique would require evaluating $f(\mathbf{r}^N)$ at all nodes of a regular grid throughout the configuration space. If 10 points (nodes) per coordinate are used, this would entail 10^{3N} function evaluations, clearly an unreasonable number even for this small–dimensional system. With Monte Carlo integration, on the other hand, one can obtain a reasonable estimate for N_{trials} much less than this. Of course, our estimate gets better as N_{trials} gets larger, but we will converge fairly rapidly to the actual value.

For higher–dimensional systems, e.g. $N = \mathcal{O}(100)$, even standard Monte Carlo integration of the type described here becomes infeasible. To see why, consider performing a MC integration evaluation of eqn 9.4 for a hard sphere fluid. The procedure would go something like this:

1. Pick 300 random numbers on $(0, L)$. Taken in triplets, these numbers specify the coordinates of all 100 hard spheres.
2. Calculate the potential energy, and thus the Boltzmann factor, for this configuration. For hard spheres, the Boltzmann factor will only be 1 if *no two hard spheres overlap*. If two of our randomly chosen molecules overlap, the potential energy will be infinite and the Boltzmann factor for that trial will be zero.
3. As the density increases, the likelihood that we get overlap increases, until almost every random configuration we generate contributes nothing to the integral.

This problem is also seen if we try to get ensemble averages from MC integration. For example, if we try to estimate $\mathcal{A}$ from

$$< \mathcal{A} >_{NVT} = \frac{\int d\mathbf{r} \mathcal{A} \exp[-\beta \mathcal{V}]}{\int d\mathbf{r} \exp[-\beta \mathcal{V}]}$$
$$\approx \frac{\sum_{i=1}^{N_{trials}} \mathcal{A}_i \exp[-\beta \mathcal{V}_i]}{\sum_{i=1}^{N_{trials}} \exp[-\beta \mathcal{V}_i]}$$

by estimating the numerator and denominator separately using the uniform sample mean method, we still run into difficulties at high densities.

The obvious solution is to choose our random coordinates from a non–uniform distribution in hopes of increasing our odds of a successful function evaluation. This is referred to as “importance sampling”.

9.3 Importance Sampling

The basic idea here is that we choose random numbers from a density distribution $\rho(x)$ which allows the function evaluation to be concentrated in the region of space that makes the biggest contribution to the integral. This is most desirable for calculating ensemble averages. We have seen that thermodynamic properties can be obtained from ensemble averages of the form

$$< f >_{ens} = \frac{\int d\mathbf{r}^N f(\mathbf{r}^N) \rho^{ens}(\mathbf{r}^N)}{\int d\mathbf{r}^N \rho^{ens}(\mathbf{r}^N)} \tag{9.5}$$

For example, with $\rho^{ens}(\mathbf{r}^N) = \rho^{NVT}(\mathbf{r}^N) = \exp[-\beta \mathcal{V}(\mathbf{r}^N)]$, we showed that

- For $f = \mathcal{V}$, we get $< f >_{NVT} = U^{ex}$, the excess internal energy.
- For $f = \frac{1}{3} \sum_i \mathbf{r}_i \mathbf{F}_i^{int}$, we get $< f >_{NVT} = PV - Nk_BT$ (the virial theorem).
- For $f = \exp[-\beta \mathcal{V}_{test}]$, we get $< f >_{NVT} = \mu^{ex}$, the excess chemical potential via the Widom insertion method.

As mentioned, is we try to sample configurations at random, very few of our choices make a contribution to the integral. Instead, we should sample our configuration space *nonuniformly*, so that the more probable states (i.e. low energy conformations) are sampled more frequently than the less probable (i.e. high energy) states. It turns out that it is most advantageous to sample states so that the frequency of sampling a state if proportional to ρ^{ens} of that state. If we can sample states according to ρ^{ens}, then calculating the ensemble average $< f >$ amounts to taking a simple *arithmetic average* over the sampled microstates.

$$< f >_{ens} = \frac{1}{N_{trials}} \sum_{i=1}^{N_{trials}} f(i)$$

An ingenious algorithm for sampling a multidimensional space according to a nonuniform probability distribution, and for calculating averages with respect to that distribution, was introduced by Metropolis and co–workers.[2] To understand the method, we must digress and talk about Markov chains.

9.3.1 Markov Chains

A Markov chain is a sequence of trials (stochastic processes) that satisfies two conditions:

1. The outcome of each trial belongs to a finite set of outcomes, called the *state space*. We describe the state space by $\{\mathbf{\Gamma}_1, \mathbf{\Gamma}_2, \cdots, \mathbf{\Gamma}_m, \mathbf{\Gamma}_n, \cdots\}$.

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[2] Metropolis, N; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; and Teller, E., *J. Chem. Phys.*, 21, 1087-1092, (1953)

2. The outcome of each trial depends only on the outcome of the *immediately preceding trial*. That is, the memory of the system only goes one step back.

A central concept is the *transition probability* which links two states $\mathbf{\Gamma}_m$ and $\mathbf{\Gamma}_n$. We define Π_{mn} as the *probability that a trial produces state n, given that the previous trial resulted in state m.* Π_{mn} depends on the values of m and n, but is independent of *where* within the sequence the considered trial lies. That is, Π_{mn} is independent of "time" or the number of trials.

By collecting values of Π_{mn} for all possible m and n, we can form a *transition probability matrix*. This matrix contains all information on the "dynamics" governing the evolution of the Markov chain. The concepts are best illustrated by an example (after Allen and Tildesley).

Let us assume that the reliability of your computer follows a certain pattern.

- If it is up and running one day, there is a 60% chance that it will be up the next day.
- If it is down one day, there is a 70% chance it will be down the next day.

In this example, our state space has only two components, "up" (U) and "down" (D). The transition probability matrix is

$$\mathbf{\Pi} = \begin{pmatrix} 0.6 \; 0.4 \\ 0.3 \; 0.7 \end{pmatrix}$$

The individual elements of the above matrix are

$$\Pi_{uu} = 0.6; \; \Pi_{ud} = 0.4$$

$$\Pi_{du} = 0.3; \; \Pi_{dd} = 0.7$$

Note that $\sum_m \Pi_{mn} = 1$; the rows of the transition probability matrix sum to 1; the system must be in some state at the end of a trial. This property makes $\mathbf{\Pi}$ a *stochastic matrix*.

Now let's assume that on day 1, the computer is equally likely to be up and down. That is

$$\boldsymbol{\rho}^{(1)} = (\rho_U \; \rho_D) = (0.5 \; 0.5) \tag{9.6}$$

What are the probabilities the computer will be up/down the next day? Applying our probability matrix, we see that

$$\boldsymbol{\rho}^{(2)} = \boldsymbol{\rho}^{(1)}\mathbf{\Pi} = (0.45, \; 0.55) \tag{9.7}$$

Thus, there is a 45% chance your computer will be up on day 2, but a 55% chance it will be down.

Repeating the process, we can compute the probabilities for day 3:

$$\boldsymbol{\rho}^{(3)} = \boldsymbol{\rho}^{(2)}\mathbf{\Pi} = \boldsymbol{\rho}^{(1)}\mathbf{\Pi}\mathbf{\Pi} = (0.435, \; 0.565) \tag{9.8}$$

We now only have a 43.5% chance of getting any work done. We can carry this out for many more days to get our chances in the long run. We find that:

$$\boldsymbol{\rho}^{(5)} = (0.4287, \; 0.5713)$$

$$\boldsymbol{\rho}^{(6)} = (0.4286, \; 0.5714)$$

$$\boldsymbol{\rho}^{(20)} = (0.4286, \; 0.5714)$$

Clearly, there is a limiting distribution which we reached, given by the formula

$$\boldsymbol{\rho} = \lim_{\tau \to \infty} \boldsymbol{\rho}^{(1)}\mathbf{\Pi}^{\tau} \tag{9.9}$$

We see from eqn 9.9 that the limiting distribution, $\boldsymbol{\rho}$, must satisfy the eigenvalue equation

$$\boldsymbol{\rho}\boldsymbol{\Pi} = \boldsymbol{\rho}$$

$$\sum_m \rho_m \Pi_{mn} = \rho_n$$

Thus, $\boldsymbol{\rho}$ is an eigenvector of the stochastic matrix $\boldsymbol{\Pi}$ corresponding to an eigenvalue of 1.

Notice that $\boldsymbol{\rho}$ is *completely determined* by $\boldsymbol{\Pi}$, and is not at all influenced by the initial condition ($\rho^{(1)}$). (Try this: start out with a different initial condition and see what you converge to). All memory of the initial state has been lost. Markov chains in which one can ultimately go from any state to any other state are called *ergodic* or *irreducible*. Such chains *always* have a limiting probability distribution.

If the transition probability matrix is full, the chain is ergodic, while if the transition probability matrix is block diagonal, the chain is non–ergodic. In the case of statistical mechanical systems, we will have a much larger transition matrix. It must be stochastic and ergodic. In this case, we do *not* know the elements of the matrix. We do know, however, the limiting distribution...(what is it?)

9.3.2 The Metropolis Monte Carlo Algorithm

The problem facing us is that we know the probability distribution in our multi–dimensional space, but we don't know what the elements of the transition matrix are. For example in the NVT ensemble, the limiting distribution of our Markov chain is the vector with elements $\rho_m = \rho_{NVT}(\boldsymbol{\Gamma}_M)$ for each point $\boldsymbol{\Gamma}_m$ in phase space. Note: the multi–dimensional space may be discrete (ρ_m is a probability in this case) or it may be continuous, ($\rho_m = \rho(\boldsymbol{\Gamma}_m)d\boldsymbol{\Gamma}$, where $\rho(\boldsymbol{\Gamma}_m)$ is a probability density and $d\boldsymbol{\Gamma}$ is an elementary volume in the multi–dimensional space centered at $\boldsymbol{\Gamma}_m$).

Our goal is to develop an efficient numerical procedure for sampling the multidimensional space, according to the probability distribution $\{\rho_m\}$. What do we mean by "sampling"? This just means that we wish to pick a finite set of points (states)

$$m_1, m_2, \cdots, m_t, \cdots, m_{N_{trials}}$$

such that the probability of finding each state m_t in the sequence is practically equal to ρ_{m_t}. Note that a given state may appear more than once in our sequence. If we can sample states in this fashion, we can calculate the average of any function f defined on the state space as

$$< f > \approx \frac{1}{N_{trials}} \sum_{t=1}^{N_{trials}} f(m_i)$$

The solution to the problem of how to do this is known as Metropolis (or MR^2T^2) Monte Carlo.[3] The idea goes as follows. Generate the representative set of points as a sequence, each from the previous one, according to certain stochastic rules. We will create a Markov chain of states,

$$m_1 \to m_2 \to \cdots \to m_t \to \cdots \to m_{N_{trials}}$$

We select the transition matrix of the Markov chain (for moving from m *to* n) as:

$$\Pi_{mn} = \begin{cases} c_{mn}, & \text{if } \rho_n \geq \rho_m, n \neq m; \\ c_{mn}\frac{\rho_n}{\rho_m}, & \text{if } \rho_n < \rho_m, n \neq m \end{cases} \tag{9.10}$$

It is also possible to stay in the same state

$$\Pi_{mm} = 1 - \sum_{m \neq n} \Pi_{mn} \tag{9.11}$$

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[3] Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E.; *J. Chem. Phys.*, 21, 1087-1092, (1953)

c is a symmetric (i.e. $c_{mn} = c_{nm}$) and a stochastic (i.e. $\sum_n c_{mn} = 1$) matrix. c_{mn} is the probability of *attempting a move* from state m to state n.

Usually, moves are attempted only between close–lying states in the multi–dimensional space. That is, most of the elements of **c** are zero; only a few which correspond to pairs of closely lying states are non-zero. Typically, c_{mn} is uniform in a small region of the space around state m – meaning that an attempted move to any of the *nearby* states n is done with equal probability.

The probability of *accepting* a move from m to n, the so–called "Metropolis selection criterion" is

$$min(1, \frac{\rho_n}{\rho_m}) \tag{9.12}$$

where "min" refers to the Fortran function which selects the minimum of the two values and we have implicitly let **c** be symmetric[4]. In words, the selection criterion states that

- If new state n is more probable that the state m from which we started, then accept the new state n as the next state in the Markov chain.
- If the new state n is less probable than the old state m, accept the new state n with probability $\frac{\rho_n}{\rho_m} < 1$.
- If the new state n is *not* accepted, state m is retained as the next state in the chain and its characteristics are entered again in the averaging procedure.

Here are the properties of the transition matrix, $\mathbf{\Pi}$:

- $\mathbf{\Pi}$ is stochastic: $\sum_n \Pi_{mn} = 1$
- $\mathbf{\Pi}$ satisfies the condition of microscopic reversibility.

  $$\rho_m \Pi_{mn} = \rho_n \Pi_{nm}$$

  That is, the probability of occurrence of the move $m \rightarrow n$ is equal to the probability of the occurrence of the move $n \rightarrow m$
- $\boldsymbol{\rho}$ is the limiting distribution corresponding to the transition matrix $\mathbf{\Pi}$. This can easily be proved by showing that, as asserted earlier, ρ is an eigenvector of the stochastic matrix $\mathbf{\Pi}$ with corresponding eigenvalue of 1. That is,

  $$\mathbf{\Pi}\boldsymbol{\rho} = \boldsymbol{\rho} \tag{9.13}$$

The Metropolis algorithm ensures that all of the above criteria are satisfied. Eqn 9.13 guarantees that, regardless of the starting point of the Markov chain, a chain long enough will asymptotically sample the probability distribution of interest, defined by ρ.

As the transition matrix $\mathbf{\Pi}$ is defined in eqn 9.10, we see that we only need to know $\boldsymbol{\rho}$ up to a multiplicative constant; only probability *ratios* appear in the Metropolis scheme. This makes the method very useful in statistical mechanical applications.

We should mention that there are other algorithms that satisfy the transition matrix criteria listed above. So–called Barker sampling yields

$$\Pi_{mn} = c_{mn}\rho_n/(\rho_n + \rho_m),\ m \neq n \tag{9.14}$$

$$\Pi_{mn} = 1 - \sum_{n \neq m} \Pi_{mn} \tag{9.15}$$

---

[4] If **c** is not symmetric, we must include it in the acceptance rules. There are times when we may prefer to have an asymmetric attempt matrix. Such methods are referred to as *biased Monte Carlo*. We won't discuss this, but note that the formulas given here are a special case of a more general set of acceptance rules.

Eqns 9.14 - 9.15 also satisfy microscopic reversibility, but in general are not as efficient as the Metropolis algorithm.

We should re–emphasize that the Metropolis technique depends on the ergodicity of the Markov chain. That is, there must be a non–zero multi–step transition probability of moving between any two allowed states of the system. If allowed states are not connected, a MC simulation will converge to a result that may be a poor estimate of a canonical average.

When the path between two allowed regions of phase space is difficult to find, we say that there is a bottleneck in the system. We always worry about bottlenecks when performing MC simulations. Bottlenecks are particularly troublesome when simulating two–phase coexistence, phase transitions, and dense systems. They are also a problem when simulating systems like polymers that have many degrees of freedom. For example, Figure 9.8 shows a schematic of the degrees of freedom of a glassy polymer. Note that in a polymeric system, the state space is really multi–dimensional, but it is shown here projected onto the x-axis for clarity.

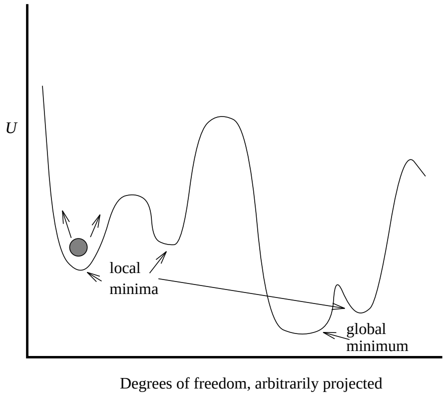

Figure 9.8: Schematic of the energy of various conformations of a polymer. The very many degrees of freedom of the system are shown "projected" onto the x–axis. In reality, the potential energy hypersurface would have very many dimensions. We see that a system with high barriers between states may not be ergodic, or may be difficult to sample.

If the thermal energy is much lower than $k_B T$ and a move consists of small local perturbations such that a Markov chain connecting local minima must pass over high energy states, a configuration will only explore the local region of the state space near its initial configuration. The average obtained from such a simulation would be dependent on the starting configuration, and would clearly not be an ensemble average. Special techniques for attacking these problems must be developed. We won't go into these methods in great detail.

Next, let's consider the basic procedure one follows in conducting Metropolis Monte Carlo. The steps are outlined in Figure 9.9 and are described in the next section.

9.3.3 Flow of Calculations in Metropolis Monte Carlo

Figure 9.9 shows the general calculation scheme used in a Metropolis Monte Carlo simulation. An algorithm would go as follows.

1. Starting from an initial state m, an elementary move is attempted.
2. A move is attempted to neighboring state n.
3. The probabilities of states m and n are compared.
4. Using the Metropolis selection criterion:
    - If state n is more probable, the move is immediately accepted.

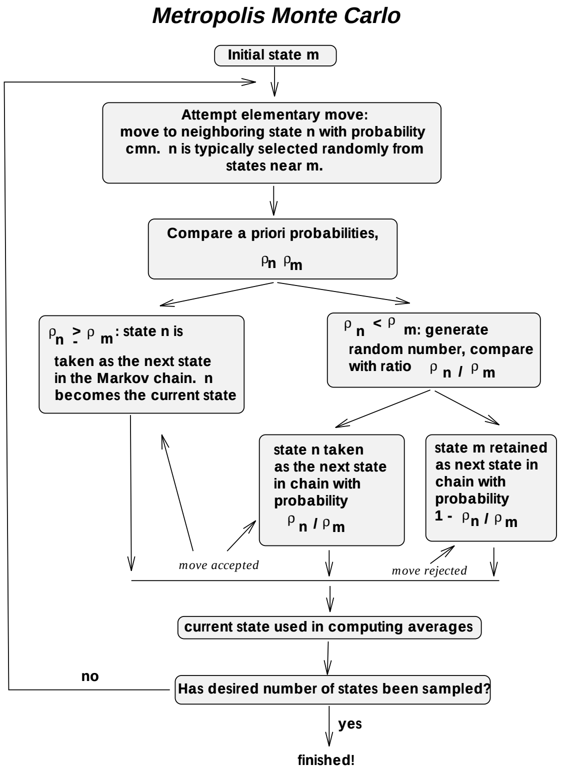

Figure 9.9: Basic flowsheet for the Metropolis method

- If state n is less probable, a random number ζ on $(0, 1)$ is generated. If $\rho_n/\rho_m \geq \zeta$ accept the move and the new state is n. If $\rho_n/\rho_m < \zeta$, reject the move.
- The "new" state (n for accepted moves, m for rejected moves) is taken as the current state, and used in computing averages.

5. We iterate many times (ca. 10^6) and compute averages. Stop when convergence is reached.

9.3.4 Example: Canonical Ensemble MC of a Simple Liquid

Let's give an example of a simple application of the Metropolis method. Assume we have a system comprised of a simple liquid (i.e. Ar). We assume we have pairwise LJ interactions. Our objective is to generate a sequence of N molecules in volume V that asymptotically samples the probability density of the canonical (NVT) ensemble.

Our multi-dimensional configuration space is given by $(\mathbf{r}_1, \cdots, \mathbf{r}_M)$. Individual "states" are simply different configurations or atomic arrangements. The probability distribution is the canonical ensemble, namely

$$\boldsymbol{\rho}_m = \rho^{NVT}(\mathbf{r}_1^{(m)}, \cdots, \mathbf{r}_N^{(m)}) d\mathbf{r}^N \tag{9.16}$$

where $d\mathbf{r}^N$ is an elementary volume element in configuration space. The ratio of two probabilities is

$$\boldsymbol{\rho}_n/\boldsymbol{\rho}_m \rightarrow \frac{\rho^{NVT}(\mathbf{r}_1^{(m)}, \cdots, \mathbf{r}_N^{(m)})}{\rho^{NVT}(\mathbf{r}_1^{(n)}, \cdots, \mathbf{r}_N^{(n)})} = \frac{\rho_n^{NVT}}{\rho_m^{NVT}} \tag{9.17}$$

where we note that

$$\rho^{NVT}(\mathbf{r}_1^{(m)}, \cdots, \mathbf{r}_N^{(m)}) \equiv \rho_m^{NVT} =$$

$$\frac{\exp[-\beta\mathcal{V}(\mathbf{r}_1,\cdots,\mathbf{r}_N)]}{Z(NVT)} \equiv \frac{\exp[-\beta\mathcal{V}_m]}{Z}$$

Thus,

$$\frac{\rho_n^{NVT}}{\rho_m^{NVT}} = \frac{\exp[-\beta\mathcal{V}_n]}{\exp[-\beta\mathcal{V}_m]} = \exp[-\beta(\mathcal{V}_n - \mathcal{V}_m)] = \exp[-\beta\Delta\mathcal{V}_{m\to n}] \tag{9.18}$$

Given this, we write the Metropolis acceptance probability as

$$min\left(1, \frac{\rho_n^{NVT}}{\rho_m^{NVT}}\right) = \begin{cases} 1, & \text{if } \mathcal{V}_n \le \mathcal{V}_m; \\ \exp[-\beta\Delta\mathcal{V}_{m\to n}], & \text{if } \mathcal{V}_n > \mathcal{V}_m \end{cases} \tag{9.19}$$

Notice that the Metropolis selection criterion *only involves potential energy* - we do not need to know the configurational integral. Using eqn 9.19, we could carry out a Metropolis Monte Carlo simulation of our atomic liquid. To see exactly how, we need to go into a few more details.

9.3.5 Metropolis Method: Implementation Specifics

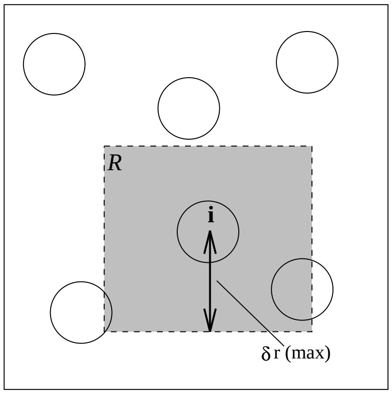

Figure 9.10: An example of a move in Metropolis Monte Carlo. The underlying stochastic matrix c allows particles to move to neighboring positions, defined here as residing inside the shaded box.

The first detail to decide upon is the form of **c**, the underlying stochastic matrix. In the typical implementation, we attempt to take the system from state m to neighboring state n with equal probability, so that $c_{mn} = c_{nm}$. Figure 9.10 shows a system with six atoms arranged inside a box. Such a configuration represents state m. To move to another state, n, we perform the following steps:

1. Choose an atom at random. Here, we pick atom i at position $\mathbf{r}_i^{(m)}$
2. Define a “local” or “neighboring” environment by a square (cube or sphere in three dimensions) centered on i. The edge length (or radius) of the local region is δr_{max}. We give the local cube the symbol $\mathcal{R}$. Note that if we use a cube (as done below), the sides are $2\delta r_{max}$ long.
3. On the computer, there is a large but finite set of new configurations, $N_{\mathcal{R}}$ within the cube $\mathcal{R}$. If each one is of equal probability, we have

$$c_{mn} = 1/N_{\mathcal{R}};\ \mathbf{r}_i^{(n)} \in \mathcal{R}$$

$$c_{mn} = 0;\ \mathbf{r}_i^{(n)} \notin \mathcal{R}$$

Such a scheme is easily implemented. An atom is chosen at random and given a uniform, random displacement along each of the Cartesian axes. An adjustable parameter, δr_{max}, controls the "boldness" of the attempted move: small displacements result in high acceptance rates but slow evolution; large displacements yield large configurational changes, but get rejected more often. δr_{max} is typically adjusted so that about 50% of the attempted moves are successful.

A piece of FORTRAN code to implement the displacements might look like:

```
rxnew = rx(i) + (2.0 * rranf(iseed) - 1.0) * drmax
rynew = ry(i) + (2.0 * rranf(iseed) - 1.0) * drmax
rznew = rz(i) + (2.0 * rranf(iseed) - 1.0) * drmax
```

After a displacement is made, the energy of the new state is compared to the energy of the old state. The Metropolis selection rule is used to decide whether or not this new state is accepted. To see that the Metropolis method does indeed work, we refer to Figure 9.11. If a move from m to n is downhill, $\delta\mathcal{V}_{nm} \leq 0$ and the move is always accepted. (That is, the transition probability for this move is

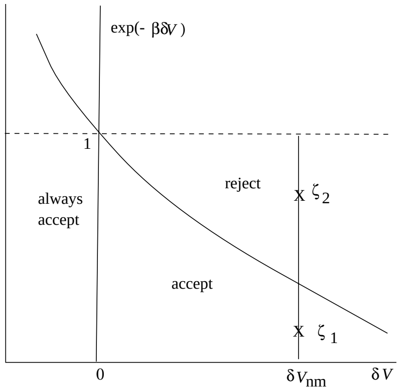

Figure 9.11: The Metropolis selection criterion does indeed sample from the proper distribution, shown here as a curve. See text for an explanation

$$\Pi_{mn} = c_{mn}$$

For "uphill" moves, a random number ζ is generated uniformly on (0,1). If $\zeta < \exp[-\beta\mathcal{V}_{nm}]$, ($\zeta_1$ in the figure), the move is accepted. Otherwise, (ζ_2), the move is rejected. Over the course of the simulation, the net result is that energy changes such as $\delta\mathcal{V}_{nm}$ are accepted with probability $\exp[-\beta\delta\mathcal{V}_{nm}]$.

9.3.6 Other Technical Considerations

For molecular systems, the elementary moves must change all the configurational degrees of freedom. That is, it isn't enough to simply translate molecules. Instead, we must perform rigid translations *as well as* rigid rotations, and conformational moves (i.e. rotations about bonds). One way is to randomly change one particular generalized coordinate and accept or reject this "move" with the standard Metropolis weighting. This is formally correct, but can you see any potential problems with this? How might you do this in a more efficient way?

The development of new and more efficient Monte Carlo moves is the subject of active research. Recent advances utilize "configurational bias" methods and various other tricks to efficiently sample these internal degrees of freedom.

Another question we have to ask is: what is the starting configuration? We know that the final result should be independent of the starting configuration, but from a practical standpoint, we have to start someplace. How do you do this? There are a few guidelines you can use. First, it is desirable to start in a high probability (low energy) state.

This will minimize the amount of time it takes for your system to "equilibrate". Since you are generally interested in equilibrium properties, you should not take any averages while the system approaches equilibrium. Thus, all the time it takes to go from the initial configuration to the "equilibrated" configuration is wasted. Starting close to equilibrium minimizes this wasted time. A traditional approach is to start all the molecules from an fcc lattice. As moves progress, the lattice "melts" and a liquid is obtained. This method ensures none of the molecules are initially overlapping, but it can often take a long time for the crystalline order to be lost. An alternative is to randomly shoot molecules into a box and then perform energy minimization to relax overlaps. This helps speed equilibration, but getting all the molecules into the box initially can be difficult at higher densities. Once a configuration has been generated and a simulation run, you can always use a "snapshot" from this simulation as a starting point for a new configuration, as long as the conditions are similar.

The next question is: once an initial configuration is generated, how do you equilibrate the system? Initially, we are in a particular state. The Markov chain will asymptotically sample the ensemble of interest. The initial period of the simulation is an equilibration period, and must be discarded when calculating ensemble averages. At the end of the equilibration period, *all memory of the starting configuration should be lost.*

To check whether the system has in fact reached equilibrium, we do the following. We monitor the potential energy and pressure. Run the equilibration until there is no systematic drift in either quantity, only fluctuations about a mean. If you started from a lattice, make sure all indications of initial order have vanished. (Translational and orientational order parameters show no order in fluid). Finally, for fluid simulations, the mean–square displacement should grow linearly with time, indicating diffusive behavior. The rule of thumb is: low–molecular weight systems require 500N – 1000N steps to equilibrate, where N is the number of molecules. (1N steps is frequently called a "cycle" in the Monte Carlo community).

9.4 Application of Metropolis Monte Carlo: Ising Lattice

It is common to study phase transformations with a simplified lattice model. An *Ising lattice* is such a model. Consider a system of N spins on a lattice. In the presence of an external magnetic field, H, the energy of a particular state ν is

$$E_\nu = -\sum_{i=1}^{N} H\mu s_i - J\sum_{ij} s_i s_j \tag{9.20}$$

The first term is the energy due to the individual spins coupling with the external field, and the second term is the energy due to interactions *between* spins. We assume that only nearest neighbors interact, so the sum is over nearest neighbor pairs. A spin system with this interaction energy is called an Ising model. J is called a coupling constant, and describes the interaction energy between pairs. When $J > 0$, it is energetically favorable for neighboring pairs to be aligned. (Recall that we already examined a system with non–interacting spins in the presence of an external field when we discussed polymeric systems).

If J is large enough (or temperature low enough), the tendency for neighboring spins to align will cause a cooperative phenomena called *spontaneous magnetization.* Physically, this is caused by interactions among nearest neighbors propagating throughout the system; a given magnetic moment can influence the alignment of spins that are separated from one another by a large distance. Such long range correlations between spins are associated with a long range order in which the lattice can have a net magnetization *even in the absence of an external magnetic field.* The magnetization is defined as

$$< M >= \sum_{i=1}^{N} \mu s_i$$

A non–zero $< M >$ when $H = 0$ is called *spontaneous magnetization*.

The temperature at which a system exhibits spontaneous magnetization is called the *Curie temperature* (or critical temperature), T_c. T_c is therefore the highest temperature for which there can be a non–zero magnetization in the absence of an external magnetic field.

For $T_c > 0$, an Ising model will undergo an *order–disorder transition*. This phenomenon is similar to a phase transition in a fluid system. Since lattice order–disorder transitions are simpler than fluid phase transitions, we study these and try to understand the basic physical processes involved in fluid phase transitions.

Ising lattices do not show an order–disorder transition in one dimension, but they do in two and higher dimensions. (To understand why, think about the energetics involved in creating an "interface" separating two regions with different spin states).

The partition function for a one–dimensional lattice can easily be solved for. In two–dimensions, the problem is more difficult; Lars Onsager showed in the 1940s that for $H = 0$, the partition function for a two–dimensional Ising Lattice is[5]

$$Q(N, \beta, 0) = [2 \cosh(\beta J) e^I]^N \tag{9.21}$$

where

$$I = (2\pi)^{-1} \int_0^{\pi} d\phi \ln(\frac{1}{2}[1 + (1 - \kappa^2 \sin^2 \phi)^{1/2}])$$

with

$$\kappa = 2 \sinh(2\beta J)/cosh^2(2\beta J)$$

This result was one of the major achievements of modern statistical mechanics.[6]

It can be shown that $T_c = 2.269 J/k_B$. Furthermore, for $T < T_c$, the magnetization scales as

$$\frac{M}{N} \sim \alpha(T_c - T)^{\lambda}$$

The three–dimensional Ising model has yet to be solved analytically; numerical simulations have shown that the critical temperature in three dimensions is roughly twice the value for two dimensions.

Physically, the Ising lattice shows many of the same characteristics as a fluid phase. In particular, the magnetic susceptibility, defined as

$$\chi = (< M^2 > - < M >^2)/k_B T$$

should diverge at the critical point. That is, local magnetization fluctuations become very large near the critical point, just as density fluctuations become large near the critical point of a fluid. Small variations in $k_B T/J$ can lead to spontaneous phase changes.

We also see in Ising lattices that the *correlation length*, the distance over which local fluctuations are correlated, must become unbounded at the transition. Physically, such a transition can be shown schematically as in Figure 9.12 The correlation length can be thought of as the "size" of the liquid droplets that form as a gas condenses; when the droplets get large enough, gravitational forces cause them to separate from the vapor, and a liquid forms.

9.5 Grand Canonical Monte Carlo Simulations

It is often convenient to conduct Monte Carlo simulations in ensembles other than the canonical ensemble. To do this, one must construct a Markov chain with a limiting distribution equal to that of the probability distribution of the chosen ensemble. We describe here two such simulation techniques: grand canonical ensemble Monte Carlo (GCMC) is described in this section, and a relatively new technique, Gibbs–ensemble Monte Carlo, will be described in the next section.

Recall that in the grand canonical ensemble, the chemical potential, μ, volume, V, and temperature, T are held constant. The probability density corresponding to the grand canonical ensemble is

$$\rho(\mathbf{r}^N; N) = \frac{1}{N!} \frac{\exp(N\beta\mu)}{\Lambda^{3N}} \exp[-\beta \mathcal{V}(\mathbf{r}_1, \cdots, \mathbf{r}_1)] \frac{1}{\Xi} \tag{9.22}$$

---

[5] I will provide you with a Metropolis code which will allow you to further investigate the properties of the 2–D Ising lattice.

[6] Onsager was trained as a chemical engineer, and goes down as one of the greatest statistical mechanicians of all time.

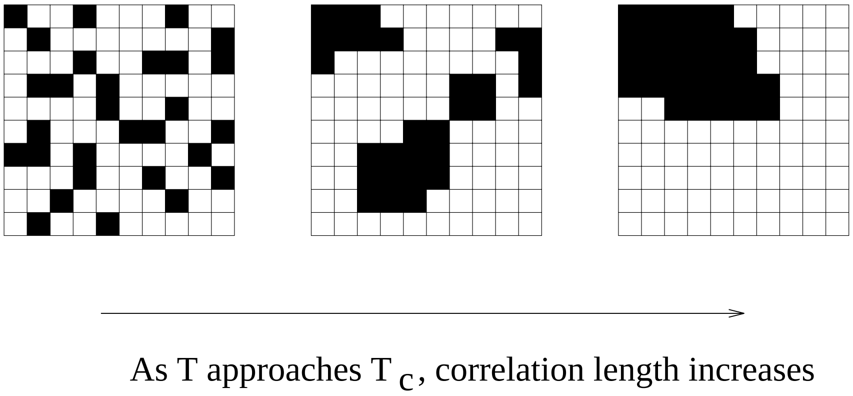

Figure 9.12: Representation of a 2-D Ising lattice. The critical temperature is being approached as we move from left to right. As this occurs, the correlation length of like regions (i.e. black and white squares) increases. At T_c, we get an order–disorder transition, analogous to condensation

For convenience, we usually work with *scaled* coordinates:

$$(\mathbf{s}_1, \cdots, \mathbf{s}_N)$$

where

$$s_{\alpha,i} = V^{-1/3} r_{\alpha,i},\ 0 \leq s_{\alpha,i} \leq 1$$

Thus we write

$$\rho(\mathbf{r}^N; N) d\mathbf{r}^N = \rho(\mathbf{s}^N; N) d\mathbf{s}^N$$

where

$$\rho(\mathbf{s}^N; N) = V^N \rho(\mathbf{r}^N; N)$$

Now we can write

$$\rho(\mathbf{s}^N; N) = \frac{\exp[-\beta(\mathcal{V}(s) - N\mu) - \ln N! - 3N \ln \Lambda + N \ln]}{\Xi}$$

We see the advantage of this; the dimensions of $\rho(\mathbf{r}^N; N)$ depend on N, whereas $\rho(\mathbf{s}^N; N)$ is dimensionless.

Now, let's consider two states m and n. If we take the ratio of the two $\rho(\mathbf{s}^N; N)$ associated with each state, we get

$$\frac{\rho_n}{\rho_m} = \frac{\exp[-\beta(\mathcal{V}_n - N_n\mu) - \ln N_n! - 3N_n \ln \Lambda + N_n \ln V]}{\exp[-\beta(\mathcal{V}_m - N_m\mu) - \ln N_m! - 3N_m \ln \Lambda + N_m \ln V]}$$

$$= \exp[-\beta(\mathcal{V}_n - \mathcal{V}_m) + \beta\mu(N_n - N_m) - \ln \frac{N_n!}{N_m!} -$$

$$3(N_n - N_m) \ln \Lambda + (N_n - N_m) \ln V]$$

Now, let's imagine we create a particle in our system; this corresponds to moving from state m with N_m particles to state n with N_n particles, where $N_n - N_m = 1$. In this case,

$$\frac{\rho_n}{\rho_m} = \exp[-\beta(\mathcal{V}_n - \mathcal{V}_m) + \beta\mu - \ln(N_m + 1) - 3 \ln \Lambda + \ln V]$$

$$= \exp\left[-\beta(\mathcal{V}_n - \mathcal{V}_m) + \ln\left(\frac{zV}{N_m + 1}\right)\right] \tag{9.23}$$

where $z = \exp[\beta\mu]/\Lambda^3$ is a constant of the simulation.

For the destruction of a molecule, we have $N_n - N_m = -1$

$$\frac{\rho_n}{\rho_m} = \exp[-\beta(\mathcal{V}_n - \mathcal{V}_m) - \beta\mu + \ln N_m + 3\ln\Lambda - \ln V] =$$

$$\exp\left[-\beta(\mathcal{V}_n - \mathcal{V}_m) + \ln\left(\frac{N_m}{zV}\right)\right] \tag{9.24}$$

We can sample from the proper distribution by conducting three elementary moves.[7]

1. A molecule is displaced
2. A molecule is destroyed, and no record of its position is kept
3. A molecule is created at a random position in the system

Pictorially, we can think of this process as is depicted in Figure 9.13 The acceptance probabilities for the three moves, given a symmetric attempt matrix, are

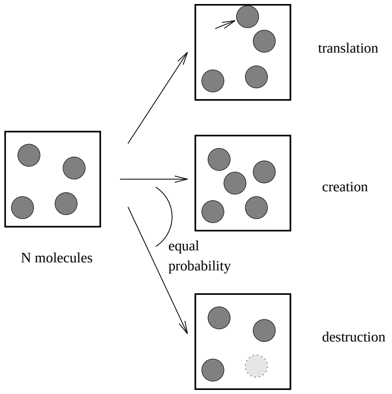

Figure 9.13: Schematic of the types of moves in GCMC: displacement, creation, and destruction

1. Translation: $min(1, \exp(-\beta\Delta\mathcal{V}))$
2. Creation: $min\left(1, \exp\left(-\beta\Delta\mathcal{V} + \ln\left(\frac{zV}{N+1}\right)\right)\right)$
3. Destruction: $min\left(1, \exp\left(-\beta\Delta\mathcal{V} + \ln\left(\frac{N}{zV}\right)\right)\right)$

The idea then is to pick a chemical potential, temperature, and volume and conduct a simulation following the above acceptance rules. The system will naturally evolve to the proper density consistent with those thermodynamic constraints.

The major advantage of GCMC simulations is that the free energy can be calculated directly once the average pressure and number of particles are collected. That is,

$$A/N = \mu - \frac{< P >_{\mu VT} V}{< N >_{\mu VT}} \tag{9.25}$$

From eqn 9.25, all the thermodynamic properties may be computed. The drawback of this approach is that random insertions and conformational changes are often accepted with very low probabilities in high density systems. This

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[7] Such an algorithm was originally proposed by Norman, G. E. and Filinov, V. S. *High Temp.* (USSR), 7, 216-222, (1969)

can cause difficulties in convergence for standard GCMC methods. Generally speaking, the various moves must be accepted with at least 0.5% for convergence to be confidently determined. There are a number of variations on the basic scheme. In particular, we just mention Adams' method[8] which is very useful for computing sorption equilibria for surfaces and pores.

9.6 Gibbs Ensemble Monte Carlo

A particularly powerful technique for studying phase equilibria was developed by Panagiotopoulos in 1987.[9] To demonstrate how it works, we will follow a slightly different derivation than the one used in the original paper.

Consider a large region, represented by the box in Figure 9.14. The box is at constant N, V, T. There are two "sub–regions" labeled I and II that have volumes V^I and V^{II}, particle numbers N^I and N^{II}, and energies E^I and E^{II}. The *total* volume is $V = V^I + V^{II}$, total number of particles is $N = N^I + N^{II}$.

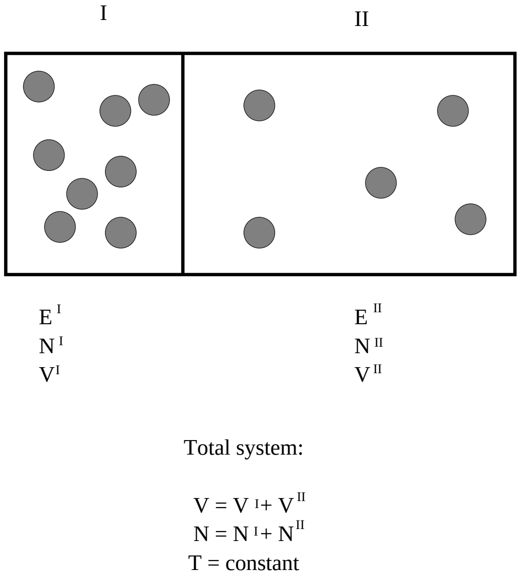

Figure 9.14: Schematic showing the system considered in the Gibbs ensemble.

We think of the individual regions as large macroscopic volumes of coexisting phases; the "surface" separating the two regions is devoid of any physical significance and does *not* represent an actual interface. We want to avoid interfaces in this method. Thus, the particles located inside the sub–regions are considered to be located deep inside the phases represented by the conditions of sub–systems I and II. The two sub–system boxes taken together form a system which is representative of the canonical ensemble at constant NVT. We now describe the three moves used in the technique.

1. Particle Displacements:

   Each sub–system box is independent in this step. Since the arguments for particle movement apply to both sub–systems, we will only consider the movement of particles in box I.

   The box is represented by the canonical $N^I V^I T$ ensemble. States in this ensemble occur with a probability proportional to $\exp[-\beta \mathcal{V}^I]$, where $\mathcal{V}^I$ is the configurational energy of the system in phase I. These states are generated using a normal Metropolis algorithm:

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[8] Adams, D. J. *Mol. Phys.*, 29, 307-311, (1975)

[9] A. Z. Panagiotopoulos, *Mol. Phys.*, 61, 813-826, (1987)

(a) A particle in box I is chosen at random.

(b) The particle is given a random displacement to a new trial position in box I.

(c) The trial move is accepted with probability $\min(1, \mathcal{P}^I_{move})$, where $\mathcal{P}^I_{move}$ is the ratio of the probabilities of the new and old state. That is

$$\mathcal{P}^I_{move} = \frac{\exp(-\beta \mathcal{V}^I_{new})}{\exp(-\beta \mathcal{V}^I_{old})}$$

or

$$\mathcal{P}^I_{move} = \exp(-\beta \Delta \mathcal{V}^I) \tag{9.26}$$

where $\Delta \mathcal{V}^I$ is the energy change for the trial move. If a move is rejected, the old state is recounted in the Markov chain of states. As mentioned, an identical procedure is applied to box II. These moves thermally equilibrate the particles in the two boxes.

2. Volume Changes:

We begin this step by considering box I as part of the isothermal–isobaric ensemble (constant $N^I PT$). Since we will see that the move for box I is perfectly correlated with the move for box II, we also note that box II is considered part of the constant $(N^{II} PT)$ ensemble.

A trial move consists of

(a) Choosing a random volume change ΔV for box I.

(b) For box I, the ratio of the probabilities of the new and old states is

$$\mathcal{P}^I_{vol} = \frac{\exp[-\beta P(V^I + \Delta V) - \beta \mathcal{V}^I_{new} + N^I \ln(V^I + \Delta V)]}{\exp[-\beta P V^I - \beta \mathcal{V}^I_{old} + N^I \ln(V^I)]}$$

$$\mathcal{P}^I_{vol} = \exp[-\beta P \Delta V - \beta \Delta \mathcal{V}^I + N^I \ln(V^I + \Delta V) - N^I \ln(V^I)] \tag{9.27}$$

(c) Note that since the total volume of the two boxes is conserved, a volume change for box I means that a simultaneous volume change of $-\Delta V$ must be performed for box II. Such a move generates states from the isothermal–isobaric $(N^{II} PT)$ ensemble.

(d) We assume that the pressure P in phases I and II are equal; this is one of the criteria for coexistence of the two phases.

(e) The probability of the volume change for box II is, using similar arguments as above:

$$\mathcal{P}^{II}_{vol} = \exp[\beta P \Delta V - \beta \Delta \mathcal{V}^{II} + N^{II} \ln(V^{II} - \Delta V) - N^{II} \ln(V^{II})] \tag{9.28}$$

(f) The *overall* ratio of the probabilities for the combined volume changes is

$$\mathcal{P}_{vol} = \mathcal{P}^I_{vol} \times \mathcal{P}^{II}_{vol}$$

$$\mathcal{P}_{vol} = \exp\left(-\beta\left[\Delta \mathcal{V}^I + \Delta \mathcal{V}^{II} - N^I k_B T \ln\frac{V^I + \Delta V}{V^I} - N^{II} k_B T \ln\frac{V^{II} - \Delta V}{V^{II}}\right]\right) \tag{9.29}$$

(g) The volume change move is accepted with probability $\min(1, \mathcal{P}_{vol})$

(h) If the trial move is rejected, the old state is recounted in the Markov chain. By multiplying the probabilities in eqn 9.29, we make the assumption that the Markov chains sampled by each region are not affected by the fact that the two volume changes are perfectly correlated. It is thought that this is a good approximation away from the critical point.

3. Particle Interchanges:

   We again consider box I, which represents the $(\mu V^I T)$ ensemble. We attempt to create a particle in box I.

   (a) A position in box I is chosen at random.

   (b) We attempt to place a particle in the randomly chosen spot.

   (c) Such a move creates a "new" configuration for box I. The ratio of the probabilities of the new and old states is

$$\mathcal{P}_{ex}^{I} =$$

$$\frac{\exp[-\beta\mathcal{V}_{new}^{I} + \beta(N^I+1)\mu - \ln(N^I+1)! - 3(N^I+1)\ln\lambda + (N^I+1)\ln V^I]}{\exp[-\beta\mathcal{V}_{old}^{I} + \beta N^I\mu - \ln N^I! - 3N^I\ln\lambda + N^I\ln V^I]}$$

$$\mathcal{P}_{ex}^{I} = \exp[-\beta\Delta\mathcal{V}^I + \ln\left(\frac{zV^I}{N^I+1}\right)] \tag{9.30}$$

   where the activity coefficient, z is defined as

$$z = \exp(\beta\mu)/\lambda^3$$

   λ is the de Broglie wavelength of the particles and μ is the chemical potential.

   (d) Because the total number of particles must be conserved, creation of a particle in box I must be accompanied by the simultaneous destruction of a particle in box II. Box II is a representative sample of the grand canonical ensemble at constant $\mu V^{II} T$. μ must be the same in each box, since the two systems are in coexistence. To complete the exchange move, an atom in box II is chosen at random and destroyed.

   (e) The ratio of the probabilities of the new and old states for box II is

$$\mathcal{P}_{ex}^{II} =$$

$$\frac{\exp[-\beta\mathcal{V}_{new}^{II} + \beta(N^{II}-1)\mu - \ln(N^{II}-1)! - 3(N^{II}-1)\ln\lambda + (N^{II}-1)\ln V^{II}]}{\exp[-\beta\mathcal{V}_{old}^{II} + \beta N^{II}\mu - \ln(N^{II})! - 3N^{II}\ln\lambda + N^{II}\ln V^{II}]}$$

$$= \exp[-\beta\Delta\mathcal{V}^{II} - \beta\mu + \ln N^{II} + 3\ln\lambda - \ln V^{II}]$$

   or

$$\mathcal{P}_{ex}^{II} = \exp[-\beta\Delta\mathcal{V}^{II} + \ln(N^{II}/zV^{II})] \tag{9.31}$$

   (f) The probability of the overall step is thus

$$\mathcal{P}_{ex} = \mathcal{P}_{ex}^{I} \times \mathcal{P}_{ex}^{II}$$

$$\mathcal{P}_{ex} = \exp\left(-\beta\left[\Delta\mathcal{V}^I + \Delta\mathcal{V}^{II} + k_bT\ln\frac{V^{II}(N^I+1)}{V^IN^{II}}\right]\right) \tag{9.32}$$

   (g) A trial exchange is then accepted with a probability of $min(1, \mathcal{P}_{ex})$. Rejected moves are recounted in the Markov chain.

(h) To satisfy microscopic reversibility, creations and destructions in the two boxes must be attempted with equal probability. This is easily achieved by choosing box I or II for the creation attempt with equal probability during a simulation.

(i) If box II is chosen for the creation, superscripts I and II are exchanged in eqn 9.32.

Nothing in the theoretical development dictates the relative number of the three moves; one chooses the ratio of moves to most rapidly equilibrate the system. Typically, one performs several NVT–moves, a single attempted volume change, and several exchange moves per cycle. One must include long–range corrections in the evaluation of the energies in the volume change and exchange steps, since both moves involve a change in density of the system [10].

Since neither the pressure or chemical potential are specified before the start of the simulation, these must be calculated using the virial theorem and Widom insertions. Since both boxes should have the same pressure and chemical potential, this is a useful check of the simulation.

9.6.1 Generalization of the Gibbs Technique

The Gibbs method can be used for atomic or molecular systems. The above derivation has focused on atomic systems. For molecular systems, NVT–type moves will also include orientational and conformational changes. μVT–type moves will also involve giving the inserted molecules random orientations. If the molecules are large compared to the void spaces, special biasing techniques will have to be used to efficiently insert the molecules (as are required in GCMC simulations). Likewise, in a dense medium, simple displacement/reptation moves may not be adequate to properly thermally equilibrate the systems. Special techniques like configurational bias and concerted rotation moves may be required.

We can also easily extend the Gibbs method to mixtures. All the moves are the same as in the single–component case, except the particle interchange. In eqn 9.32, N^I and N^{II} are now the number of molecules *of the species being exchanged*. For example, with a mixture of A and B we would have N_A^I, N_A^{II}, N_B^I, N_B^{II} with $N = N_A^I + N_A^{II} + N_B^I + N_B^{II}$. To ensure microscopic reversibility, the following steps must be taken in the exchange moves

1. Choose either box I or II for the trial creation with equal probability.
2. Select with a fixed but otherwise arbitrary probability which species is to be exchanged. That is, we could select A 20% of the time and B 80% of the time. Alternatively, we could select each half the time. We *cannot* simply choose a particle at random from one of the boxes for interchange, since microscopic reversibility must apply to the creation and destruction of each *species* separately.
3. Once a species is chosen, we randomly pick a location for creation and randomly pick one of those species for destruction.

Note that it is possible to "empty" one box of a species completely. This would happen frequently in a multi–component simulation in which one of the species was present in small amounts (low concentrations). It is stated that when a box is emptied, "the calculation should continue in the normal fashion". This can be justified by considering the limiting case of an infinite dilution distribution coefficient calculation. In this limit, a single particle could be used for that species in the total system.

The method can be generalized to include a constant pressure ensemble for mixtures. This would be useful for specifying the coexistence pressure in advance of the simulation. In such a simulation, the total system volume would no longer be constant, and volume changes of the two boxes would occur independently of one another. The acceptance rules are the same as for an NPT simulation of two independent regions. Note that a constant pressure Gibbs ensemble only has meaning in the case of mixtures, since for pure components the number of *intensive* variables that can be independently specified, in addition to the condition of two–phase equilibrium, is one – the

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[10] See Allen and Tildesley, pp 64-65

temperature. (Recall that the Gibbs phase rule is $F = C - P + 2$. Thus, for a pure system, $F = 1 - 2 + 2 = 1$. A two–component, two–phase mixture, however, would allow T and P to be specified).

A membrane system could also be simulated using an extension of the Gibbs technique. For a semi–permeable membrane, only the chemical potentials of the membrane–permeable species would be equal in the two coexisting phases. The other species would have no constraint on chemical potentials. Both regions can be maintained at constant volume. Particle exchanges would take place for the membrane–permeating species only. The pressure of the two phases is therefore not constrained, and a pressure difference consistent with the equality of chemical potentials of the permeating components exists. The osmotic pressure could therefore be computed.

One could also *impose* a pressure difference across the membrane (i.e. set the osmotic pressure). In this case, only the permeable species gets exchanged. In addition, the volume rearrangement step should take into account the osmotic pressure $\Pi = P^I - P^{II}$. Volume rearrangements are accepted with a probability given by $min(1, \mathcal{P}_{vol})$, where

$$\mathcal{P}_{vol} =$$

$$\exp\left(-\beta\left[\Delta E^I + \Delta E^{II} - N^I k_B T \ln\frac{V^I + \Delta V}{V^I} - N^{II} k_B T \ln\frac{V^{II} - \Delta V}{V^{II}} + \Pi\Delta V\right]\right) \tag{9.33}$$

9.6.2 Additional Computational Details for Monte Carlo Simulations

As mentioned before, a simple way of starting the simulation is to start with a face–centered lattice configuration, with the desired number of particles for each region placed randomly on the lattice.

Simulation cycles consist of sequential displacements (i.e. NVT moves) of all particles, a single volume fluctuation, and a number of exchanges. Displacements are selected randomly from a uniform distribution. The maximum displacement is adjusted in both regions to give an average acceptance ratio of 50%. After all the particles have had displacements attempted, a single trial volume change is performed. The attempted volume change is again selected at random from a uniform distribution, and maximum displacements are adjusted to give a 50% acceptance ratio. Note that energy and pressure calculations must be performed after a volume change. Long range corrections to the potential need to be used. This is done by integrating the potential from one–half the box edge length (the potential cutoff) to infinity and setting $g(r) = 1.0$. Finally, a number of exchange attempts are made. To do this, it is decided at random and with equal probability which box will receive a particle (and consequently, which box will donate a particle). A point is then chosen at random in the recipient box, and a particle is chosen for destruction at random in the donor box. For multi–component exchanges, the donor/recipient boxes are again chosen at random and with equal probability, then the *identity* of the exchange particle is determined at random, using a fixed probability for each species. The probability is best set so that approximately the same number of successful exchanges takes place for all species.

The chemical potential can be easily and efficiently computed during the course of the simulation and used to provide internal consistency checks on the simulation. To do this, the interaction energies calculated during the particle exchange steps are equivalent to the "ghost" particle energy of the Widom insertion method. That is, the potential energy of a potential exchange step of particle i, $\mathcal{V}_{i,ex}$ can be used in the following formula

$$\beta\mu_{i,r} = -\ln\langle\exp(-\beta\mathcal{V}_{i,ex})\rangle \tag{9.34}$$

where $\mu_{i,r}$ is the residual chemical potential of species i. $\mathcal{V}_{i,ex}$ is the interaction potential of species i with the rest of the fluid in the recipient box, *including long range corrections*. The chemical potential can therefore be evaluated in both regions with no additional computational cost. This can serve as a check for equilibration. It should be noted that eqn 9.34 is strictly only valid in the NVT ensemble; it needs to be modified for application in the NPT ensemble. However, since the volume fluctuations in the Gibbs method are small away from the critical point, eqn 9.34 gives essentially identical results to the other expressions. Thus, one can use eqn 9.34 as an approximate means of checking for internal consistency.

For mixtures, constant–pressure calculations appear to be the best suited over constant total volume. Constant pressure simulations give lower uncertainties for the compositions of the coexisting phases, and no uncertainty for the coexistence pressure. However, constant pressure simulations give somewhat higher uncertainties for densities.

Chapter 10

Molecular Dynamics Methods

10.1 Introduction

Up to this point, we have been interested in computing thermodynamic information for our model system. The Monte Carlo methods mentioned in the last section are very powerful tools for addressing these issues. There is another technique that is commonly used to simulate both equilibrium and *nonequilibrium* properties of fluids and materials; the technique is referred to as *molecular dynamics*.

The objective of molecular dynamics methods is to simulate the evolution of an atomistic model in time. To do this, we "simply" solve the classical equations of motion for a given atomistic model. During such a simulation, we wish to accumulate estimates of structural, thermodynamic, transport, and dynamic properties. We do this by taking *time averages*. Remember that one of our major assumptions was that *time averages* were equivalent to *ensemble averages*. Thus we should obtain the same thermodynamic information from a molecular dynamics (MD) simulation as we do from a Monte Carlo (MC) simulation *using the same model*. In addition, MD simulations can give us dynamic information that MC simulations cannot. Of course, there are tradeoffs, which we will discuss in detail later. However, one of the biggest tradeoffs is that MD simulations tend to be more complex to program and conduct, and efficient sampling can be more difficult.

10.2 Formulation of the Molecular Dynamics Method

We wish to solve the classical equations of motion for a system of N particles interacting via a potential $\mathcal{V}$. The most fundamental way of writing these equations is to use the Lagrangian form (see eqn 3.26):

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{q}_k}\right) = \frac{\partial \mathcal{L}}{\partial q_k} \tag{10.1}$$

where the Lagrangian function $\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)$ is defined in terms of the kinetic and potential energies as

$$\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t) = \mathcal{K}(\mathbf{q}, \dot{\mathbf{q}}, t) - \mathcal{V}((\mathbf{q}, t)$$

In general, $\mathcal{L}$ is a function of the generalized coordinates q_k, their time derivatives $\dot{q}_k$, and time t.

Now consider a system of atoms described by Cartesian coordinates $\mathbf{r}_i$. Recall that for this case,

$$\mathcal{K} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i}$$

$$\mathcal{V} = \sum_{i=1}^{N} v_1(\mathbf{r}_i) + \sum_{j>i} v_2(\mathbf{r}_i, \mathbf{r}_j) + \cdots$$

Eqn 10.1 can therefore be written as

$$m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i \tag{10.2}$$

m_i is the mass of atom i and the force on atom i is

$$\mathbf{f}_i = \nabla_{\mathbf{r}_i} \mathcal{L} = -\nabla_{\mathbf{r}_i} \mathcal{V}$$

This set of equations are often called Newton's equations of motion.

These equations apply to the center of mass of the molecule; $\mathbf{f}_i$ is the total force acting on the center of mass of molecule i due to all the interactions in the system. (Note that similar equations for molecular systems that can exhibit rotational motion, etc. can also be written using eqn 10.1; we will address this topic shortly).

Now, we can also write the equations in terms of the Hamiltonian. Recall that the definition of momentum conjugate to the generalized coordinate q_k was:

$$p_k = \frac{\partial \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)}{\partial \dot{q}_k}$$

Recall also that the Hamiltonian was defined in terms of the Lagrangian formulation as

$$\mathcal{H}(\mathbf{q}, \dot{\mathbf{q}}, t) = \sum_k \dot{q}_k p_k - \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)$$

We have already seen that if the generalized coordinate definitions do not depend explicitly on time and if the forces are derivable from a conservative potential $\mathcal{V}(\mathbf{q})$ then the Hamiltonian is *a constant of the motion*. In such an instance, the Hamiltonian is equal to the energy of the system:

$$\mathcal{H}(\mathbf{q}, \dot{\mathbf{q}}, t) = E = constant$$

and Hamilton's equations are

$$\dot{q}_k = \frac{\partial \mathcal{H}}{\partial p_k}$$

$$\dot{p}_k = -\frac{\partial \mathcal{H}}{\partial q_k}$$

If the Hamiltonian does not depend explicitly on time (depends on time only through the time dependence of $\mathbf{p}$ and $\mathbf{q}$), then it is a constant of the motion and the system is *conservative*. Given a conservative system, we can write the Cartesian equations of motion from Hamilton's equations as

$$\dot{\mathbf{r}}_i = \frac{\dot{\mathbf{p}}_i}{m_i} \tag{10.3}$$

$$\dot{\mathbf{p}}_i = -\nabla_{\mathbf{r}_i} \mathcal{V} = \mathbf{f}_i \tag{10.4}$$

We can therefore compute center of mass trajectories by either solving a set of $3N$ second order differential equations (eqn 10.2) or $6N$ first order differential equations (eqns 10.3-10.4).

As we will see shortly, we often impose *constraints* on our system (for efficiency reasons). In this case, the Newtonian equations of motion would still be

$$m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i$$

but

$$\mathbf{f}_i = -\nabla_{\mathbf{r}_i} \mathcal{V} + \mathbf{g}_i$$

where $\mathbf{g}_i$ is a constraint force. Notice that with constraints, not all $\mathbf{r}_i$ are independent.

10.3 Some General Features of the Equations of Motion

In an *isolated system* of interacting molecules, in the absence of any external fields, the following quantities are conserved

- $\mathcal{H}$, the total energy
- $\mathbf{P} = \sum_i \mathbf{p}_i$, the total linear momentum
- $\mathbf{L} = \sum_i \mathbf{r}_i \times \mathbf{p}_i$, the total angular momentum

Energy conservation applies whether or not we have an external field. The only requirement is that there be no time– or velocity–dependent forces acting on the system. These last two conditions can be rationalized by the following argument: For any set of particles, we can can always choose six generalized coordinates such that changes in these coordinates correspond to translations of the center of mass and rotations about the center of mass of the system as a whole. Changes in the other $3N$-6 coordinates would then only involve motion of the particles *relative* to one another. If $\mathcal{V}$ only depends on the magnitude of separation of these particles, and again there is no external field, then $\mathcal{V}$, $\mathcal{L}$, and $\mathcal{K}$ must be *independent of these six generalized coordinates*. If we then take the center of mass of our system as the origin, we see that the total angular and linear momentum *must* be conserved. However, *rarely* do we encounter a completely isolated system with no external fields!

For a system of molecules confined to a box with periodic boundary conditions that evolves in time subject only to interparticle interactions, you can show that $\mathcal{H}$ and $\mathbf{P}$ are conserved, *but total linear momentum*, $\mathbf{L}$, *is not conserved*. This is because we do not have spherical symmetry in a periodic cube. (Can you imagine a way of creating a spherically symmetric periodic system in Euclidean space?) In general, then, total angular momentum is usually *not* conserved in MD simulations. $\mathcal{H}$ and $\mathbf{P}$ usually are conserved. Thus a typical MD simulation is carried out under conditions of constant N, V, E, and $\mathbf{P}$. It samples from the microcanonical ensemble, with the added constraint of constant total momentum.

Another important fact is that, formally, the equations of motion are completely reversible in time. As we will see in the next section, we must integrate the equations numerically, which introduces imprecision in our solution so that our trajectories are only approximately reversible in time.

Another thing to be aware of before we proceed: we use spatial derivatives of the potential, so some care must be used in handling non–continuous potential functions. As we will see shortly, use of a finite–time step algorithm for numerically integrating the equations of motion can lead to problems with sharply varying potentials (such as hard sphere potentials).

10.4 Difference Methods for the Integration of Dynamical Equations

MD can be thought of as a numerical solution to an initial value problem. For a molecular system with no constraints, the initial value problem can be written as

$$\ddot{\mathbf{r}}_i = \frac{\mathbf{f}_i(\mathbf{r}_i, \cdots, \mathbf{r}_N)}{m_i} \tag{10.5}$$

with $\mathbf{r}_i(0)$ and $\dot{\mathbf{r}}_i(0)$ specified. Exactly how these get specified will be discussed later...but let's assume for now we can do this. A variety of *finite difference* methods can be used to solve such equations[1] having the form

$$\frac{dy_i(x)}{dt} = f(y_1, \cdots, y_N, t) \tag{10.6}$$

The basic idea is that one steps along the independent variable (time) in small, finite steps δt. This step size can be either constant or changed adaptively during the simulation.

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[1] See *Numerical Recipes*, Press et al.

The most common method for solution of such problems is probably Runge–Kutta. R–K methods propagate a solution over an interval by combining the information from several Euler–type steps

$$y_{n+1} = y_n + \delta t f'(t_n, y_n)$$

This advances the solution from t_n to $t_{n+1} \equiv t_n + \delta t$. Each step involves one evaluation of the f's, and this information is then used to obtain a match of a Taylor series up to some high order. The most common R–K method (and practically useful) is probably *fourth–order* Runge–Kutta:

$$y_{n+1} = y_n + \frac{k_1}{6} + \frac{k_2}{3} + \frac{k_3}{3} + \frac{k_4}{6} + \mathcal{O}(\delta t^5) \tag{10.7}$$

where each k involves a function evaluation. We see that this method then takes 4 function evaluations to move ahead one time step δt. This makes Runge–Kutta a particularly *bad* method for use in MD, since function evaluations (i.e. force calculations) make up the bulk of the computational load.[2]

An alternative method that is better is a *predictor–corrector* type algorithm. These methods minimize the number of function evaluations. We will describe these methods in a moment, but first we consider some general features of MD simulations.

10.4.1 Algorithmic Considerations in MD

There are a number of practical issues that must be addressed when developing an MD algorithm. First and foremost, one should reduce the total number of force evaluations in a simulation. The most time–consuming part of the simulation is the evaluation of forces. Thus, *the speed of the integration algorithm is immaterial compared to the force calculations*. We seek to minimize the ratio of the number of force evaluations over the total simulation time. This is why R–K techniques are not generally used. A second important factor is that the integration algorithm should employ a long integration time step δt. This enables us to simulate a longer time for a given number of integration time steps. Third, the algorithm must be accurate; a small error should result in the numerical evaluation for a large δt. Fourth, the algorithm must be *stable*. The error in the integration must not blow up with increasing δt. ODE's where stability is a problem are referred to as "stiff" equations. Generally speaking, this means the problem has two or more widely disparate time scales. MD problems typically fit this classification. This can be solved through the use of *implicit* algorithms

$$y_{n+1} = y_n + \frac{\delta t}{2}[f(y_n, t_n) + f(y_{n+1}, t_{n+1})] \tag{10.8}$$

rather than explicit algorithms

$$y_{n+1} = y_n + \delta t f(y_n, t_n) \tag{10.9}$$

Implicit algorithms are generally not used, however, because they involve more (costly) function evaluations than explicit algorithms. Fifth, the algorithm should not require a lot of memory, if very large systems are to be simulated. This is becoming less of a concern as computer memory becomes more readily available. Other important factors: The conservation laws for energy and momentum, as well as time reversibility, should be satisfied; it would be nice if the algorithm were simple and easy to program; and the algorithm should duplicate the "exact" trajectory as close as possible.

It turns out that MD problems are *highly nonlinear*: there is a tremendous sensitivity to the initial conditions. That is, any two classical trajectories that are initially close will diverge exponentially with time. This means it is practically impossible to trace out the "real" trajectory of the system. This is not a problem! As long as the trajectory stays reasonably close to the "real" trajectory over the correlation times of interest and energy is conserved, then the trajectory provides correct sampling of the NVE ensemble.

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[2] Press at al. are even blunter: "Runge–Kutta is what you use when you don't know any better, ... or you have a trivial problem where computational efficiency is of no concern."

10.4.2 Gear Predictor–Corrector Methods

We wish to use a finite difference approach to solve the differential equations of MD. That is, given molecular positions, velocities, (and other dynamic information) at time t, we seek a method for obtaining the positions, velocities, etc. at some later time $t + \delta t$ to a sufficient degree of accuracy. To do this, we solve the equations on a step–by–step basis. δt will depend somewhat on the method we choose, but it will need to be smaller than the fastest mode of motion.

One particularly good method is a *predictor–corrector* algorithm, of which the form given by Gear[3] is most commonly used. In the particular method we will discuss here (the so–called Nordsieck representation), molecular positions and several time derivatives, all evaluated at the same time, are stored. Remember: we can only apply such methods to *continuous* potentials. The method goes as follows:

1. Given the positions, velocities, etc. at time t, estimate the new positions, velocities, etc. at time $t + dt$ by a Taylor expansion about time t

$$\mathbf{r}^p(t+\delta t) = \mathbf{r}(t) + \delta t \mathbf{v}(t) + \frac{1}{2}\delta t^2 \mathbf{a}(t) + \frac{1}{6}\delta t^3 \mathbf{b}(t) + \cdots$$

$$\mathbf{v}^p(t+\delta t) = \mathbf{v}(t) + \delta t \mathbf{a}(t) + \frac{1}{2}\delta t^2 \mathbf{b}(t) + \cdots$$

$$\mathbf{a}^p(t+\delta t) = \mathbf{a}(t) + \delta t \mathbf{b}(t) + \cdots$$

$$\mathbf{b}^p(t+\delta t) = \mathbf{b}(t) + \cdots$$

   Note that the superscripts denote “predicted” values. We will “correct” these in a minute. The vectors $\mathbf{r}$ and $\mathbf{v}$ stand for the full position and velocity vectors. $\mathbf{a}$ is the accelerations and $\mathbf{b}$ is the third time derivative. Since we store four values, this is an example of a four–value predictor–corrector; in principle, we can go to higher orders, although this doesn’t necessarily imply higher accuracy.

   We have now advanced our positions and velocities to the next time step. However, repeated use of these equations will not generate the proper trajectories; we have not yet used the equations of motion! The equations of motion enter through the corrector step.

2. Calculate, using the predicted positions, $\mathbf{r}^p$, the forces at time $t + \delta t$. This will give the correct accelerations at this time ($\mathbf{a}^c(t + \delta t)$).

3. Compare the corrected accelerations with the predicted accelerations

$$\Delta \mathbf{a}(t+\delta t) = \mathbf{a}^c(t+\delta t) - \mathbf{a}^p(t+\delta t)$$

4. This error, along with the predicted quantities, are fed into the corrector routine, which typically has the form

$$\mathbf{r}^c(t+\delta t) = \mathbf{r}^p(t+\delta t) + c_0 \Delta \mathbf{a}(t+\delta t)$$

$$\mathbf{v}^c(t+\delta t) = \mathbf{v}^p(t+\delta t) + c_1 \Delta \mathbf{a}(t+\delta t)$$

$$\mathbf{a}^c(t+\delta t) = \mathbf{a}^p(t+\delta t) + c_2 \Delta \mathbf{a}(t+\delta t)$$

$$\mathbf{b}^c(t+\delta t) = \mathbf{b}^p(t+\delta t) + c_3 \Delta \mathbf{a}(t+\delta t)$$

   What are these coefficients, c_0, etc? The values depend upon the order of the equation being integrated. Coefficients for first and second order equations are given in Allen and Tildesley.

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[3] Gear, C. W.; *Numerical Initial Value Problems in Ordinary Differential Equations*, Prentice-Hall, 1971

5. After the corrector step, the values $\mathbf{r}^c(t+\delta t)$, etc. should now be closer to the "true" values. We may iterate on the corrector step; "new" corrected accelerations can be computed using the corrected positions $\mathbf{r}^c(t+\delta t)$, and the process repeated to refine the quantities. Convergence should be quite quick. In principle, then, the "predicted" positions don't have to be very good – convergence will be rapid even for a bad initial guess. However, since force evaluations are the most expensive part of a MD simulation, we only want to "correct" our values once (or at most, twice). Thus, an accurate predictor step (such as the Taylor series used here) is important.

6. We thus have the guts of an MD simulation:
   (a) Predict positions, velocities, etc. at time $t+\delta t$
   (b) evaluate forces (accelerations) from the new positions
   (c) correct positions, velocities, etc. using the new accelerations
   (d) Collect averages, if desired, then go back to the predictor step

The Gear predictor–corrector algorithm is not the only integration method, nor is it the most widely used. The *Verlet algorithm*, described next, holds this honor.

10.4.3 The Verlet Algorithm

The Verlet algorithm[4], of which there are many flavors, is the most commonly used integration scheme for MD. It is a direct solution of the second order MD equations, eqn 10.2. The basic equation for advancing the positions is

$$\mathbf{r}(t+\delta t) = 2\mathbf{r}(t) - \mathbf{r}(t-\delta t) + \delta t^2 \mathbf{a}(t) \tag{10.10}$$

We see that the method requires positions from the previous step, $\mathbf{r}(t-\delta t)$, and the accelerations at the current step. Interestingly, velocities do not appear explicitly in eqn 10.10. Where did they go? Eqn 10.10 is obtained by performing Taylor expansions about $\mathbf{r}(t)$:

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \delta \mathbf{v}(t) + (1/2)\delta t^2 \mathbf{a}(t) + (1/6)\delta t^3 \mathbf{b}(t) + \cdots$$

$$\mathbf{r}(t-\delta t) = \mathbf{r}(t) - \delta \mathbf{v}(t) + (1/2)\delta t^2 \mathbf{a}(t) - (1/6)\delta t^3 \mathbf{b}(t) + \cdots$$

Adding these two equations gives eqn 10.10, which we see eliminates velocities.

We do not really need velocities unless we wish to compute the temperature or total energy of the system. For these cases, we can estimate the velocities (and hence the kinetic energy) from

$$\mathbf{v}(t) = \frac{\mathbf{r}(t+\delta t) - \mathbf{r}(t-\delta t)}{2\delta t}$$

The Verlet algorithm (eqn 10.10) is accurate up to orders of δt^4, is time–reversible, and has excellent energy conservation properties. In addition, positions get advanced in one step, rather than two (as is the case in predictor–corrector methods). It is also easy to code (an example FORTRAN program is given in Allen and Tildesley). One problem is that a small value ($\mathcal{O}\delta t^2$) term is added to the difference of two relatively large ($\mathcal{O}\delta t$) terms; this can cause numerical imprecision.

To get around this last problem (and the awkward handling of velocities), Hockney introduced a modified form called the "leap–frog" Verlet.[5]

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[4] Verlet, L. *Phys. Rev.*, 159, 98-103, (1967)

[5] Hockney, R. W. *Methods Comput. Phys.*, 9, 136-211, (1970)

10.4.4 The Leap–Frog Verlet Algorithm

The term “leap–frog” is evident from the form of the equations

$$\mathbf{r}(t+\delta t)=\mathbf{r}(t)+\delta t\mathbf{v}(t+\frac{1}{2}\delta t) \tag{10.11}$$

$$\mathbf{v}(t+\frac{1}{2}\delta t)=\mathbf{v}(t-\frac{1}{2}\delta t)+\delta t\mathbf{a}(t) \tag{10.12}$$

To implement the method, we first advance velocities a half time step using eqn 10.11. The velocities ’leap over” the positions to give mid–step values (see the accompanying figure and eqn 10.12). During this step, the current velocities may be calculated from

$$\mathbf{v}(t)=\frac{1}{2}(\mathbf{v}(t+\frac{1}{2}\delta t)+\mathbf{v}(t-\frac{1}{2}\delta t)) \tag{10.13}$$

The half–step velocities are then used to propel the positions ahead to $t+\delta t$, using eqn 10.11. Accelerations at this step are evaluated and used to get the next half–step velocities, and the process is repeated.

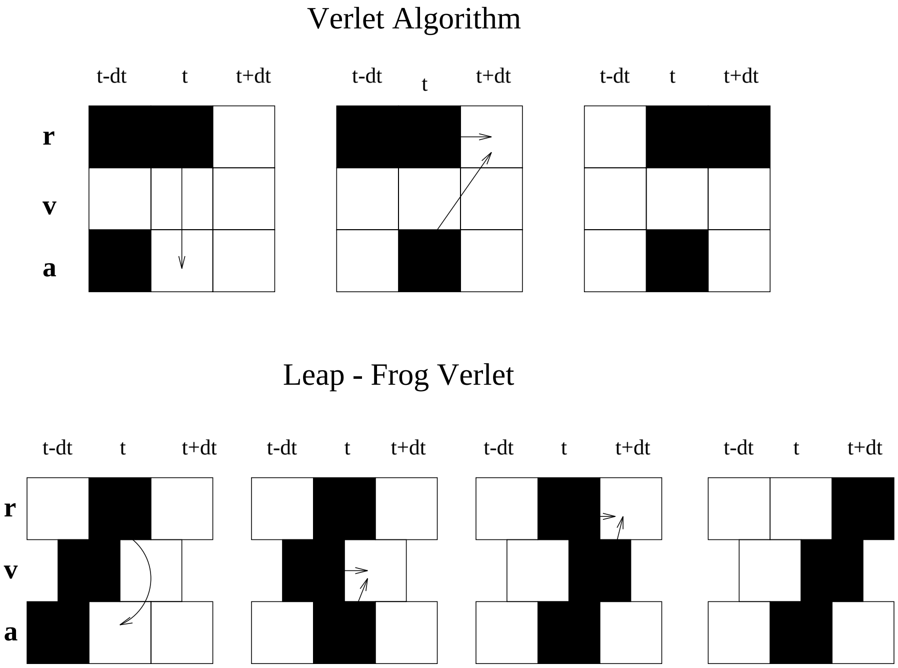

Figure 10.1: Pictorial representation of the flow of calculations involved in advancing positions in the Verlet technique (top) and the leap–frog method (bottom)

The standard Verlet method and the leap–frog method are compared in Figure 10.1 The leap–frog algorithm is algebraically equivalent to the Verlet algorithm. However, it does not involve taking the difference between large numbers to estimate a small quantity. Again, however, velocities are handled rather clumsily with eqn 10.13.

Perhaps the best Verlet algorithm proposed to date is the “velocity Verlet” algorithm of Swope, Andersen, Berens, and Wilson.[6] This algorithm has the form

$$\mathbf{r}(t+\delta t)=\mathbf{r}(t)+\delta t\mathbf{v}(t)+\frac{1}{2}\delta t^2\mathbf{a}(t)\mathbf{v}(t+\delta t)=\mathbf{v}(t)+\frac{1}{2}\delta t[\mathbf{a}(t)+\mathbf{a}(t+\delta t)] \tag{10.14}$$

To implement, the following steps are taken

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[6] see J. Chem. Phys., 76, 637-649 (1982)

1. Get the new positions at time $t + \delta t$ using

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \delta t \mathbf{v}(t) + \frac{1}{2}\delta t^2 \mathbf{a}(t)$$

2. Compute the velocities at mid–step:

$$\mathbf{v}(t + \frac{1}{2}\delta t) = \mathbf{v}(t) + \frac{1}{2}\delta t \mathbf{a}(t)$$

3. Compute the forces and accelerations at time $t + \delta t$
4. Get the velocity at $t + \delta t$

$$\mathbf{v}(t + \delta t) = \mathbf{v}(t + \frac{1}{2}\delta t) + \frac{1}{2}\delta t \mathbf{a}(t + \delta t)$$

5. Repeat the process...

The method is in some ways similar to predictor–corrector methods, since two steps are required to move the positions ahead one time step.

10.5 Molecular Dynamics of Rigid Non-Linear Polyatomic Molecules

We have so far focused on MD of simple molecules that can be represented as spheres. How does one go about conducting MD with polyatomic molecules? If we have potential expressions for all bonded forces, then the system can just be treated as a collection of atoms all interacting with each other. There are a number of problems with this. First, an extremely small time step is needed to track the fast vibrational modes. Recall that we want to use a large time step to enable us to simulate long time phenomena. If we have to simulate these fast modes, we "waste" a lot of time watching relatively uninteresting vibrational modes (unless, of course, that is what we are most interested in studying!). A second problem is that it is really somewhat questionable to allow such vibrations to occur "classically" anyway.

One solution to this problem is to "fix" the hard degrees of freedom and only track the slower, soft degrees of freedom. For things like bond lengths, this is a pretty reasonable thing to do. For bond angles, it is less reasonable and for torsion angles, it is probably unacceptable. Another approach, which we will discuss in class if we have time but which won't be covered in these notes, is to use *multiple time step* algorithms to solve the equations of motion. This method was proposed by Berne and co-workers[7], and involves a "breaking up" of the Liouvillian operator into hard and soft degrees of freedom. The hard degrees of freedom are integrated with a small time step and the soft degrees of freedom are integrated with a long time step. Intermolecular force calculations, which take the bulk of computational time, are integrated with the long time step, so the method enables long time trajectories to be generated while still handling fluctuations in the hard degrees of freedom "exactly". (Our group has found that this method, called r-RESPA for reversible reference system propagator algorithm, can significantly speed up MD calculations. It is about as fast as constraint methods, but easier to program and it does allow hard degrees of freedom to fluctuate. From my standpoint, I can see no reason why constraint dynamics are used anymore. Nevertheless, they are still used, so we will discuss them here).

Fixing bond lengths and/or angles amounts to introducing constraints among the Cartesian coordinates of atoms. That is, all coordinates are no longer independent. (e.g. If the bond between atoms 1 and 2 is fixed, then there is a constraint such that $\mathbf{r}_1 - \mathbf{r}_2| = d$) For now, let's consider rigid, non-linear polyatomic molecules. The orientation of a rigid body specifies the relation between an axis system fixed in space and one fixed with respect to the body. We may specify any unit vector $\mathbf{v}$ in terms of components in body–fixed or space–fixed frames. We will use the notation

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[7] *J. Chem. Phys.*, 94, 6811, (1991).

$\mathbf{v}^b$ and $\mathbf{v}^s$ to refer to the body-fixed and space-fixed representations of this vector. The relationship between the two frames of reference are given by a rotation matrix, $\mathbf{A}$

$$\mathbf{v}^b = \mathbf{A} \cdot \mathbf{v}^s$$

There are nine components in the rotation matrix, which completely define the orientation of the molecule. There are only *three independent* quantities (generalized coordinates) necessary to specify $\mathbf{A}$, however. Following Goldstein,[8] we define the generalized coordinates as the Euler angles ϕ, θ, ψ (see Figure 10.2). We see that the primed coordinates in the figure represent the body-fixed frame, while the unprimed coordinates are the fixed-space frame. The transformation matrix has the form

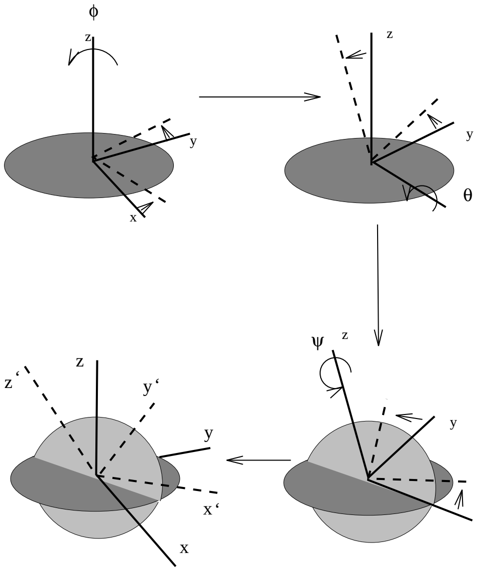

Figure 10.2: Definitions of the Eulerian angles (after Goldstein)

$$\mathbf{A} =$$
$$\begin{pmatrix} \cos\phi\cos\psi - \sin\phi\cos\theta\sin\psi & \sin\phi\cos\psi + \cos\phi\cos\theta\sin\psi & \sin\theta\sin\psi \\ -\cos\phi\sin\psi - \sin\phi\cos\theta\cos\psi & -\sin\phi\sin\psi + \cos\phi\cos\theta\cos\psi & \sin\theta\cos\psi \\ \sin\phi\sin\theta & cos\phi\sin\theta & \cos\theta \end{pmatrix}$$

$\mathbf{A}$ is orthogonal: $\mathbf{A}^{-1} = \mathbf{A}^T$

We can categorize motion as

1. Center-of-mass translation

   Here we consider the total force acting on the center of mass, $\mathbf{F}_i$. The relevant equation is

   $$m\ddot{\mathbf{r}}_i = \mathbf{F}_i$$

   This gives us a linear velocity for the center of mass, $\dot{\mathbf{r}}_{cm}$

2. Rotational motion is governed by the torque τ_i about the center of mass $\mathbf{r}_i$. If the force acting on site α is $\mathbf{F}_\alpha$, then the torque is simply

   $$\tau_i = \sum_\alpha (\mathbf{r}_{i\alpha} - \mathbf{r}_i) \times \mathbf{F}_{i\alpha} = \sum_\alpha \mathbf{r}'_\alpha \times \mathbf{F}_\alpha$$

   This gives us an angular velocity, ω.

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[8] Goldstein, H. *Classical Mechanics*, 1980

Before writing down the equations of motion, let us define some quantities

- Angular momentum

$$\mathbf{L} = \sum_\alpha m_\alpha \mathbf{r}'_\alpha \times \dot{\mathbf{r}}'_\alpha$$

From this, one can show

$$\mathbf{L} = \mathbf{I} \cdot \omega$$

where **I** is the moment of inertia tensor

$$\mathbf{I} = \sum_\alpha m_\alpha ((r'_\alpha)^2 \mathbf{1} - \mathbf{r}'_\alpha \mathbf{r}'_\alpha)$$

One can finally write the full set of dynamical equations of rotational motion in the generalized coordinates ϕ, θ, ψ as

- Torque:

$$\tau^s = \sum_\alpha (\mathbf{r}^s_\alpha - \mathbf{r}^s_{cm}) \times \mathbf{F}_\alpha$$

(Recall that $\tau^b = \mathbf{A} \cdot \tau^s$)

- Rate of change of angular velocity (the so–called Euler equations)

$$\dot{\omega}^b_x = \frac{\tau^b_x}{I_{xx}} + \left(\frac{I_{yy} - I_{zz}}{I_{xx}}\right) \omega^b_y \omega^b_z$$

$$\dot{\omega}^b_y = \frac{\tau^b_y}{I_{yy}} + \left(\frac{I_{zz} - I_{xx}}{I_{yy}}\right) \omega^b_z \omega^b_x$$

$$\dot{\omega}^b_z = \frac{\tau^b_z}{I_{zz}} + \left(\frac{I_{xx} - I_{yy}}{I_{zz}}\right) \omega^b_x \omega^b_y$$

where I_{xx}, I_{yy}, I_{zz} are the three principle moments of inertia.

- Euler angles change with time as

$$\dot{\phi} = -\omega^s_x \frac{\sin\phi \cos\theta}{\sin\theta} + \omega^s_y \frac{\cos\phi \cos\theta}{\sin\theta} + \omega^s_z$$

$$\dot{\theta} = \omega^s_x \cos\phi + \omega^s_y \sin\phi$$

$$\dot{\psi} = \omega^s_x \frac{\sin\phi}{\sin\theta} - \omega^s_y \frac{\cos\phi}{\sin\theta}$$

The above equations apply to each molecule and can be solved in a stepwise fashion just as we have done with translational motion. There is a problem. The $\sin\theta$ term in the denominators causes numerical problems when θ is close to 0 or π (at these points, ϕ and ψ become degenerate).[9]

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[9] There are special techniques that can handle this problem See Evans, D. J. *Mol. Phys.*, 34, 317-325 (1977)

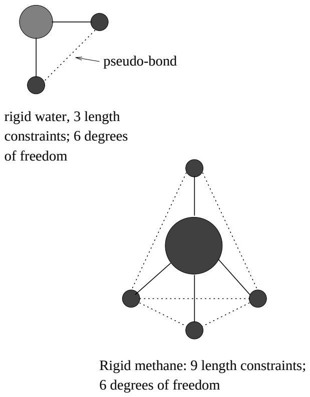

Figure 10.3: Pseudo-bonds showing how constraints would be imposed on a 3-atom “bent” molecule and a tetrahedrally oriented molecule (like methane)

10.5.1 Constraint Dynamics

For molecules with torsional degrees of freedom, formulating the dynamical equations of motion in generalized coordinates is very laborious. An alternative, and simpler, approach is to formulate and carry out the MD simulation in Cartesian coordinates and the RESPA method to handle the disparate time scales. We could also constrain the hard degrees of freedom to positions at or near their equilibrium values. So–called “constraint dynamics” enables one to do this fairly easily. We seek to integrate the equations of motion for a system of particles subject to constraints. The advantages:

- No laborious transformations required between fixed and internal coordinates.
- Algorithm ensures that constraints are satisfied (i.e. molecular shape is preserved)
- Applicable to any arbitrarily selected degrees of freedom; others allowed to remain flexible.

How does one impose constraints? To impose bond length constraints is relatively simple. We try to fix bonded atomic distances about the equilibrium value. For bond angles, we can use “pseudo–bonds” to triangulate the molecule, as in Figure 10.3 Each length constraint will result in a force acting along the bond or pseudo-bond. These constraint forces must therefore appear in the Newtonian equations of motion for the molecule.

As an example, consider the equations for water with fixed bond lengths (but flexible bond angles), as shown in Figure 10.4. In this figure, $\mathbf{g}_1$ is the constraint force on atom 1 due to bond 12; $-\mathbf{g}_1$ is the constraint force on atom 2 due to bond 12; $\mathbf{g}_3$ is the constraint force on atom 3 due to bond 23; and $-\mathbf{g}_3$ is the constraint force on atom 2 due to bond 23. The dynamical equations can therefore be written as:

1. 9 differential equations

$$m_1\ddot{\mathbf{r}}_1 = \mathbf{F}_1 + \mathbf{g}_1$$

$$m_3\ddot{\mathbf{r}}_3 = \mathbf{F}_3 + \mathbf{g}_3$$

$$m_2\ddot{\mathbf{r}}_2 = \mathbf{F}_2 - \mathbf{g}_1 - \mathbf{g}_3$$

2. 6 equations in terms of the undetermined multipliers, λ

$$\mathbf{g}_1 = \lambda_{12}(\mathbf{r}_1 - \mathbf{r}_2)$$

$$\mathbf{g}_3 = \lambda_{23}(\mathbf{r}_3 - \mathbf{r}_2)$$

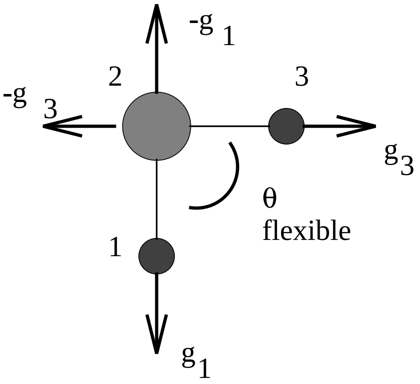

Figure 10.4: Constraint forces along the bonds of a water molecule having fixed bond lengths

3. 2 constraint equations

$$\chi_{12} = (\mathbf{r}_1 - \mathbf{r}_2)^2 - d_{12}^2 = 0$$

$$\chi_{23} = (\mathbf{r}_3 - \mathbf{r}_2)^2 - d_{23}^2 = 0$$

Note that one could also formally start with the Lagrangian formulation, where the magnitudes of constraint forces appear as undetermined (Lagrange) multipliers. In this case, one would write the Lagrangian as

$$\mathcal{L} = \mathcal{K} - \mathcal{V} + \frac{1}{2}\lambda_{12}\chi_{12} + \frac{1}{2}\lambda_{23}\chi_{23} \tag{10.15}$$

and the equations of motion would just come from

$$\frac{d}{dt}(\nabla_{\dot{\mathbf{r}}_i}\mathcal{L}) - \frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} = 0; \; i = 1, 2, 3 \tag{10.16}$$

Algorithms For Implementing Constraint Dynamics

The constraint equations we developed are exact. However, if we try to solve them using finite difference techniques (which only solve the equations of motion approximately), our "constrained" degrees of freedom will eventually distort (i.e "constrained" bond lengths will fly apart). A straightforward way of circumventing this problem is as follows:

1. Advance the positions 1 step using a Verlet algorithm. Ignore the constraint forces.

$$\mathbf{r}_i'(t + \delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \delta t) + \frac{\delta t^2}{m_i}\mathbf{F}_i(t)$$

This gives us "distorted" molecules at positions $\mathbf{r}'$ at $t + \delta t$.

2. The *actual* positions of the atoms, if we took into account constraint forces, would be

$$\mathbf{r}_i(t + \delta t; \lambda_{ij}) = \mathbf{r}_i'(t + \delta t) + \frac{\delta t^2}{m_i}\mathbf{g}_i(t; \lambda_{ij})$$

$$= \mathbf{r}_i'(t + \delta t) - \frac{\delta t^2}{m_i}\sum_j \lambda_{ij}\mathbf{r}_{ij}(t)$$

where the λ_{ij} are not yet determined.

3. Substitute the above expression for $\mathbf{r}_i(t+\delta t;\lambda_{ij})$ into the constraint equations. The result

   $$[\mathbf{r}_i(t+\delta t;\lambda_{ij}) - \mathbf{r}_j(t+\delta t;\lambda_{ij})]^2 - d_{ij}^2 = 0$$

   This is a set of quadratic algebraic equations in λ_{ij}. The solution must be obtained iteratively, usually by successive substitutions. Thus, the solution of a set of $n_c \times n_c$ linear equations is required at each iteration, where n_c is the number of constraints in a given molecule. Finally, substitute the determined λ_{ij} into the expressions for $\mathbf{r}_i(t+\delta t;\lambda_{ij})$ and get the actual atomic positions at $t+\delta t$. This completes one integration step.

Inversion of a matrix of dimension $n_c \times n_c$ becomes very time consuming for large, polyatomic molecules. We would like to use another approach for more complex molecules.

Other Constraint Dynamics Techniques

As an alternative, we could go through the constraints one–by–one, cyclically adjusting the coordinates so as to satisfy each in turn. The procedure could be iterated until all the constraints are satisfied within a given tolerance. Such a procedure was outlined by Ryckaert et al.[10] and was given the name SHAKE. The SHAKE algorithm is very popular and is used extensively in polymeric and biological simulations. It is easy to code and works well. It can be inefficient, especially in the presence of bond angle constraints. It is easiest to apply to Verlet integration schemes.

Andersen[11] extended the SHAKE algorithm for use with the velocity Verlet integration algorithm. This algorithm is known as RATTLE.

To improve the efficiency of the constraint methods, Edberg et al. (*J. Chem. Phys.*, 84, 6933, (1986)) proposed the following technique (which doesn't have a cute name, but which is extremely useful).

1. In place of the quadratic equations for the constraint forces $\{\lambda_{ij}\}$, use a *linear* system of equations in $\{\lambda_{ij}\}$

2. Instead of the constraint equations, use their second time derivatives. That is

   $$(\mathbf{r}_i - \mathbf{r}_j)^2 - d_{ij}^2 = \mathbf{r}_{ij}^2 - d_{ij}^2 = 0$$

   is instead written as

   $$\mathbf{r}_{ij} \cdot \ddot{\mathbf{r}}_{ij} + (\dot{\mathbf{r}}_{ij})^2 = 0$$

3. The idea is to then solve the following system of differential and algebraic equations simultaneously

   $$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i + \sum_j \lambda_{ij} \mathbf{r}_{ij}$$

   $$\mathbf{r}_{ij} \cdot \ddot{\mathbf{r}}_{ij} + (\dot{\mathbf{r}}_{ij})^2 = 0$$

4. Notice that the velocities enter the formulation explicitly. Determination of the set $\{\lambda_{ij}\}$ requires the solution of a linear matrix equation, which can be done quite rapidly on a computer with canned packages. The standard predictor–corrector or velocity Verlet algorithm may be used with this technique.

5. Molecular shape will gradually distort as numerical error accumulates. (The bond lengths d_{ij} do not appear in the dynamical equations!) We must periodically restore the correct molecular geometry by minimizing the following penalty functions

   Bond:

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[10] *J. Comput. Phys.*, 23, 327, (1977)

[11] *J. Comput. Phys.*, 52, 24-34, (1983)

$$\Phi = \sum_{ij} (\mathbf{r}_{ij}^2 - d_{ij}^2)^2$$

Velocity:

$$\Psi = \sum_{ij} (\mathbf{r}_{ij} \cdot \dot{\mathbf{r}}_{ij})^2$$

10.5.2 General Comments on the Choice of Algorithms

Here are some rule-of-thumb recommendations.

- For simple fluids (monatomic), use the velocity Verlet algorithm.
- For rigid polyatomics, there are two choices that are comparable:
  1. MD in generalized coordinates, with the "fix" for $\sin\theta$ diverging (we didn't talk about this) or
  2. Constraint methods that set a rigid core of "primary" atoms.
- For flexible, polyatomics, constraint methods such as EEM, or RATTLE are OK, but the newer r-RESPA technique is preferable.
- It is better to constrain bonds only and not bond angles if you can at all help it. This more accurately reflects the dynamics of the system.

10.6 Molecular Dynamics In Other Ensembles

A problem with standard MD is that it occurs in the *microcanonical* ensemble. That is, the temperature of the simulation fluctuates, while the energy stays constant. Recall that the temperature in an NVE simulation is

$$T = < \mathcal{T} >$$

where $< \mathcal{T} >$ is an ensemble average temperature, estimated as a time average at equilibrium. The instantaneous temperature is

$$\mathcal{T} = \frac{2\mathcal{K}}{(3N - N_c)k_B} = \frac{1}{(3N - N_c)k_b} \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{m_i} \tag{10.17}$$

where N is the number of atoms in the system, each with mass m_i and momentum $\mathbf{p}_i$. N_c is the total number of constraints. This includes *internal constraints,* such as fixed bond lengths, *and global constraints* such as fixed total momentum. In an $NVE\mathbf{P}$ simulation with $\mathbf{P} = 0$, $N_c = 3$

Also recall that from the virial theorem that

$$P = < \mathcal{P} >$$

where the instantaneous pressure, $\mathcal{P}$ is given by

$$\mathcal{P} = \rho k_B \mathcal{T} + \frac{1}{3V} \sum_i \sum_{j>i} (\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_{ij} \tag{10.18}$$

where $\mathbf{F}_{ij}$ is the force on i due to j.

We saw how to relate fluctuations in the potential energy (or kinetic energy) to the heat capacity:

$$< \delta\mathcal{V}^2 >=< \delta\mathcal{K}^2 >= \frac{3}{2}Nk_B^2T^2\left(1 - \frac{3Nk_B}{2C_v}\right) \tag{10.19}$$

The problem with NVE MD is that if one wants to conduct a simulation at a given temperature, you can only get “close” to this value. That is, you are not free to set the temperature at the beginning of a simulation. Instead, the temperature will fluctuate about some value which you take as the “average” temperature of the system. It would be desirable to adapt MD so that the simulations could be conducted in the *canonical ensemble*. There are a number of ways of doing this.

10.6.1 Stochastic Methods

We can think of the canonical ensemble as corresponding to a system of molecules that have a weak interaction with a heat bath at a given temperature. Using this picture, we can construct an MD simulation that can be shown to sample from the canonical ensemble. The idea is as follows.

At certain intervals, we pick a molecule. We then assume that this molecule has “thermalized” with a heat bath; we re-assign it’s velocity from a Maxwell–Boltzmann distribution corresponding to the desired temperature. (This attempts to simulate the collision of the molecule with an imaginary heat bath particle). The system moves through phase space on a constant energy hypersurface until the velocity of one molecule is changed. At this point, the system jumps onto another energy surface, and the Hamiltonian motion proceeds. The system samples all the regions of phase space about the mean temperature. One can show that such a method does indeed sample from the canonical ensemble.

The choice of “collision frequency” is somewhat arbitrary. Infrequent collisions translate to slow energy fluctuations but relatively large kinetic energy fluctuations. Frequent collisions cause the dynamics to be dominated by the heat bath, rather than by the systematic forces present in the system. To mimic a real fluid, it is suggested that the collision rate be given by

$$r \propto \frac{\lambda_T}{\rho^{\frac{1}{3}}N^{\frac{2}{3}}} \tag{10.20}$$

where λ_T is the thermal conductivity. Too high a collision rate leads to an exponential decay in the correlation functions (to be discussed later) which is not observed experimentally.

We can also alter the velocities of *all* the molecules at the same time, less frequently, at equally spaced intervals. These rescaling events correspond to “massive stochastic collisions”. In between such rescaling events, normal statistics (i.e correlation functions) may be computed. Such a method also provides averages consistent with the canonical ensemble. However, such a method is very crude in that the dynamics of the system are greatly perturbed.

10.6.2 Extended System Methods

A somewhat better method of coupling the molecules to a heat bath is to use so–called “extended system” methods. In this approach, an extra degree of freedom, representing a thermal reservoir, is added to the simulation. Other constraints can be imposed by adding additional degrees of freedom, representing other “reservoirs”. Each new degree of freedom has associated with it a “coordinate”, a “velocity” (i.e. rate of change), and a “mass” (i.e. inertia).

A common method is the one introduced by Nosé.[12] In this method, the extra degree of freedom is given the the symbol s. The conjugate momentum is denoted p_s, and the velocities of the real molecules are related to the time derivatives of the positions by

$$\mathbf{v} = s\dot{\mathbf{r}} = \mathbf{p}/ms \tag{10.21}$$

In essence, s is a scaling factor for time. A real time step equals a simulation time step divided by s.

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[12] Nosé, S. *Mol. Phys.*, 52, 255, (1984)

There is an extra potential energy associated with s

$$\mathcal{V}_s = (3N - N_c + 1)k_BT \ln s \tag{10.22}$$

where the desired temperature is given by T. A kinetic energy term also can be written as

$$\mathcal{K}_s = \frac{1}{2}Q\dot{s}^2 = p_s^2/2Q \tag{10.23}$$

where Q is a "thermal inertia" parameter. Q has units of (energy)×(time)^2, and controls the rate of temperature fluctuations. In can be shown that the proper equations of motion for this system are

$$\ddot{\mathbf{r}}_i = \frac{\mathbf{F}_i}{m_i s^2} - \frac{2\dot{s}\dot{\mathbf{r}}_i}{s} \tag{10.24}$$

$$Q\ddot{s} = \sum_i m\dot{\mathbf{r}}_i^2 s - \frac{(3N - N_c + 1)k_BT}{s} \tag{10.25}$$

These equations can be integrated using a standard integration algorithm.

The extended Hamiltonian of the system is conserved (rather than the "real" Hamiltonian):

$$\mathcal{H}_s = \mathcal{K} + \mathcal{K}_s + \mathcal{V} + \mathcal{V}_s \tag{10.26}$$

Nosé proved that the partition function corresponding to this Hamiltonian yields a canonical distribution in the variables $\mathbf{p}'$ and $\mathbf{r}$, where

$$\mathbf{p}' = \frac{\mathbf{p}}{s}$$

Thus, the simulation time in Nosé's algorithm is not the "real" time; equal simulation time steps may be unequal in real time. The averaged real time duration of a simulation is obtained by multiplying the simulation time by $< s^{-1} >$.

Just as in the case of stochastic methods, the choice of the inertia parameter, Q, will affect the results. We can examine a few limiting cases. When $Q \rightarrow \infty$, there is a large inertia which resists change in temperature. In this case, NVE MD is recovered. When $Q \rightarrow 0$, there is an "instantaneous" thermalization which perturbs the dynamics severely. This is the same as re-scaling the velocities of all the molecules at every time step. For "reasonable" choices of Q, it is thought that the dynamical properties determined with this method agree with NVE MD. "Reasonable" values of Q can be obtained by looking at fluctuations in s. The period in s–oscillations is

$$t_0 = 2\pi \left(\frac{Q < s^2 >}{2(3N - N_c)k_B < \mathcal{T} >} \right)^{1/2} \tag{10.27}$$

Nosé recommends t_0 of 1 ps.

10.6.3 Constraint Methods

A simple means for fixing the temperature during an MD simulation is to rescale the velocities at each time step by $(T/\mathcal{T})^{1/2}$. This so-called "velocity rescaling" approach is a good method for equilibrating an MD simulation, and has been used as a crude means for performing NVT MD. However, simple velocity rescaling is not the best way of constraining the kinetic energy, however. A better method was proposed by Hoover[13] and elaborated on by Evans and Morriss.[14] In this approach, the equations of motion for constant kinetic energy simulations are

$$\dot{\mathbf{r}}_i = \mathbf{p}_i/m_i \tag{10.28}$$

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[13] *A. Rev. Phys. Chem.*, 34, 103-127, (1983)

[14] *Comput. Phys. Rep.*, 1, 297-344 (1984).

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \xi(\mathbf{r},\mathbf{p})\mathbf{p} \tag{10.29}$$

where $\xi(\mathbf{r},\mathbf{p})$ is a "friction coefficient" that serves to constrain the instantaneous temperature, $\mathcal{T}$, to a constant value. One can show that

$$\xi = \frac{\sum_i \mathbf{p}_i \mathbf{F}_i}{\sum_i |\mathbf{p}_i|^2} \tag{10.30}$$

These equations of motion generate a trajectory in the constant $NV\mathcal{T}$ ensemble, which can be shown to have the same configurational properties as the canonical ensemble. Allen and Tildesley provide a leap–frog algorithm that uses this method.

There are other constant–temperature MD algorithms and there are also extended system and constraint methods for carrying out constant *pressure* molecular dynamics.

10.7 Structural Information From MD (and MC)

When an MD simulation is carried out, the information we get is the molecular positions, velocities, and energies as a function of time. Normally, we write this information out to a file periodically. The question is, what do we do with this information? A more immediate question is: how frequently should I write this information to file?

You might think that we should write every single configuration to file. There are two problems with this. First, writes or reads from disk (called "I/O" for input/output) are very slow. Excessive I/O will significantly slow down any simulation. We'd like to minimize these operations. Another more mundane reason that you don't want to do this is that you only have a finite amount of disk space to work with. A simple back of the envelop calculation shows that the three Cartesian positions and velocities for a molecule, along with the time, consumes $7 \times 8 = 56$ bytes of space for each "write" to disk. For a system with 1000 atoms, this means that approximately 50 Kbytes are required for each write. A typical MD simulation may require 1-100 million time steps to complete. Clearly, disk space becomes a concern for these simulations! On the other hand, configuration "dumps" should be done frequently enough so that good statistics are obtained and the modes you are interested in can be analyzed.

You may ask: why write anything to disk at all? Why not calculate all the properties of interest during the course of the simulation? This can be done, but there are risks involved. First of all, when performing long simulations (as these tend to be) you must protect yourself from "crashes". Although computer systems are pretty stable, jobs can "crash" for a variety of reasons, including power failure, etc. Writing results to disk enables you to restart crashed jobs, and thus save potentially "wasted" simulation time. More importantly, however, this type of "tape" file can be analyzed at your leisure after a simulation to obtain structural and dynamic information. The advantage of this approach is that you don't have to remember to do everything during the simulation. If interesting phenomena are uncovered, detailed probing ("mining") of the results can be easily accomplished.

We will being by considering the way on which static, structural quantities are computed from a set of MD configurations. In this discussion, there is no difference between the way in which this is done from an MD or MC simulation. That is, in an MC simulation, we also want to write out position "snapshots" (there are no velocities!) as a function of MC cycle. After this, we will then on to consider ways in which dynamical properties are computed from an MD trajectory.

10.7.1 Pair Distribution Functions

Recall that in an isotropic material, the pair distribution function is defined as

$$g(r) = \frac{\rho(r)}{\rho}$$

where $\rho(r)$ is the local density of particles within a spherical shell of radius r to $r + dr$, centered at a given particle in the fluid, and averaged over all configurations (refer to Figure 10.5) and ρ is the mean (macroscopic) density.

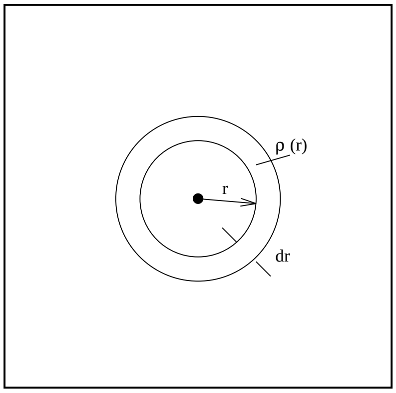

Figure 10.5: A schematic showing a differential "ring" about a molecule where a local density can be defined and used to compute a pair distribution function

We wish to answer: How do you compute $g(r)$ from a tape file? To do this, you analyze the stored configurations to determine distances between the minimum image pairs. $g(r)$ is equal to the number of particles at distance r to $r + dr$ from a central particle, divided by the number of particles at distance r to $r + dr$ from a central particle in an ideal gas system *of the same density*. To compute the numerator of $g(r)$, you first discretize the r-axis from 0 to r_{max} into bins of width dr. (Below, we let b be the index of a bin between r and $r + dr$. Then, loop over all stored configurations and perform the following steps:

1. Within this loop, loop over all pairs (i, j) in a given configuration.
2. Calculate the minimum image distance $(r_{ij})_{min}$.
3. Sort this distance; that is, determine which bin b the distance falls in.
4. Add 2 to the contents of this bin. (1 for each molecule).

$$n_{his}(b) = n_{his}(b) + 2$$

After this, go back to the next stored configuration until you've looped over them all. The numerator for each bin of $g(r)$ is then

$$n(b) = \frac{n_{his}(b)}{N\tau_{run}}$$

where N is the total number of particles and τ_{run} is the total number of configurations analyzed.

For the denominator (distribution of molecules in ideal gas phase at the same density) we simply have for each bin

$$n^{id}(b) = \frac{4\pi\rho}{3}\left[(r + dr)^3 - r^3\right]$$

where the term in brackets yields the volume of a spherical shell between r and $r + dr$. ρ is the average density. Note that this expression is only valid for $r_{max} \leq L/2$, To compute $g(r)$, use the histogram of information:

$$g(r + \frac{1}{2}dr) = \frac{n(b)}{n^{id}(b)}$$

For molecular fluids, we may compute site-site distribution functions $g_{\alpha\beta}(r)$ in the same way. As we showed earlier, $g(r)$ is extremely important for computing thermodynamic properties, and for making comparisons with experiment.

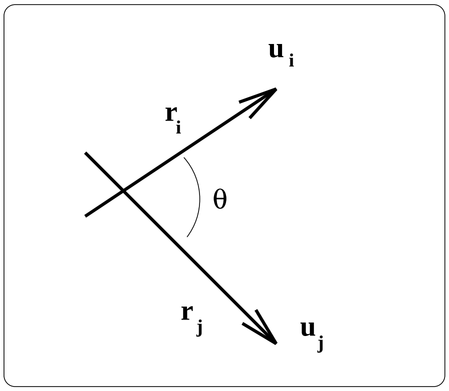

Figure 10.6: The angle between two vectors, defining some molecular order or structure, can be examined as a means of determining the structure of a fluid.

10.7.2 Molecular Orientation

Often, we are interested in quantifying the molecular structure. One way of doing this is through the use of *order parameters*. Consider Figure 10.6. Let $\mathbf{u}_i$ be a unit vector attached to a molecule (i.e. a bond vector, end–to–end vector, etc.). The angle formed by two such vectors is θ. A useful order parameter for studying the decorrelation of molecular structure is to form the 2nd Legendre polynomial of the first kind of the cosine of θ. That is

$$P_2(\cos\theta) = \frac{1}{2}[3(\mathbf{u}_i \cdot \mathbf{u}_j)^2 - 1] \tag{10.31}$$

This provides information on the orientation of i and j.

A useful order parameter to track might be

$$< P_2(\cos\theta) >_{|\mathbf{r}_i - \mathbf{r}_j| = r} = \frac{1}{2}[3 < \mathbf{u}_i \cdot \mathbf{u}_j >^2_{|\mathbf{r}_i - \mathbf{r}_j| = r} -1] \tag{10.32}$$

as a function of r. This order parameter equals 1 for parallel orientations, -1/2 for perpendicular, and 0 for random orientations.[15]

10.8 Dynamical Information From Equilibrium MD

Dynamical information usually refers to *time correlation functions*.[16] Consider a system at equilibrium under some given external constraint. The probability distribution of the system in phase space will conform to an equilibrium ensemble with probability density $\rho^{eq}(\mathbf{p}^N, \mathbf{q}^N)$.

Let us consider two quantities $\mathcal{A}$ and $\mathcal{B}$ which are functions of the phase–space representative point. That is, $\mathcal{A}(\mathbf{p}^N, \mathbf{q}^N)$ and $\mathcal{B}(\mathbf{p}^N, \mathbf{q}^N)$

As the microscopic state changes with time, so does the value of $\mathcal{A}$ and $\mathcal{B}$. We will use the notation

$$\mathcal{A}(t) \equiv \mathcal{A}(\mathbf{p}^N, \mathbf{q}^N)$$

$$\mathcal{B}(t) \equiv \mathcal{B}(\mathbf{p}^N, \mathbf{q}^N)$$

---

[15] Recall that for two randomly oriented vectors having an angle θ between them, $< \cos\theta >= 1/3$

[16] see McQuarrie for good information of the statistical mechanics of time correlation functions

In addition, we will denote the deviations between the instantaneous values of $\mathcal{A}$ and $\mathcal{B}$ along a dynamical trajectory and the corresponding ensemble averaged values as

$$\delta\mathcal{A}(t) \equiv \mathcal{A}(t) - < \mathcal{A}(t) > = \mathcal{A}(t) - < \mathcal{A} >$$

$$\delta\mathcal{B}(t) \equiv \mathcal{B}(t) - < \mathcal{B}(t) > = \mathcal{B}(t) - < \mathcal{B} >$$

where we have used the fact that ensemble averages are invariant with time. Next, we *define* the non–normalized time correlation function between $\mathcal{A}$ and $\mathcal{B}$ by

$$C_{\mathcal{A}\mathcal{B}}(t) \equiv < \delta\mathcal{A}(t_1)\delta\mathcal{B}(t_1+t) > = \langle [\mathcal{A}(t_1) - < \mathcal{A} >][\mathcal{B}(t_1+t) - < \mathcal{B} >] \rangle \tag{10.33}$$

There are two key points about this last equation:

1. For a system at equilibrium, the ensemble average on the right–hand side of the last equation will *not depend on the time origin* t_1*, but only on the time separation* t.
2. By the ergodic hypothesis, *the ensemble averages in the last equation can be substituted by time averages over all time origins* t_1.

Therefore, we may write

$$C_{\mathcal{A}\mathcal{B}}(t) = C_{\mathcal{A}\mathcal{B}}(-t) = \langle \delta\mathcal{A}(0)\delta\mathcal{B}(t) \rangle = \langle \delta\mathcal{A}(t)\delta\mathcal{B}(0) \rangle \tag{10.34}$$

You should convince yourself that this expression is true.

If we restrict our attention to the special case where $\mathcal{A}$ and $\mathcal{B}$ are the same quantity, we have

$$C_{\mathcal{A}\mathcal{A}}(t) = \langle \delta\mathcal{A}(t_1)\delta\mathcal{A}(t_1+t) \rangle = \langle \delta\mathcal{A}(0)\delta\mathcal{A}(t) \rangle \tag{10.35}$$

We will call $C_{\mathcal{A}\mathcal{A}}(t)$ the non–normalized (time) autocorrelation function of $\mathcal{A}$.

We define the normalized autocorrelation function of $\mathcal{A}$ as

$$c_{\mathcal{A}\mathcal{A}}(t) = \frac{C_{\mathcal{A}\mathcal{A}}(t)}{C_{\mathcal{A}\mathcal{A}}(0)} = \frac{\langle \delta\mathcal{A}(t)\delta\mathcal{A}(0) \rangle}{\langle (\delta\mathcal{A})^2 \rangle} \tag{10.36}$$

(Notice that the term $\langle (\delta\mathcal{A})^2 \rangle$ is a measure of the fluctuation of $\mathcal{A}$ and has its own thermodynamic meaning.)

Physically, what does $c_{\mathcal{A}\mathcal{A}}(t)$ represent? We see that for $t = 0$, $c_{\mathcal{A}\mathcal{A}}(t) = 1$. When $c_{\mathcal{A}\mathcal{A}} = 1$, there is a perfect correlation of the quantity $\mathcal{A}$ with it's value at the time origin. For $t > 0$, $c_{\mathcal{A}\mathcal{A}}$ typically decays from 1, eventually reaching zero as $t \to \infty$. $c_{\mathcal{A}\mathcal{A}}$ *measures how the property* $\mathcal{A}$ *loses memory of its initial value* as a result of molecular motion in the system. The characteristic time over which memory persists is called the correlation time, and is defined by

$$\tau_{\mathcal{A}} = \int_0^\infty c_{\mathcal{A}\mathcal{A}}(t)dt \tag{10.37}$$

For many (but certainly not all) systems, $c_{\mathcal{A}\mathcal{A}}(t)$ is found to decay exponentially with time at long times, as is shown in Figure 10.7.

Why do we care about autocorrelation functions? There are three primary reasons. First, they give a picture of molecular motion in a system. Second, the time integrals $\tau_{\mathcal{A}}$ are often directly related to macroscopic transport coefficients (more on this later). Finally, the Fourier transform of $c_{\mathcal{A}\mathcal{A}}(t) = \hat{c}_{\mathcal{A}\mathcal{A}}(\omega)$ are often related to experimental spectra.

Consider as an example the *velocity autocorrelation function* for a fluid. Here, our quantity $\mathcal{A}$ is the velocity.

$$C_{v_\alpha v_\alpha}(t) = \langle v_{i\alpha}(t)v_{i\alpha}(0) \rangle \tag{10.38}$$

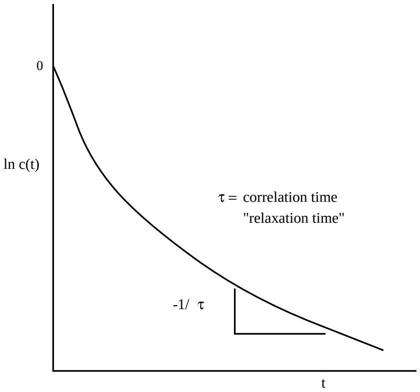

Figure 10.7: By plotting the logarithm of an exponentially–decaying time correlation function, one may obtain an estimate of the decorrelation time by determining the slope

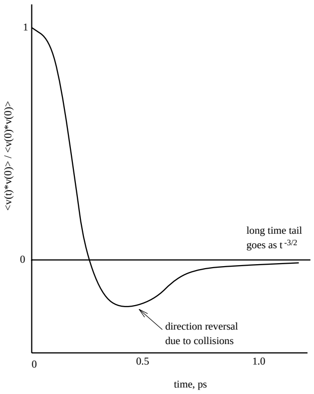

Figure 10.8: The velocity autocorrelation function for argon near the triple point. The negative region indicates a "backscattering" motion in which molecules collide with neighbors. The long–time decay to zero indicates complete decorrelation

where $\delta v_{i\alpha} \equiv v_{i\alpha}$, since $\langle v_{i\alpha} \rangle = 0$. In a simulation, we can average over all equivalent species to increase the sample size and improve statistics

$$C_{v_\alpha v_\alpha}(t) = \frac{1}{N} \langle \sum_{i=1}^{N} v_{i\alpha}(t) v_{i\alpha}(0) \rangle \tag{10.39}$$

The overall velocity autocorrelation function is the sum of the three components

$$C_{\mathbf{v}\mathbf{v}}(t) = \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle = C_{v_x v_x}(t) + C_{v_y v_y}(t) + C_{v_z v_z}(t) \tag{10.40}$$

Normalizing

$$\begin{aligned} c_{\mathbf{v}\mathbf{v}}(t) &= \frac{C_{\mathbf{v}\mathbf{v}}(t)}{C_{\mathbf{v}\mathbf{v}}(0)} = \frac{C_{\mathbf{v}\mathbf{v}}(t)}{\langle \mathbf{v}^2 \rangle} \\ &= \frac{C_{\mathbf{v}\mathbf{v}}(t)}{\frac{3k_BT}{m}} = \frac{m}{3k_BT} \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle \end{aligned} \tag{10.41}$$

This is the function we are interested in. What does it look like? Figure 10.8 shows a schematic of $c_{\mathbf{v}\mathbf{v}}(t)$ for liquid argon near the triple point. We can take the Fourier transform of this to get frequency information

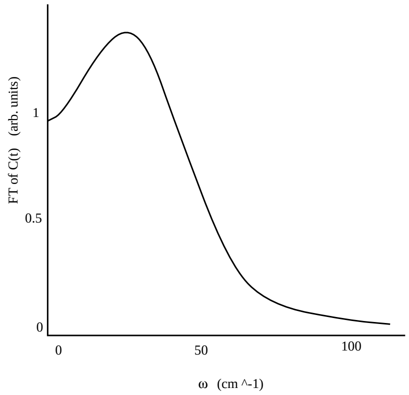

Figure 10.9: The Fourier transform of the velocity autocorrelation function for argon near the triple point

$$\hat{C}_{\mathbf{vv}}(\omega) = \int_{-\infty}^{+\infty} C_{\mathbf{vv}}(t) e^{-i\omega t} d \tag{10.42}$$

For an even function, we have

$$\hat{C}_{\mathbf{vv}}(\omega) = 2\int_{0}^{+\infty} C_{\mathbf{vv}}(t) \cos \omega t dt$$

The Fourier transform of Figure 10.8 is shown in Figure 10.9. You should think about what would the velocity autocorrelation function look like for a gas and a solid.

10.9 Transport Coefficients From Correlation Functions

Transport coefficients (diffusion coefficients, viscosities, thermal conductivities) describe the response ("flux) elicited in a system by the imposition of a perturbation ("driving force") that causes the system to depart from equilibrium. Autocorrelation functions describe the rate at which *spontaneous fluctuations* created within a system *at equilibrium* die out with time. *Linear response theory* describes the relationship between autocorrelation functions and transport coefficients in a system not too far from equilibrium. Autocorrelation functions of the time derivatives of quantities, having the form

$$\langle \dot{\mathcal{A}}(t)\dot{\mathcal{A}}(0)\rangle$$

will play a major role in our analysis of this relationship. Again, recall that

$$\delta\dot{\mathcal{A}}(t) = \dot{\mathcal{A}}(t);\ <\dot{\mathcal{A}}>= 0$$

It turns out that transport coefficients are linked to autocorrelation functions (via linear response theory) through so–called Green–Kubo relations, which have the form

$$\gamma = \int_0^{\infty} dt\ \langle \dot{\mathcal{A}}(t)\dot{\mathcal{A}}(0)\rangle = \int_0^{\infty} dt\ C_{\dot{\mathcal{A}}\dot{\mathcal{A}}}(t) \tag{10.43}$$

where γ is a transport coefficient (within a multiplicative constant).

As an example, let's consider the self–diffusivity. The self–diffusivity along the x–direction would be

$$D_{s,xx} = \int_0^{\infty} dt\ \ < \dot{x}_i(t)\dot{x}_i(0) >= \int_0^{\infty} dt\ \ < v_{i,x}(t) v_{i,x}(0) >$$

and the overall self–diffusivity would be

$$D_s = \frac{1}{3}\int_0^{\infty} dt\ \ < \mathbf{v}_i(t)\cdot\mathbf{v}_i(0) >=$$

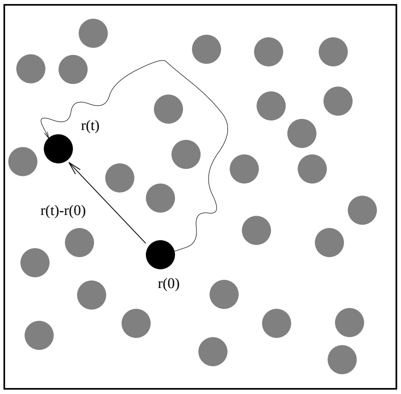

Figure 10.10: A tagged particle moves in a stochastic ("diffusive") manner in a sea of identical untagged particles. The magnitude of the mean square displacement is proportional to the self–diffusivity.

$$\frac{1}{3}(D_{s,xx}+D_{s,yy}+D_{s,zz})=\frac{1}{3}Tr(\mathbf{D}_s) \tag{10.44}$$

Eqn 10.44 is the Green–Kubo relation for the orientationally–averaged self–diffusivity.

One can show that an equivalent expression for eqn 10.43 is the following "Einstein relation"

$$2\gamma t=\langle[\mathcal{A}(t)-\mathcal{A}(0)]^2\rangle \tag{10.45}$$

Eqn 10.45 is valid only for long times (i.e. $t \gg t_{\dot{\mathcal{A}}}$). Applied to the diffusivity, we get

$$D_{s,xx}=\lim_{t\to\infty}\left(\langle[x_i(t)-x_i(0)]^2\rangle/2t\right)$$

and the orientationally averaged diffusivity can be written as

$$D_s=\lim_{t\to\infty}\frac{\langle[\mathbf{r}_i(t)-\mathbf{r}_i(0)]^2\rangle}{6t} \tag{10.46}$$

Eqn 10.46 is referred to as the Einstein equation for self–diffusivity. This is more useful D_s from simulations than the equivalent Green–Kubo expression, due to the difficulty of integrating the long–time tail of the GK expression.

10.9.1 Transport Coefficients From MD

Several transport coefficients can be directly obtained through application of linear response theory.

1. Self–Diffusivity, D_s

   The self–diffusivity is related to the mobility of a single "tagged" particle in a sea of identical "untagged" particles, as can be seen schematically in Figure 10.10. The greater the mean square displacement as a function of time, the greater is the self–diffusivity. From the Green–Kubo expression we have

$$D_s=\frac{1}{3}\int_0^\infty dt\ \langle\mathbf{v}_i(t)\cdot\mathbf{v}_i(0)\rangle$$

$$=\frac{1}{3}\int_0^\infty dt\ \langle\frac{1}{N}\sum_{i=1}^{N}\mathbf{v}_i(t)\cdot\mathbf{v}_i(0)\rangle$$

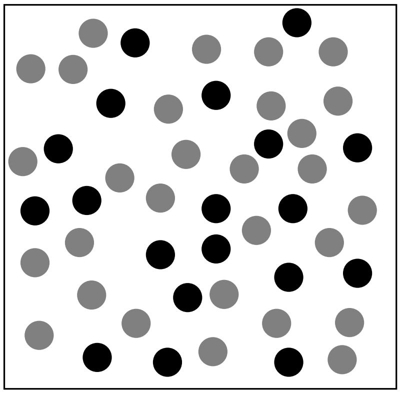

Figure 10.11: In a binary system, the interdiffusion coefficient, representative of the rate at which different species "mix", can also be determined from equilibrium MD simulations

The equivalent Einstein relation yields

$$\begin{aligned} D_s &= \lim_{t\to\infty} \frac{\langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle}{6t} \\ &= \lim_{t\to\infty} \frac{\langle \frac{1}{N}\sum_{i=1}^{N} [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle}{6t} \\ &= \frac{1}{6} \lim_{t\to\infty} \frac{d}{dt} \langle \frac{1}{N} \sum_{i=1}^{N} [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle \end{aligned}$$

In general, the "6" in the numerator is $2d$, d being the dimensionality of the system.

The self–diffusivity is one of the easiest properties to compute, because of the possibility of averaging over all equivalent particles. The Einstein relation is practically more useful than the Green–Kubo formula, since the integration requires an accurate knowledge of the function at long times. The "slope" expression is used more than the ratio expression; linearity of the mean–square displacement with time is an indication that diffusive motion is taking place.

2. Interdiffusion Coefficient, D, for a Binary System

The appropriate Green–Kubo relation is

$$D = \frac{1}{3} \left(\frac{\partial^2 (\beta G/N)}{\partial x_i^2} \right)_{P,T} \int_0^\infty \langle \mathbf{j}^c(t) \cdot \mathbf{j}^c(0) \rangle \, dt \tag{10.47}$$

where G is the total Gibbs energy, N is the number of molecules, x_i is the mole fraction of species i, $i = 1, 2$, $x_i = \frac{N_i}{N}$ and $\mathbf{j}^c(t)$ is the microscopic interdiffusion current, defined as

$$\mathbf{j}^c(t) = x_2 \mathbf{j}^1(t) - x_1 \mathbf{j}^2(t)$$

Each component flux is defined by the number of molecules of species i times the velocity of the center of mass of species i:

$$\mathbf{j}^i(t) = \sum_{k=1}^{N_i} \mathbf{u}_k(t)$$

3. Shear Viscosity, η

   The Green–Kubo expression is

$$\eta = \frac{V}{k_B T}\int_0^\infty dt < \mathcal{P}_{\alpha\beta}(t)\mathcal{P}_{\alpha\beta}(0) >, \ \alpha \neq \beta \tag{10.48}$$

   where $\mathcal{P}_{\alpha\beta}$ is a non–diagonal component of the instantaneous pressure tensor

$$\mathcal{P}_{\alpha\beta} = \frac{1}{V}\left(\sum_i \frac{p_{i\alpha}p_{i\beta}}{m_i} + \sum_i r_{i\alpha} f_{i\alpha}\right)$$

   (Compare this expression with the virial theorem).

   The equivalent Einstein relation is

$$2t\eta = \frac{V}{k_B T}\langle(\mathcal{Q}_{\alpha\beta}(t) - \mathcal{Q}_{\alpha\beta}(0))^2\rangle \tag{10.49}$$

   where $\mathcal{Q}_{\alpha\beta} = \frac{1}{V}\sum_i r_{i\alpha}p_{i\alpha}$. Note that in the expression for viscosity, p is momentum.

4. Thermal Conductivity, λ_T

   Green–Kubo:

$$\lambda_T = \frac{V}{k_B T^2}\int_0^\infty dt \langle j_\alpha^\epsilon(t) j_\alpha^\epsilon(0)\rangle \tag{10.50}$$

   where the “energy current” along axis α is

$$j_\alpha^\epsilon = \frac{d}{dt}\left[\frac{1}{V}\sum_i r_{i\alpha}(\epsilon_i - < \epsilon_i >)\right]$$

   and the energy per molecule is

$$\epsilon_i = \frac{p_i^2}{2m_i} + \frac{1}{2}\sum_{j\neq i}\mathcal{V}(r_{ij})$$

   The Einstein relation

$$2t\lambda_T = \frac{V}{k_B T^2}\langle(\delta\epsilon_\alpha(t) - \delta\epsilon_\alpha(0))^2\rangle$$

   where $\delta\epsilon_\alpha = \frac{1}{V}\sum_i r_{i\alpha}(\epsilon_i - < \epsilon_i >)$

Notice that, as opposed to D_s, the properties D, η, and λ_T are *collective properties of the system*, and are not properties of individual particles. Consequently, we cannot average over many particles. Their accurate estimation requires a much longer simulation.

Special *nonequilibrium molecular dynamics* (NEMD) techniques may be used effectively in computing these quantities. If we have time, we will discuss these methods in greater detail in class.

10.9.2 Computing Correlation Functions From MD Runs

Computing time correlation functions is pretty straightforward. However, there are a few tricks that are used to improve the statistics that are not obvious.

- Let there be τ writes (position, velocity, etc.) to our “tape” file.
- Let δt be the *time interval* between configurations stored on tape.

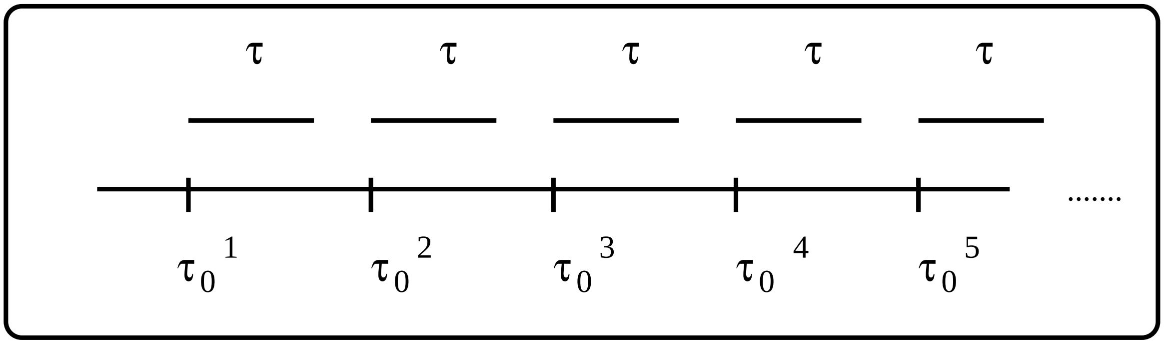

Figure 10.12: Schematic showing the way in which block averaging is used to improve the statistics of a correlation function. Multiple time origins (τ_0) are used and the results over correlation time τ are computed.

- Then $t = \delta t \tau$
- We substitute an ensemble average by a time average

  $$C_{\mathcal{AA}}(\tau) = \langle \mathcal{A}(\tau)\mathcal{A}(0)\rangle = \frac{1}{\tau_{max}} \sum_{\tau_0=1}^{\tau_{max}} \mathcal{A}(\tau_0)\mathcal{A}(\tau_0+\tau)$$

  Here, we average $\mathcal{A}(\tau_0)\mathcal{A}(\tau_0+\tau)$ over τ_{max} time origins.
- Note that $\tau_{max} \leq \tau_{run} - \tau$, where τ_{run} is the total number of “tape” file writes. This means that short–time correlations are available with greater precision; there is a very small sample size at large τ.
- To safely estimate the entire $C_{\mathcal{AA}}(t)$, the length of the simulation must be such that $\tau_{corr} \ll \tau_{run}$.
- A typical loop structure goes like:

```
do t0 = 1, trun, tskip              ! Loop over origins of time
 do t = 0,min(tcor,trun-t0) ! Loop over time intervals
   sum(t) = sum(t) + (A(t0)*A(t0+t)  ! compute corr fun
   N(t) = N(t) + 1.0
 enddo
enddo
c(t) = sum(t) / N(t)
```

10.9.3 General Considerations For Writing an MD Code

The goal: make the code a *fast* as possible so that long times can be accessed.

- Since long runs are inevitable, design the code so that a minimal amount of information is lost in the event of a crash. Make it so that it can be restarted following a crash with minimal difficulty.
- Minimize the amount of I/O (for speed)
- Write $\mathcal{V}$, $\mathcal{H}$, $\mathcal{P}$, $\mathcal{T}$ at frequent intervals, accumulate averages, and write these averages out at the end of the run.

- Store configurations and average accumulators periodically in crash file for restart purposes.
- Write positions, velocities, accelerations to tape file; typically every 10-15 steps, although long–time information can be obtained with less frequent writes.

10.9.4 Structuring the Program

1. Always read and then write information about run to a log file for future reference.
2. Precalculate auxiliary values, initialize everything.
3. Calculate/print forces, positions, velocities, etc. for initial step.
4. Main body of the code
   (a) move atoms
   (b) update running averages
   (c) print out instantaneous properties and current averages (if required)
   (d) print out detailed info to tape (if required)
   (e) save current configuration to crash file (if required)
5. Accumulate final averages, fluctuations, statistics of run
6. close files and exit...