Introduction to Molecular Simulation and Statistical Thermodynamics

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Contents

Preface

Statistical thermodynamics aims at describing the macroscopic properties of systems that consist of many individual entities (e.g. particles, molecules, atoms). Nevertheless, the properties of the system are related to the microscopic properties and interactions of the individual entities. Therefore, statistical thermodynamics bridges a gap between descriptions at two distinct length scales (microscopic and macroscopic).

In statistical thermodynamics systems consist of a large number of entities that can exchange energy with each other. The entities are often atoms, molecules or ions. The theory however is not restricted to these everyday ingredients for materials scientists. In colloid science the entities may be colloidal particles that consist millions of atoms. In fusion or fission reactors, the entities are photons, protons, neutrons and other elementary particles. At the other extreme, in astronomy some of the properties of galaxies and galaxy clusters are described using stars as entities.

The aim of statistical thermodynamics is to derive macroscopic properties of systems from the microscopic properties of the particles that constitute the system. The macroscopic properties of a system consisting of many particles is based on probability distributions. Two types of distributions form the basis of the theory of statistical thermodynamics:

1. The *Gaussian* or *normal* distribution;

2. The *Boltzmann* distribution.

In order to get a feeling for the significance of these distributions we illustrate them with an all-day-live system.

Imagine that we are in a kindergarten in Vienna, February 20, 1849. As always, the child that has its birthday chooses a game to play together. Today, at his fifth anniversary, Ludwig Boltzmann chooses to play *Balls & Bucket*. A number of, say M, children of the kindergarten are sitting in a circle. Each child has a bucket in front of him or her. Initially the teacher randomly distributes n balls over the buckets. The teacher selects one of the children at random. Unless the child's bucket is empty, the child gives at random one ball to his/her left or right neighbor. The teacher randomly selects another child and this child also gives at random one ball to his/her left or right neighbor (unless the child's bucket is empty). This process is continued and after t selections the teacher decides that the play is over. At this point, the total number of balls g collected by all girls is counted, as well as the number of balls collected by the child having his/her birthday (here denoted as B).

Ludwig, being fond of numbers, has remembered all results of today's and earlier *Balls & Bucket* plays. It was easy enough for him to calculate some averages. It seemed natural to him that the average number of balls $\langle B \rangle$ collected by the child having his/her birthday was close to n/M. He was not surprised either by his observation that the average number of balls $\langle g \rangle$ collected by the girls was close to $n/3$, since his class had twice as many boys as girls.

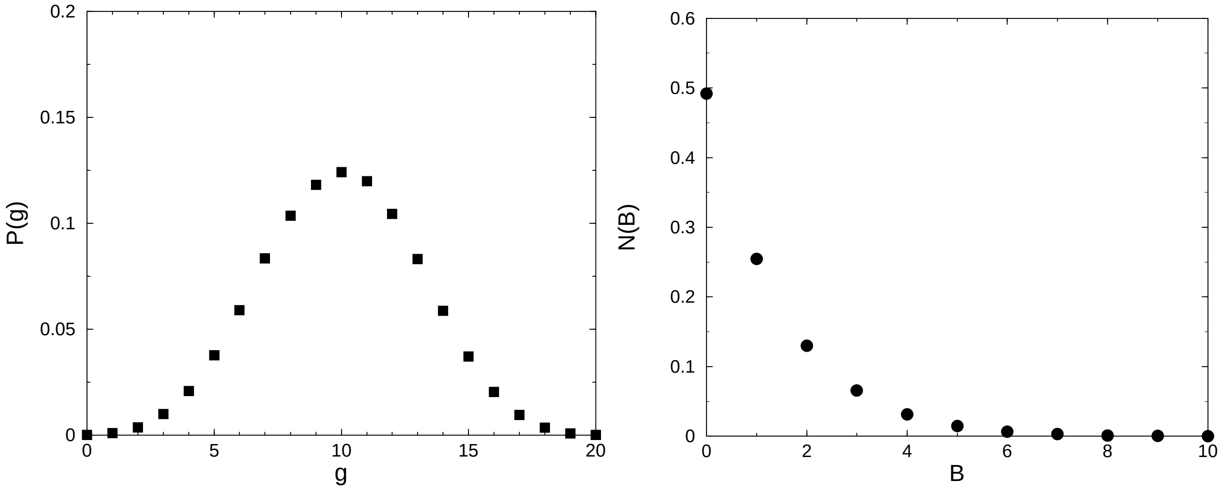

Figure 1: Example of the Balls & Bucket game for $M = 20$ children (10 girls and 10 boys) and $n = 20$ balls. Left: Probability $P(g)$ that the girls collected g balls. Right: Probability $N(B)$ that Ludwig collected B balls.

Ludwig noticed also that a play in which $g = 0$ was very rare. The number of times that the child having its birthday collected no balls, $B = 0$, was *larger* than the number of times that this child collected the average number of balls $\langle B \rangle = n/M$. Ludwig understood that such general results would become more predictable if the number of selections t and the number of children M are very large. He supposed that in that case the probability distribution of g is sharply peaked around $g = \langle g \rangle$, whereas the probability distribution of B would have its maximum at $B = 0$ and would decay monotonously with B, see Fig. 1.

In chapters 1 and 2 we shall investigate in more detail the results we can expect for this game. These results are at the heart of statistical thermodynamics. Therefore we take the opportunity to introduce some of the central formulas and concepts already here. In statistical thermodynamics we refer to the limit of many children in a class ($M \to \infty$) as the *thermodynamic limit*. Let us assume that the initial distribution of the balls over the buckets and the selection of the children are perfectly random. Then the number of balls g collected by the girls after $t = 1$ selection is *Gaussian* distributed around the average $\langle g \rangle = xn$ with x being the fraction of girls in the class:

$$P(g) = C \times \exp\left[-\frac{(g - \langle g \rangle)^2}{2\sigma^2}\right] \tag{1}$$

Here $P(g)$ is the probability that the girls collected g balls and C is a normalization constant and $\sigma = \sqrt{xn}$ is the standard deviation for this *Balls & Bucket* game. If the number of selections t is large enough, i.e. in the limit $t \to \infty$, then the number of balls in Ludwigs bucket is *Boltzmann* distributed:

$$N(B) = C' \times \exp\left[-\frac{B}{\langle B \rangle}\right] \tag{2}$$

in which C' is a normalization constant.

If the teacher is not ideal, the initial distribution of balls is biased. E.g. the teacher may give more balls to the boys than to the girls. The effect of this unbalanced initialization will die out after a certain number of selections. In statistical thermodynamics this means that sometimes a *transient time* $t \gg 1$ is necessary before relevant averages can be taken. With a little reflection the reader will convince him/herself that the Boltzmann distribution of balls in Ludwigs bucket after many selections t (Eq. 2), also applies to the distribution of balls over the buckets of all M children in his class at a given moment of time. More explicitly, let the number of selections t be equal to the number of children M in the class. Then the number of times that Ludwig finds B balls in his bucket after $t = M$ selections, is the same as the number of children finding B balls in their buckets after $t = 1$ selections (provided that the initial distribution is unbiased). This illustrates the equivalence of studying one particle for a long time and many particles for a short time. In statistical mechanics this equivalence is referred to as the *ergodicity* principle.

Finally one might wonder how general the Boltzmann and Gaussian distributions are. Though we can not investigate or prove this rigorously, some plausible deductions can be made from the kindergarten example. The first key ingredient is that no balls disappear, they only are redistributed. This translates to the conservation of energy in an isolated system. The second is that no ball can be removed from an empty bucket, corresponding to the fact that a molecule can not have a lower energy than its (well-defined) ground state energy. Would the Boltzmann also occur for poker players? The role of the balls is played by the value of the different coins that they use. As long as there is no bank that absorbs some of the money, the total value in the play is constant. Furthermore, the ground state of each player is well-defined (i.e. when the player is broke). If all players are equally strong their personal capitals eventually will be Boltzmann distributed. This property of the players translates to the *equal a priori probability* of states with equal amount of money.

Chemists and physicists are often more interested in systems of interacting particles (atoms or molecules) and how these microscopic interactions result in macroscopic (thermodynamic) properties. We will show that we can calculate all thermodynamic properties of a system once all possible states of the system and their energy are known. However, systems with more than two interacting particles can usually not be solved analytically (i.e. finding all possible states and energies using pen and paper only) as the number of states is too large. Often, drastic approximations have to be made for the model that describes our system of particles, as well as severe approximations to solve the theory analytically. There are only a few systems that can be solved exactly, e.g. the ideal gas, the harmonic oscillator (which closely resembles the *Balls & Bucket* game), the Einstein crystal and the two-dimensional Ising system. To circumvent this problem, one has to resort to other methods. This is the reason why computer simulations play an important role in providing essentially "exact" results for problems in statistical thermodynamics which are otherwise only solvable by approximate methods, or are unsolvable anyway. The properties and structure of interacting systems can easily be obtained in molecular simulations, and hence, simulations are ideal to study materials science. This tool to study many-body systems became available in the early fifties of the twentieth century. In a computer simulation, we mimic the real world. We define a model for the system we wish to study and we tell the computer the physical laws that should be satisfied. Simulations can therefore act as a bridge between experiments and theory.

There are three possible applications of simulations: *(1)* Simulations can be used to obtain predictions of (bulk) properties of existing or new materials, when we feed in a guess for the interactions between the atoms or molecules. These predictions are "exact" as no approximations are made. Moreover, we can carry out experiments on the computer that are difficult, impossible, or expensive in the laboratory (for example at extreme temperatures or pressures). *(2)* Computer simulations can be used as a test of theories. A good theory gives us an explanation at a fundamental level of the generic phenomena we observe in our experiments. However, to make a theory that can be solved analytically, we have to make drastic assumptions. As a test of our theory we can compare our theoretical results with experiments. However, when a disagreement is found, it is often not clear what the reason is of this discrepancy. Is the model wrong, are the input parameters wrong, or are the assumptions too drastic? Computer simulations can help us to discriminate between the good and bad assumptions in the theory. *(3)* Computer simulations can also be used to predict new phenomena, which can stimulate new experiments and the development of new theories. Examples of new phenomena found in simulations are, for instance, the freezing transition of hard spheres [1–4], the liquid crystalline phase behavior of hard rods [5,6] and diffusion-limited aggregation [7].

This textbook consists of three parts. The aim of Part I is to familiarize the reader with the basics of statistical thermodynamics with the help of computer simulations. The computer programs and detailed instructions on how to run them can be downloaded from our website. In contrast to "traditional" textbooks on statistical thermodynamics, rigorous proofs have been replaced by computer exercises from which many of the basics concepts follow directly. For example, an important postulate of statistical thermodynamics is that an isolated system is equally likely to be found in any of its eigenstates. It can be shown mathematically that this postulate results in the second law of thermodynamics: an isolated system evolves in such a way that the entropy is at a maximum. Furthermore, the Boltzmann distribution (Eq. 2) follows directly from this. In this book, we will use the following alternative approach to illustrate the consequences of this postulate. First, we introduce a system of harmonic oscillators that can exchange energy packets as a model for an isolated system. A computer program will be used to simulate and to visualize the time-evolution of this system. During this process, the number of visited states is recorded, from which the entropy change is computed directly. Such a simulation shows that it is extremely unlikely that the entropy of an isolated system decreases. In the same simulation, the Boltzmann distribution for the energy of a single oscillator is found, but only when the number of oscillators is large enough to act as a "heat bath" at a fixed temperature. At the end of Part I we will show that as the number of states of typical systems is extremely large, the Metropolis Monte Carlo method will be required to compute thermodynamic averages.

In Part II a brief introduction to molecular simulations is presented. Simulation techniques like Monte Carlo and Molecular Dynamics simulations are discussed. In particular, we focus on simulations to study systems in various ensembles (canonical, isothermal-isobaric, grand-canonical and the Gibbs ensemble) and we compute statistical properties of interacting Lennard-Jones particles (equation of state, phase diagram, diffusion coefficient). In Part III some advanced assignments are presented, as well as appendices that describe the basics of classical thermodynamics and the basics of mathematics.

We aim at undergraduate chemistry and physics students with some basic knowledge of classical thermodynamics. No knowledge about computer programming is required. We feel that this book will provide *(1)* the necessary background for more advanced courses in statistical thermodynamics and/or molecular simulation *(2)* sufficient background for studying the book "Understanding Molecular Simulations" by Daan Frenkel and Berend Smit [8]. For a more in-depth discussion of molecular simulation techniques we also refer the reader to Refs. [9–11].

Part I

Statistical Thermodynamics

Chapter 1

Probability of States in Isolated Systems

1.1 Isolated Systems

We first consider isolated systems that do not exchange energy with the environment. This means that the system is perfectly isolated from the environment so that there is no heat transfer with the environment and no radiation enters or escapes the system. Moreover, no work (either mechanical or chemical) is performed on or by the system. Mechanical work can be achieved by compressing or expanding the system while chemical work corresponds to a flux of particles that go in or out of the system. Therefore, isolated systems have a constant volume V (and shape), a constant number of particles N, and a constant energy E.

Although the total energy of an isolated system is constant, the individual atoms may have different energies. E.g. in a gas the collisions between the particles will lead to energy exchanges and to many different positions, velocities and energies of the individual atoms. If one could make a high speed movie with atomic resolution, each of the images would be different (as all atomic positions and velocities would be different). One might think that the distribution of positions and velocities depends on the type of collisions in the gas. Many experimental and theoretical investigations have made it plausible that this idea is incorrect. Instead, we have the so-called hypothesis of equal *a priori* probability (also called the *fundamental assumption*): *All possible configurations of the system which have the same total energy are equally likely*. Here a configuration means a complete description of all the degrees of freedom of all entities in the system. In the case of a classical description of a mono-atomic gas this means that a configuration is fully described by all positions and velocities of all atoms. For a quantum mechanical gas of non-interacting molecules all quantum numbers for all atoms should be given.

Question 1 (Balls & Bucket)
Explain that the Balls & Bucket game of the preface can be considered as an isolated system.

Question 2 (Throwing a Die)
Throw three dice many times and look only at those throws where the total of the eyes (the "energy" of the throw) is 12*. The following throws are possible: (*6 *and* 5 *and* 1*), (*6 *and* 4 *and* 2*), (*6 *and* 3 *and* 3*), (*5 *and* 5 *and* 2*), (*5 *and* 4 *and* 3*) and (*4 *and* 4 *and* 4*). Does the hypothesis of equal* a priori *probability say that these six throws are equally likely? If not, what is the probability for each of the throws?*

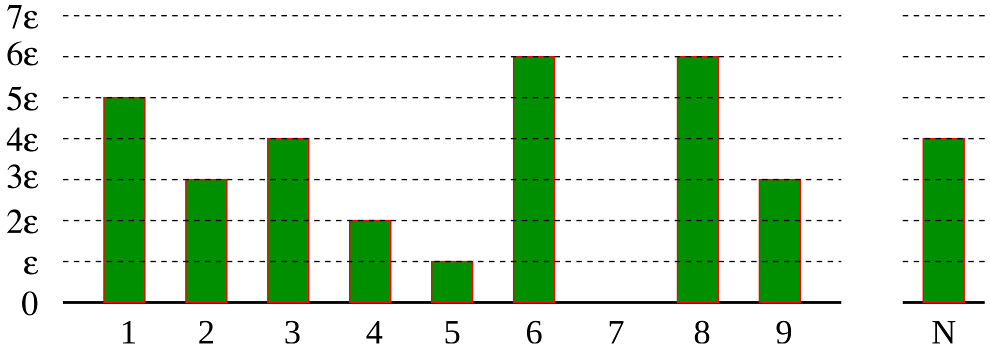

Figure 1.1: Snapshot of a system of N harmonic oscillators, each with energy levels $0, \epsilon, 2\epsilon, 3\epsilon \cdots$. The oscillators can exchange energy packets (of size $\epsilon = \hbar\omega$) but the total energy remains constant.

1.2 Harmonic Oscillators

From elementary quantum mechanics, we know that a harmonic oscillator has equally spaced energy levels:

$$E_k = \left(k + \frac{1}{2}\right)\hbar\omega \quad \text{with} \quad k = 0, 1, ... \tag{1.1}$$

where $\hbar = h/(2\pi)$ is Planck's constant and ω is the eigenfrequency of the oscillator. Suppose that we have a system of N independent harmonic oscillators. Each harmonic oscillator can emit a photon that can be absorbed immediately by another oscillator. In this system the individual oscillators may have different energies. A configuration of the system is given by $(k_1, k_2, ..., k_N)$, where k_n is the state of oscillator n. The energy of oscillator n is denoted by $E(n) = E_{k_n}$. If the system is isolated, the total energy E is constant and is given by

$$E = E(k_1, k_2, ..., k_N) = \sum_{n=1}^{N} E_{k_n} = E_0 + \sum_{n=1}^{N} \hbar\omega k_n = E_0 + \epsilon \sum_{n=1}^{N} k_n \tag{1.2}$$

Here $E_0 = N\hbar\omega/2$ is the energy of N oscillators in the ground state. The example above with the three dice (question 2) corresponds to a system of $N = 3$ harmonic oscillators with $\hbar\omega = \epsilon = 1$ and $E_0 = 0$. In this example the individual energy levels are restricted to $k = 1, 2 \cdots 6$ and the total energy is $E = 12$. The probability for each of the six possible energy distributions can be calculated explicitly. This is not possible in general. Using smart analytical approaches one may derive the form of the most probable distribution (see section 1.4). Before following this route we investigate the possible energy distributions "experimentally", i.e. using a simple computer simulation (question 4). The computer program simulates a system of N harmonic oscillators, each of which may have an energy $E(n) = 0, \hbar\omega, 2\hbar\omega, \cdots$ (note that we did not lose any information by choosing the ground state energy at $E_0 = 0$), see Fig. 1.1. The total energy E and the number of oscillators N are input for the program. One step in the simulation consists of selecting two different oscillators A and B at random. Next, the program attempts to increase the energy of oscillator A by $\hbar\omega$ and at the same time decrease the energy of B by $\hbar\omega$. If the energy of B becomes negative, the trial is rejected. Output of the program are "snapshots", i.e. the energies of all individual oscillators, after t simulation steps.

Question 3 (Statistical description of the Balls & Bucket game)
Explain why the Balls & Bucket game is equivalent to the computer simulation of harmonic oscillators described above.

Question 4 (Simulation of a System of Oscillators)
Consider a system of N *harmonic oscillators at constant total energy* E*. The value of* $\epsilon = \hbar\omega$ *is set to* 1*.*

1. *Run the given computer program and produce "movies" of snapshots like in Fig. 1.1. Find out how they can be influenced by changing* N *and* E*.*
2. *Make a "movie" of the energy of the first oscillator by showing a plot of the energy* $E_1(t)$*. Hint: do not take too many or too few oscillators and take* E/N *not more than a few times* ϵ*.*
3. *Make a histogram of* $P(k)$*, the probability that a given oscillator has an energy* ϵk*. Determine by trial and error how many configurations must be taken in order to have a reasonable signal to noise ratio in* $P(k)$*. Is your result influenced by the value of* N*?*
4. *By plotting, verify that* $\ln(P(k))$ *depends linearly on* k *and determine for a few choices of* E/N *the fitting constants* β *and* q *in the equation* $\ln(P(k)) = -\beta\epsilon k - \ln(q)$*. We shall see later why we write the linear relationship in this particular form.*
5. *Make a histogram of* $P_{1+2}(K)$*, the probability that the sum of the energies of first two oscillators is* ϵK *with* $K = k_1 + k_2$*. How does this quantity relate to the Balls & Bucket game? Explain the differences with the result for a single oscillator. We will come back to this in question 17.*

From our simulation experiment in question 4 it follows that the probability distribution for a given state k of a single harmonic oscillator reads

$$P(k) = \frac{\exp[-\beta E_k]}{q} \tag{1.3}$$

with constants β and q. In statistical thermodynamics the numerator $\exp[-\beta E_k]$ is called the *Boltzmann factor*. The constant q is called the *molecular partition function* or *molecular partition sum*, defined as the sum of Boltzmann factors over all states of the oscillator

$$q = \sum_{k=0}^{\infty} \exp[-\beta E_k] \tag{1.4}$$

Substituting $x = \exp[-\beta\hbar\omega]$ one can rewrite the partition sum q of a harmonic oscillator as a geometric series (section C.5). Using Eq. C.20 it can be shown that

$$q = \frac{1}{1 - \exp[-\beta\hbar\omega]} \tag{1.5}$$

The average energy $\langle E_i \rangle$ of a single oscillator can be related to β using the same substitution as above and employing Eq. C.21:

$$\langle E_i \rangle = \sum_{k=0}^{\infty} \hbar\omega k P(k) = \hbar\omega \frac{\sum_{k=0}^{\infty} k \exp[-\beta\hbar\omega k]}{\sum_{k=0}^{\infty} \exp[-\beta\hbar\omega k]} = \frac{\hbar\omega}{\exp[\beta\hbar\omega] - 1} \tag{1.6}$$

In section 1.5 we show that the fitting constant β is related to the temperature T by

$$\beta = \frac{1}{k_B T} \tag{1.7}$$

This means that for a sufficiently large number of oscillators, a single oscillator i is surrounded by a "heat bath" consisting of all other $N - 1$ oscillators, see Fig. 1.2. The temperature of this heat bath follows from the total energy E, which in turn determines $\langle E_i \rangle$ and β.

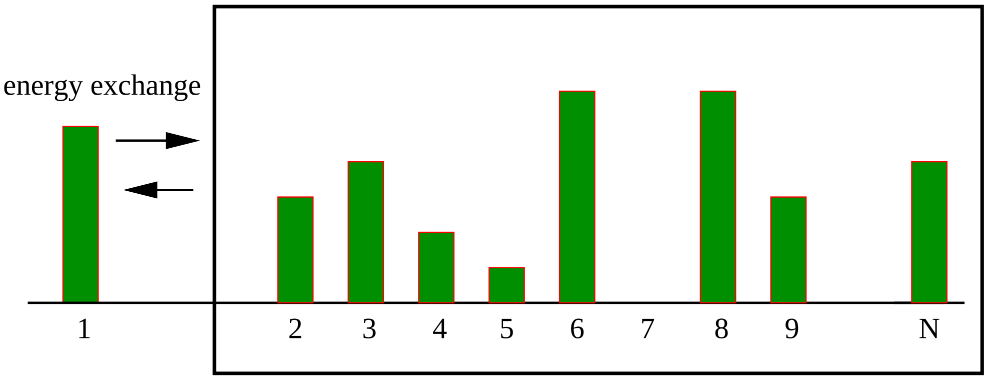

Figure 1.2: A single oscillator is surrounded by a heat bath consisting of all other oscillators. For a large number of oscillators N the energy of this heat bath is approximately constant and equal to $E - E_{k_1} \approx E$. The value of β follows directly from the average energy E/N.

Question 5 (Average Energy)
Explain that $\langle E_i \rangle = E/N$.

Question 6 (Fitting Constant)
For a number of system energies $E = E(k_1, k_2, \cdots, k_N)$, *use simulation data to find* $\langle E_i \rangle$ *and* β. *Check that your results are consistent with Eq. 1.6.*

1.3 The Ideal Gas

A very important model system in the development of (statistical) thermodynamics is the ideal gas. By definition an ideal gas is a system of non-interacting particles. More precisely, it is a system of which the potential energy is independent of the positions of the particles. If the particles are point particles (i.e. they are structureless, and without any internal energy eigenstates), then the system is known in quantum mechanics as the "particles in a box" problem. For a cubic box of volume $V = L^3$ with N independent distinguishable point particles the quantum mechanical problem is easily solved. The wave function of the system is a product of wave functions for the individual particles and the system energy is the sum of the particle energies. For one particle the possible energy levels are

$$E_{\mathbf{k}} = \left(k_x^2 + k_y^2 + k_z^2\right) \frac{h^2}{8mL^2} \tag{1.8}$$

with $k_i = 1, 2, 3, \cdots$ for $i = x, y, z$. Here $\mathbf{k} = (k_x, k_y, k_z)$ comprises the three integer quantum numbers that define the eigenstate of the particle. In an ideal gas the particles can exchange energy by collisions. In real collisions both the total energy and the total momentum of the particles is conserved. The ideal gas assumption however, does not take the precise motion and position of the particles into account. Therefore, only energy conservation has to be considered. The situation is very similar to the harmonic oscillators that exchange energy by radiation. A subtle difference is that the energy levels of a particle in a box are not equidistant. This implies that the energy loss of particle i during a binary collision with particle j can not always be exactly compensated by an energy gain of particle j.

Question 7 (Ideal Gas)
Suppose that a certain particle (here denoted as i*) is in state* $\mathbf{k} = (2, 2, 3)$ *and another particle (denoted*

by j*) is in the ground state* $(1,1,1)$*. Verify that when particle* i *changes to state* $(2,2,2)$ *then the energy loss* $\Delta E_i = 5h^2/8mL^2$ *can not be compensated by an energy gain of particle* j*.*

A method exists to deal with this problem, called the Maxwell demon method [12]. The method will not be discussed here but it has been included in the enclosed computer program for simulating a quantum mechanical ideal gas of distinguishable point particles.

Question 8 (Ideal Gas Energy)
Consider an ideal gas for which the particles can exchange energy. The energy of each particle is given by Eq. 1.8 and the value of $h^2/8mL^2$ *is set to* 1*.*

1. *Make "movies" of the energy of each particle, analogous to the movies for the system of harmonic oscillators in question 4.*
2. *From the simulation output, measure* $P(\mathbf{k})$*, the probability that a given particle is in state* $\mathbf{k}$*, for the states* $\mathbf{k}$ *that appear in the simulation.*
3. *Plot* $P(\mathbf{k})$ *as a function of the energy* $E_{\mathbf{k}}$ *of state* $\mathbf{k}$*. Note that sometimes different* $\mathbf{k}$ *have the same* $E_{\mathbf{k}}$ *(e.g.* $E_{2,3,4} = E_{4,2,3} = 29h^2/8mL^2$*).*
4. *Verify that* $\ln P(\mathbf{k})$ *depends linearly on* $E_{\mathbf{k}}$ *and determine for a few choices of* E/N *the fitting constants* β *and* q *in the equation* $\ln P(\mathbf{k}) = -\beta E_{\mathbf{k}} - \ln q$*.*

We reach the conclusion that the probability distribution for particle states and the molecular partition function in an ideal gas have the same form (Eqs. 1.3 and 1.4) as for the system of harmonic oscillators. We can write

$$q = \sum_{\mathbf{k}} \exp[-\beta E_{\mathbf{k}}] = \sum_{\mathbf{k}} \exp\left[-\frac{\beta h^2(k_x^2+k_y^2+k_z^2)}{8mL^2}\right] = \left(\sum_{k=1}^{\infty} \exp\left[-\frac{\beta h^2 k^2}{8mL^2}\right]\right)^3 \tag{1.9}$$

where the power of 3 is due to the fact that the summations over the three quantum numbers k_x, k_y, k_z are independent of eachother. For the average energy of one particle we find:

$$\langle E\rangle = \frac{1}{q}\sum_{\mathbf{k}} E_{\mathbf{k}} \exp[-\beta E_{\mathbf{k}}] = \frac{3}{q^{1/3}}\sum_{k=1}^{\infty} \frac{h^2k^2}{8mL^2}\exp\left[-\frac{\beta h^2k^2}{8mL^2}\right] \tag{1.10}$$

These expressions are exact. For the harmonic oscillator, we could do the summations analytically. Here, as for almost all physically relevant systems, this is not possible. An excellent approximation for all circumstances can be found as follows.

Question 9 (Number of Terms in q for the Ideal Gas)
Take as an example hydrogen gas in a box of 1 cm^3 *at temperature* 1K*. Calculate the factor* $\alpha = \beta h^2/\left(8mL^2\right)$ *that appears in the exponents of Eq. 1.9 (note that* $\beta = 1/(k_BT)$*). Estimate after how many terms the last term is half the first term. At which temperature is the spacing between the first two energy levels equal to* k_BT*?*

We see that for all practical circumstances, i.e. realistic system size and temperature, many terms will contribute to the summations in Eqs. 1.9 and 1.10. We can then treat the energies of ideal gas molecules as continuous variables. Hence, in these expressions for the partition function and the energy we may replace summations by integrations. Indeed for $\alpha \ll 1$ we may use the approximations (see section C.8)

$$\sum_{k=1}^{\infty} \exp[-\alpha k^2] \approx \int_0^{\infty} dk \exp[-\alpha k^2] = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} \tag{1.11}$$

$$\sum_{k=1}^{\infty} k^2 \exp[-\alpha k^2] \approx \int_0^{\infty} dk k^2 \exp[-\alpha k^2] = \frac{1}{4\alpha}\sqrt{\frac{\pi}{\alpha}} \tag{1.12}$$

Substituting these approximations into Eq. 1.9 and Eq. 1.10 we find for the molecular partition function

$$q = \left(\frac{\pi}{4\alpha}\right)^{3/2} = \left(\frac{L}{\Lambda}\right)^3 = \frac{V}{\Lambda^3} \tag{1.13}$$

where

$$\Lambda \equiv \frac{h}{\sqrt{2\pi m k_B T}} = \frac{h}{\sqrt{2\pi m/\beta}} \tag{1.14}$$

is often called the thermal wavelength, and

$$\langle E \rangle = \frac{3}{2\beta} = \frac{3}{2} k_B T \tag{1.15}$$

for the average molecular energy in which we used Eq. 1.7 for β. This remarkably simple expression is in line with the classical thermodynamics result that the energy of an ideal gas depends on temperature only, and not on volume or pressure (see Eq. B.2).

Another advantage of treating the energy as a continuous, rather than a discrete variable, is that we can simulate an ideal gas at constant energy without having to invoke a Maxwell demon. Indeed, whereas for discrete energy levels the energy loss and energy gain of two colliding particles can not always be matched exactly, this poses no problem in the continuous case. This simplifies the simulation of an ideal gas, which becomes essentially the same as for the harmonic oscillators. In both systems a binary collision may lead to an exchange of particle energies, the only difference being that for harmonic oscillators only discrete amounts of energy can be exchanged, whereas for an ideal gas arbitrary energy exchange is possible.

1.4 Entropy and the Most Probable Distribution

In the previous section we have found "experimentally" that after some time the distribution of states in an isolated system reaches a certain form, that does depend on the total energy of the system. On the other hand according to the fundamental assumption all accessible states with the same energy are equally likely. This may seem contradictory. The subtlety however is that the distribution of states deals with *particle states* and the fundamental assumption with *system states*.

Consider e.g. a system of N particles with three non-degenerate energy levels: $E_0 = 0$, $E_1 = \epsilon$ and $E_2 = 3\epsilon$. A *system state* $\mathcal{S} = (k_1, k_2, \cdots k_N)$ gives the state k_n for each particle $n = 1, 2, \cdots, N$ in the system. A *system distribution* $\mathcal{N} = (N_0, N_1, \cdots N_k \cdots)$ is given by the numbers N_k of particles that are found in each of the particle states k. As the total number of particles is constant, $\sum_k N_k = N$. Fig. 1.3 shows an example of the *system state* and *system distribution* for $N = 4$.

Next, we consider the situation of all possible system states at a *fixed* total energy E. If the total energy is $E = 3\epsilon$ above the ground state, then one possibility is that the energy 3ϵ is absorbed by one of the particles. It is also possible that the same energy is distributed over three particles of the system, see table 1.1. In the first case the system distribution is $\mathcal{N} = (N-1, 0, 1)$, in the second case it is $\mathcal{N} = (N-3, 3, 0)$.

We denote the number of system states corresponding to the system distribution $\mathcal{N}$ as $W(\mathcal{N})$. There are $W(\mathcal{N}) = N$ system states corresponding to $\mathcal{N} = (N-1, 0, 1)$ and $W(\mathcal{N}) = N(N-1)(N-2)/6$ system states corresponding to $\mathcal{N} = (N-3, 3, 0)$. Obviously, for large N the probability to find the system with the latter distribution is much larger than to find it with the first.

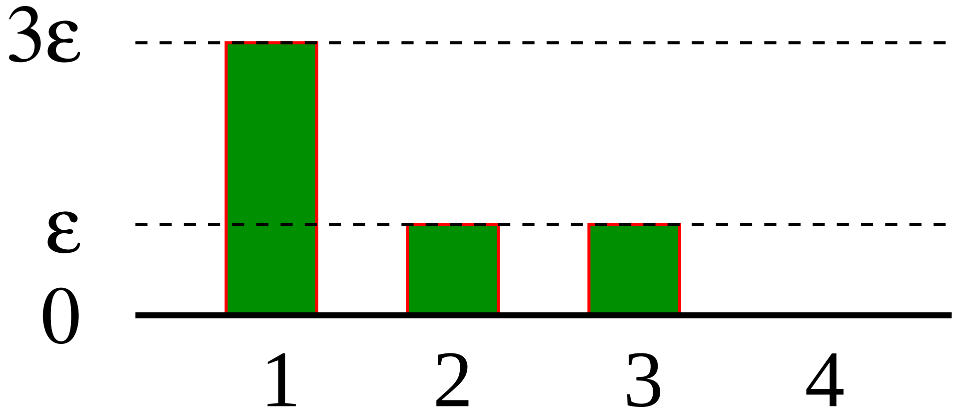

Figure 1.3: System of $N = 4$ particles with three non-degenerate energy levels: $E_0 = 0$, $E_1 = \epsilon$ and $E_2 = 3\epsilon$. The system state $\mathcal{S}$ gives the state k_n for each particle so here $\mathcal{S} = (2, 1, 1, 0)$. The total energy of the system is therefore $E = \sum_k E_k N_k = 2 \times 3\epsilon + 1 \times \epsilon + 1 \times \epsilon + 0 \times \epsilon = 8\epsilon$. The system distribution $\mathcal{N}$ gives the number of particles in each of the states. As there is $N_0 = 1$ particle in the ground state, $N_1 = 2$ particles in the state with energy E_1 and $N_2 = 1$ particle in state with energy E_2, the the system distribution reads $\mathcal{N} = (N_0, N_1, N_2) = (1, 2, 1)$.

	$\mathcal{S}$				$\mathcal{N}$		
possibility	k_1	k_2	k_3	k_4	N_0	N_1	N_2
1	0	0	0	2	3	0	1
2	0	0	2	0	3	0	1
3	0	2	0	0	3	0	1
4	2	0	0	0	3	0	1
5	1	1	1	0	1	3	0
6	1	1	0	1	1	3	0
7	1	0	1	1	1	3	0
8	0	1	1	1	1	3	0

Table 1.1: All possible system states $\mathcal{S}$ for $N = 4$ particles that are distributed over 3 energy levels with energies $E_0 = 0$, $E_1 = \epsilon$ and $E_2 = 3\epsilon$ such that the total energy equals 3ϵ. The system state $\mathcal{S} = (k_1, k_2, k_3, k_4)$ gives the state for each particle $n = 1, 2, 3, 4$ in the system. For example, $k_3 = 2$ means that particle 3 has an energy of $E_{k_3} = E_2 = 3\epsilon$. The system distribution $\mathcal{N} = (N_0, N_1, N_2)$ gives the number of particles in each of the particle states E_0, E_1, E_2. For example, N_0=1 means that there is only a single particle in energy level E_0 (there are 4 possibilities for this).

Question 10 (Number of states)

Explain without using formulas that for large N *there are much more system states corresponding to* $\mathcal{N} = (\mathsf{N}-3,3,0)$ *than to* $\mathcal{N} = (\mathsf{N}-1,0,1)$.

For a *given* system distribution $\mathcal{N}$, the probability distribution $\mathsf{P}(\mathsf{k}|\mathcal{N})$ to find a given particle in state k equals

$$\mathsf{P}\left(\mathsf{k}|\mathcal{N}\right) \equiv \frac{\mathsf{N}_\mathsf{k}(\mathcal{N})}{\mathsf{N}} \tag{1.16}$$

in which $\sum_\mathsf{k} \mathsf{N}_\mathsf{k} = \mathsf{N}$. For the example given above, we see that

$$\begin{aligned}
\mathcal{N} = (\mathsf{N}-1,0,1) \quad &\rightarrow \quad \mathsf{P}(0|\mathcal{N}) = \frac{\mathsf{N}-1}{\mathsf{N}} \quad \mathsf{P}(1|\mathcal{N}) = 0 \quad \mathsf{P}(2|\mathcal{N}) = \frac{1}{\mathsf{N}} \\
\mathcal{N} = (\mathsf{N}-3,3,0) \quad &\rightarrow \quad \mathsf{P}(0|\mathcal{N}) = \frac{\mathsf{N}-3}{\mathsf{N}} \quad \mathsf{P}(1|\mathcal{N}) = \frac{3}{\mathsf{N}} \quad \mathsf{P}(2|\mathcal{N}) = 0
\end{aligned} \tag{1.17}$$

It turns out that for a large number of particles, a single system distribution becomes dominant which means that the majority of system states correspond to that system distribution. Therefore, the probability distribution $\mathsf{P}(\mathsf{k})$ that we measured in questions 4 and 8 will be related to the most probable system distribution (denoted as $\mathcal{N}^\star$). The hypothesis of equal *a priori* probabilities implies that the *most probable* system distribution for a given system energy E is the one corresponding to the *largest number of system states* $W(\mathcal{N})$. An elementary combinatorial formula (section C.6) learns that

$$W(\mathcal{N}) = \frac{\mathsf{N}!}{\prod_{\mathsf{k}=0}^{\infty} \mathsf{N}_\mathsf{k}!} \tag{1.18}$$

The discussion so far leads to the expectation that during each of the simulations above the number $W(\mathcal{N})$ increases with "time". As this number is very large it is more practical to follow its logarithm in time. Using Stirling's approximation, Eq. C.48 for $\ln \mathsf{N}!$ we find that

$$\begin{aligned}
\ln W(\mathcal{N}) &= \ln \mathsf{N}! - \ln \prod_{\mathsf{k}=0}^{\infty} \mathsf{N}_\mathsf{k}! \\
&= \mathsf{N}\ln\mathsf{N} - \mathsf{N} - \sum_{\mathsf{k}=0}^{\infty} \left[\mathsf{N}_\mathsf{k}\ln\mathsf{N}_\mathsf{k} - \mathsf{N}_\mathsf{k}\right] \\
&= \mathsf{N}\ln\mathsf{N} - \sum_{\mathsf{k}=0}^{\infty} \left[\mathsf{N}_\mathsf{k}\ln\mathsf{N}_\mathsf{k}\right] \\
&= -\sum_{\mathsf{k}=0}^{\infty} \left[\mathsf{N}_\mathsf{k}\left(\ln\mathsf{N}_\mathsf{k} - \ln\mathsf{N}\right)\right] \\
&= -\mathsf{N}\sum_{\mathsf{k}=0}^{\infty} \frac{\mathsf{N}_\mathsf{k}}{\mathsf{N}} \ln\frac{\mathsf{N}_\mathsf{k}}{\mathsf{N}} \\
&= -\mathsf{N}\sum_{\mathsf{k}=0}^{\infty} \mathsf{P}(\mathsf{k}|\mathcal{N}) \ln \mathsf{P}(\mathsf{k}|\mathcal{N})
\end{aligned} \tag{1.19}$$

Since the redistribution of states over the particles is a spontaneous process at constant volume, number of particles and total energy, the second law of classical thermodynamics tells us that the entropy should increase (see appendix B). Entropy is an extensive variable (proportional to the system size, see section B.1). These properties are seen to be satisfied by $\ln W$ as well. Therefore, we follow Boltzmann's brilliant suggestion that the (statistical) entropy of a system distribution $\mathcal{N}$ is given by

$$\mathsf{S}(\mathcal{N}) = \mathsf{k}_\mathsf{B} \ln W(\mathcal{N}) \tag{1.20}$$

The thermodynamic (i.e. equilibrium) entropy $S = S(U, V, N)$ corresponds to the most probable system distribution, say $\mathcal{N} = \mathcal{N}^\star(U, V, N)$

$$S(U, V, N) = k_B \ln W(\mathcal{N}^\star) = -N k_B \sum_k P(k) \ln[P(k)] \tag{1.21}$$

where the summation is over all possible system states that are present in $\mathcal{N}^\star$. The probabilities that appear at the right hand side are the ensemble probabilities $P(k) = P(k|\mathcal{N}^\star) = N_k(\mathcal{N}^\star)/N$, as given by Eq. 1.16.

Question 11 ($\ln W(\mathcal{N})$ Increases with Time)
In this question, we will consider a system of N *harmonic oscillators with total energy* E*. At time zero, all energy is inside the first oscillator so* $\mathcal{N} = (N-1, 0, 0, \cdots, 0, 1)$*. At each timestep, a single unit of energy is exchanged between two oscillators. This process (starting from* $\mathcal{N} = (N-1, 0, 0, \cdots, 0, 1)$ *and exchanging energy packets) is repeated a large number of times. The program calculates* $\ln W(\mathcal{N})$ *as a function of time, as well as the system distribution* $\mathcal{N}$ *at the end of the simulation.*

1. *Run the simulation for* $N = 5000$ *and* $E = 5000$ *and verify that for very short simulations, the final system distribution* $\mathcal{N}$ *is not Boltzmann distributed (*$N_k \neq \exp[-\beta E_k]$*).*

2. *Show that for a large number of cycles* $\ln W(\mathcal{N})$ *is going to a maximum and that at this point, the system distribution* $\mathcal{N}$ *approaches a Boltzmann distribution (*$N_k \propto \exp[-\beta E_k]$*). Verify that for different simulations, the final system distributions* $\mathcal{N}$ *do not differ much.*

3. *Verify that* $\ln W(\mathcal{N})$ *(and therefore* S*) is an extensive quantity (section B.1) by running a simulation for* $N = 2500$ *and* $E = 2500$*.*

It is important to realize that the result that we found in question 11 is a direct demonstration of the *second law* of thermodynamics; *only a single system distribution* $\mathcal{N}^\star$ *(here: the Boltzmann distribution) corresponding to a maximum entropy is important.* It also gives a statistical interpretation of this macroscopic law. The increase of entropy of an isolated system during irreversible processes, is nothing else than the approach to the most probable system distribution $\mathcal{N}^\star$.

1.4.1 Boltzmann Distribution corresponds to a Maximum in $\ln W(\mathcal{N})$

We have *measured* in our simulations, that the probability of a particle state is proportional to its Boltzmann factor, Eq. 1.3, with β is a fitting parameter for given U, V and N. It is also possible to *proof* mathematically that Eq. 1.3 corresponds to the system distribution $\mathcal{N} = \mathcal{N}^\star(U, V, N)$ for which the number of system states $W(\mathcal{N})$ is maximal. The proof is as follows. We maximize $\ln W$ rather than W itself. On the outset all non-negative integer values for any of the N_k are possible, but there are two restrictions:

$$N - \sum_k N_k = 0 \tag{1.22}$$

$$E - \sum_k N_k E_k = 0 \tag{1.23}$$

Introducing two Lagrange multipliers α and β (see section C.10), we maximize

$$\begin{aligned}\Phi(\mathcal{N}) &= \ln W(\mathcal{N}) - \alpha\left(N - \sum_k N_k\right) + \beta\left(E - \sum_k N_k E_k\right) \\ &= -\sum_k N_k \ln\frac{N_k}{N} - \alpha\left(N - \sum_k N_k\right) + \beta\left(E - \sum_k N_k E_k\right) \end{aligned} \tag{1.24}$$

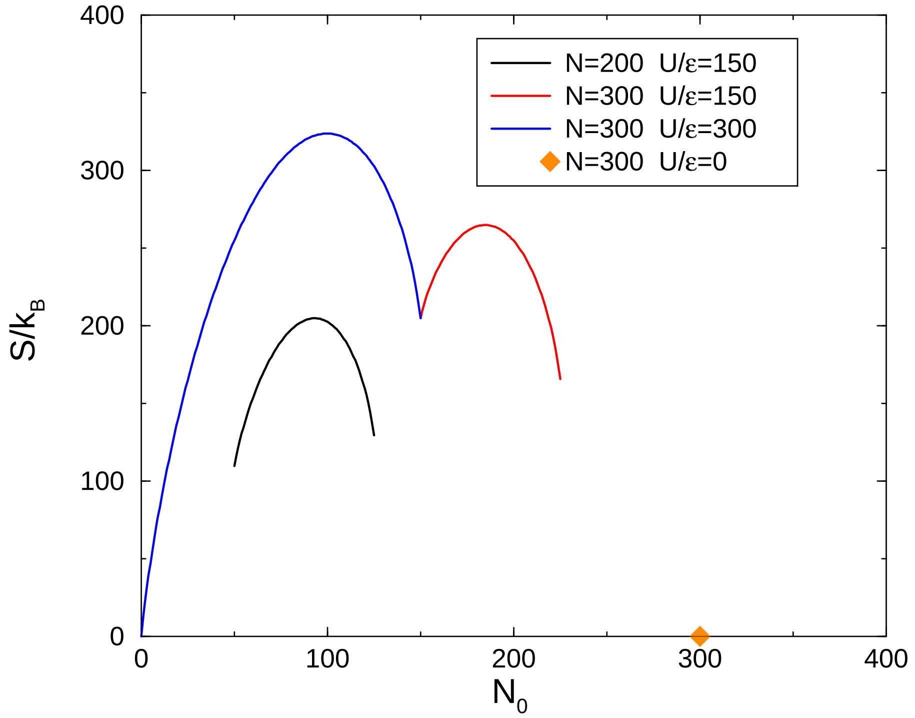

Figure 1.4: Entropy as a function of N_0 (question 12).

without taking the restrictions into account. Taking the derivative with respect to a single N_k leads to

$$\frac{\partial \Phi}{\partial N_k} = -\ln \frac{N_k}{N} - 1 + \alpha - \beta E_k = 0 \tag{1.25}$$

This relation shows that $P(k) = N_k/N$ is proportional to $\exp[-\beta E_k]$. The constant energy condition Eq. 1.23 relates β to the system energy E. In the next section the physical interpretation of β as the inverse temperature will be developed.

Question 12 (Entropy of an Isolated System)
Consider a system of N *molecules. The total energy* U *of the system is constant. Each of the molecules can be in one of the following states:* $k = 0$, $k = 1$ *and* $k = 2$ *with energies* $E_0 = 0$, $E_1 = \epsilon$ *and* $E_2 = 2\epsilon$ *respectively. The number of molecules in state* k *is denoted as* N_k.

1. *Show that for this system*

$$N_0 + N_1 + N_2 = N \tag{1.26}$$

$$N_1 \epsilon + 2N_2 \epsilon = U \tag{1.27}$$

2. *Show that the system distribution* $\mathcal{N}$ *only depends on* N_0 *according to*

$$\mathcal{N} = \left(N_0, 2N - 2N_0 - \frac{U}{\epsilon}, N_0 - N + \frac{U}{\epsilon} \right) \tag{1.28}$$

3. *Show that the entropy of the system is given by*

$$S = k_B \ln \left[\frac{N!}{N_0! \left(2N - 2N_0 - \frac{U}{\epsilon}\right)! \left(N_0 - N + \frac{U}{\epsilon}\right)!} \right] \tag{1.29}$$

Fig. 1.4 shows the entropy S as a function of N_0 *for several values of* N *and* U.

5. *For* $U/\epsilon = 0$ *and* $N = 300$, *this figure consists only of a single point. Explain why.*
6. *For* $U/\epsilon = 300$ *and* $N = 300$, *the entropy is at a maximum for* $N_0 = 100$. *What is the most probable system distribution* $\mathcal{N}^\star$ *in this case? To which temperature does this system distribution correspond?*
7. *Consider the systems with* $U/\epsilon = 150$ *and a different number of molecules,* $N = 300$ *and* $N = 200$ *respectively. For both systems, estimate the probability that a molecule is in the ground state. Explain why this probability is larger for* $N = 300$.

1.5 The Temperature of a Distribution

In sections 1.2 and 1.3 we have presented expressions for the average energy of particles in a system and in section 1.4 for the entropy. Energy differences, volume and number of molecules are well-defined and, at least in principle, accurately measurable both in experiments and in numerical simulations. In experiments one can also measure temperature, and using these measurements one can determine the entropy of a system. In numerical simulations temperature is not an *a priori* defined object, and it has to be defined in accordance with the entropy, which we defined in Eq. 1.21. At constant system volume V and number of particles N we can use the thermodynamic definition of temperature (section B.6)

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \frac{\left(\frac{\partial U}{\partial \beta}\right)_{V,N}}{\left(\frac{\partial S}{\partial \beta}\right)_{V,N}} \tag{1.30}$$

in which U is the *macroscopic internal energy*. If the system is sufficiently large, the average energy $\langle E \rangle$ will be equal to the macroscopic internal energy U. This means that for the calculation of the numerator of Eq. 1.30 we can use

$$U \approx N \sum_k E_k P(k) \tag{1.31}$$

to get

$$\left(\frac{\partial U}{\partial \beta}\right)_{V,N} = N \sum_k E_k \frac{\partial P(k)}{\partial \beta} \tag{1.32}$$

whereas for the denominator it follows from Eq. 1.21 that

$$\left(\frac{\partial S}{\partial \beta}\right)_{V,N} = -Nk_B \sum_k (\ln P(k) + 1) \times \frac{\partial P(k)}{\partial \beta} \tag{1.33}$$

With $\sum_k \partial P(k)/\partial \beta = 0$, which follows from the normalization $\sum_k P(k) = 1$ of the probability distribution, this can be simplified to

$$\left(\frac{\partial S}{\partial \beta}\right)_{V,N} = -Nk_B \sum_k \ln P(k) \frac{\partial P(k)}{\partial \beta} \tag{1.34}$$

The next step is to substitute the explicit form of Eq. 1.3 for the probability $P(k)$ and to use once more that $\sum_k \partial P(k)/\partial \beta = 0$:

$$\left(\frac{\partial S}{\partial \beta}\right)_{V,N} = -Nk_B \sum_k (-\beta E_k - \ln q) \frac{\partial P(K)}{\partial \beta} = Nk_B \beta \sum_k E_k \frac{\partial P(K)}{\partial \beta} \tag{1.35}$$

which can be used directly in Eq. 1.30 leading to

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \frac{(\partial U/\partial \beta)_{V,N}}{(\partial S/\partial \beta)_{V,N}} = \frac{N\sum_k E_k \frac{\partial P(K)}{\partial \beta}}{Nk_B\beta \sum_k E_k \frac{\partial P(K)}{\partial \beta}} = \frac{1}{k_B \beta} \tag{1.36}$$

Thus we obtain the following simple relation between β and T:

$$\beta = \frac{1}{k_B T} \tag{1.37}$$

Question 13 (Temperature of a Distribution)
Consider the simulation of question 11 with $N = 5000$ *and* $E = 5000$.

1. *Determine the value of* $\ln W(\mathcal{N})$ *and the fitting constant* β *from a fit of the final system distribution to* $N_k \propto \exp[-\beta E_k]$. *Make sure that the simulation has enough cycles so* $W(\mathcal{N})$ *is at a maximum.*
2. *Repeat the simulation for* $N = 5000$ *and* $E = 5500$ *and measure the final entropy. Check whether the value of* β *that you found in the previous subquestion is consistent with the thermodynamic definition of the temperature (Eq. 1.36):*

$$\beta = \left(\frac{\partial S/k_B}{\partial E}\right)_N = \left(\frac{\partial \ln W(\mathcal{N})}{\partial E}\right)_N \approx \left(\frac{\Delta(\ln W(\mathcal{N}))}{\Delta E}\right)_N \tag{1.38}$$

Question 14 (Entropy for an Ideal Gas)
Boltzmann's formula for the entropy (Eq. 1.20) is in line with classical thermodynamics. To show this, consider the compression of an ideal gas at constant temperature from volume V_1 *to volume* V_2.

1. *Show that the entropy change for this process equals*

$$\Delta S = \int_{V_1}^{V_2} dV \left(\frac{\partial S}{\partial V}\right)_{T,N} = \int_{V_1}^{V_2} dV \left(\frac{\partial P}{\partial T}\right)_{V,N} = \int_{V_1}^{V_2} dV \frac{Nk_B}{V} = Nk_B \ln \frac{V_2}{V_1} \tag{1.39}$$

   Hint: have a look at sections B.5, B.6 and B.7.

2. *Explain that for* N *point particles in volume* V, $W(\mathcal{N}) \propto V^N$.
3. *Show that the result from classical thermodynamics (Eq. 1.39) is in agreement with Eq. 1.20.*

In retrospect, we have shown that for an isolated system (which has a constant volume V and number of particles N), the system energy E determines the temperature T *via* the fitting parameter β. Then the probability distribution $P(k)$ of the system states and all thermodynamic variables are determined as well. This result can also be used the other way around. The temperature of a system at given volume V and number of particles N determines the whole probability distribution $P(k)$ and from this distribution the system energy E and all other thermodynamic variables can be derived. In this way the temperature controls the energy of the system, in the same way as the energy of an isolated system controls the temperature of that system.

Chapter 2

Systems at Constant Temperature

In the previous chapter we have investigated the probability distribution for the states of non-interacting harmonic oscillators or molecules in a system containing many of them. This result can be generalized in order to describe systems whose particles *do* interact. First, each individual particle is replaced by a molecular system with a fixed volume V and fixed number of (possibly interacting) molecules N. Second, a large set of such molecular systems is considered. Such a set is called an *ensemble* and averages calculated from these sets are often called *ensemble averages*. If the systems in the ensemble can exchange energy, but no particles or volume, then the ensemble is called the *canonical ensemble*. The energy E of each of the systems in the ensemble fluctuates around the average system energy U in the ensemble. From the analogy of the canonical ensemble of systems that only exchange energy with a system of particles that only exchange energy, it is understood that the most probable distribution of energies over the system in the ensemble is the Boltzmann distribution. From the perspective of one system in the ensemble the exchange of energy with the other systems in the ensemble can be interpreted as heat exchange with a thermostat bath at the temperature T that corresponds to U, V and N. Therefore, the average system energy in the ensemble is the thermodynamic energy $U = U(N, V, T)$ of the molecular system.

2.1 Boltzmann Probability in the Canonical Ensemble

In quantum mechanics the state of a system is completely determined when all the quantum numbers are given. In classical mechanics this is the case when all the positions and momenta of all particles are known. For ease of notation we use one symbol k, which comprises all this detailed information to label the state of a system. In chapter 1 we found Eq. 1.3 for the probability $P(k)$ to find an individual harmonic oscillator or an individual ideal gas molecule in a molecular state k. Analogously, the probability to find a system of a canonical ensemble in a state k with energy E_k is given by

$$P(k) = \frac{\exp[-\beta E_k]}{Q} \tag{2.1}$$

where β is a constant that is determined by the total energy of all systems in the ensemble, and $Q = Q(N, V, T)$ is a normalization constant, called the *canonical partition function*, which is given by a sum over all possible (quantum) states k of a system in the ensemble

$$Q = \sum_k \exp[-\beta E_k] \tag{2.2}$$

Combining Eqs. 2.1 and 2.2 leads to $\sum_k P(E_k) = 1$, e.g. the probability distribution is normalized. The probability distribution Eq. 2.1 is known as the *Boltzmann distribution*. Note that the summation in Eq. 2.2 is over the states of an individual system, but the value of β is related to the total energy of the ensemble or, which amounts to the same, to the *average energy of a system in the ensemble*.

2.2 Thermodynamic Variables Follow from Q

2.2.1 Energy can be Derived from the Partition Function

The thermodynamic energy, also called internal energy, of a system is the average energy that a system has in the proper ensemble. This quantity is often called the *ensemble average of the energy*. In the canonical ensemble the (ensemble) average energy of a system can be derived from the canonical partition function by

$$U = \langle E \rangle = \sum_k E_k P(E_k) = \frac{\sum_k E_k \exp[-\beta E_k]}{Q} = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_{V,N} = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N} \tag{2.3}$$

At this point we have given a statistical interpretation of the thermodynamic variables like energy, volume, number of particles and temperature. The summation includes the individual quantum states of all the molecules in one system. Therefore, we obtain the average energy of systems in the ensemble, which is proportional to N.

2.2.2 Entropy can be Derived from the Partition Function

In an isolated system we have argued that the entropy is given by Eq. 1.21. We can generalize this relation for the canonical ensemble. If we substitute Eq. 2.1 directly in Eq. 1.21, we obtain the total entropy S_{ens} of the ensemble. If N_{ens} is the number of systems in the ensemble we then see that

$$S_{\text{ens}} = -k_B N_{\text{ens}} \sum_k \frac{\exp[-\beta E_k]}{Q} \ln\left[\frac{\exp[-\beta E_k]}{Q}\right] \tag{2.4}$$

In this expression k runs over all possible system states, E_k is the system energy of state k and Q is the sum over all system states (Eq. 2.2). As all the systems in the ensemble are identical, the entropy S of one system is obtained from $S = S_{\text{ens}}/N_{\text{ens}}$. The logarithm in Eq. 2.4 equals $-\beta E_k - \ln Q$, so the resulting expression for S can be split into two terms:

$$S = \frac{S_{\text{ens}}}{N_{\text{ens}}} = k_B \sum_k \left(\frac{\exp[-\beta E_k]}{Q}\beta E_k\right) + k_B\left(\frac{\sum_k \exp[-\beta E_k]}{Q}\ln Q\right) = \frac{U}{T} + k_B \ln Q \tag{2.5}$$

The factor N that appears in Eq. 1.21 is absent here. The reason is that the system entropy in Eq. 2.5 is the entropy of one of the systems in a big ensemble, whereas S in Eq. 1.21 is the total entropy of N individual particles. Since Eq. 2.3 relates the thermodynamic system energy U to the canonical partition function Q, we have now an expression for the system entropy S in terms of Q as well.

2.2.3 Free Energy is the Logarithm of the Partition Function

In classical thermodynamics one can derive the other thermodynamic variables from the dependence of the free energy F on temperature T, volume V and number of particles N. In the definition of F (Eq. B.15) we can substitute Eq. 2.3 for U and Eq. 2.5 for S to get a remarkably simple expression for the free energy

$$F = U - TS = -k_B T \ln Q \tag{2.6}$$

In the canonical ensemble N, V and T are fixed. From classical thermodynamics we know that for these variables the free energy F is the characteristic thermodynamic state function, see section B.5, which forms the starting point of treating systems for which N, V and T are the control variables.

2.2.4 Chemical Potential follows directly from the Free Energy

From the definition of the free energy (Eq. B.15) it follows directly that

$$dF = -SdT - PdV + \mu dN \tag{2.7}$$

Therefore, the chemical potential μ follows from

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \tag{2.8}$$

Alternatively, consider the process in which the system is (mentally) built up by adding molecules, meanwhile adjusting the volume and adding heat in such a way that P and T remain constant. This results in the alternative expression

$$\mu = \frac{F + PV}{N} = \frac{F}{N} + \frac{P}{\rho} \tag{2.9}$$

which will be used extensively in chapter 9.

2.2.5 Other Thermodynamic Variables

Following standard routes in classical thermodynamics, expressions for many thermodynamic variables, at given N, V and T, can be derived from $F(N, V, T)$. Operating in the same way on the statistical expression $-k_BT \ln Q$ for F we obtain statistical expressions for all these thermodynamic variables. We conclude that all thermodynamic functions and variables can be deduced from the dependence on N, V and T of the canonical partition function Q.

A first example of a thermodynamic variable that can be derived from the canonical partition function is the pressure P. Upon substituting the thermodynamic definition

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \tag{2.10}$$

in Eq. 2.6 we find

$$P = k_BT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} \tag{2.11}$$

Once we have an expression for the dependence of Q on V, N and T we can derive how P depends on these thermodynamic variables*. This relation is the *equation of state* that we know from thermodynamics, see section B.1. For an ideal gas Eq. 1.13 shows that the translational part of the molecular partition function depends on V, but the internal part is independent of V. Therefore the pressure of an ideal gas does not depend on the internal structure of the molecules.

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*In section 6.4 we will show that even for systems with interactions, the pressure can be written as an ensemble average that can be easily computed in a simulation.

Question 15 (The Pressure of a Gas)
In chapter 3 we will show how the canonical partition function Q *of an ideal gas is related to the molecular partition function* q. *Upon combining Eq. 1.13 with Eq. 3.6 it follows that*

$$Q = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N \tag{2.12}$$

is the partition function of an ideal gas of N *point particles in volume* V. *The thermal wavelength* Λ *is given by Eq. 1.14.*

1. *Show that the partition function of the ideal gas leads to the ideal gas law (*$P = \rho k_B T$ *in which* $\rho = N/V$*).*

We can also calculate the equation of state for non-ideal gases, once Q *is known. A simple example is a (model) gas of hard spheres for which the canonical partition function is approximately given by*

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{V - N\cdot b}{\Lambda^3}\right)^N \tag{2.13}$$

in which b *is related to the (excluded) volume per particle.*

2. *Starting from the ideal gas expression for* Q *(Eq. 2.12), justify that taking into account the total volume occupied by the hard sphere molecules leads to an expression of the form of Eq. 2.13.*

3. *Show that Eq. 2.13 results in the following equation of state, giving* P *as a function of* N, V *and* T.

$$P = \frac{N k_B T}{V - N\cdot b} \tag{2.14}$$

4. *Is the pressure of a system of* N *hard spheres in volume* V *and temperature* T *larger, smaller or equal to that of an ideal gas at the same density and temperature?*

5. *Show that the energy of this system is equal to the energy if the system would behave as an ideal gas (Eq. 1.15).*

A second example is the specific heat at constant volume. Its thermodynamic definition is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} \tag{2.15}$$

Using this in Eq. 2.3 we find

$$C_V = \frac{1}{k_B T^2}\frac{\partial^2 \ln Q}{\partial \beta^2} \tag{2.16}$$

Question 16 (Heat Capacity)
Simulate systems of harmonic oscillators at a number of different choices of the system energy U *(see question 4). Determine the temperature for each of these systems. Plot* U *versus* T *to calculate the molar heat capacity* $\overline{C}_V = C_V/N$ *using the thermodynamic definition Eq. 2.15. Also use the molecular version of Eq. 2.16, i.e. with* Q *replaced by* q *(Eq. 1.4) to deduce* C_V *from a plot of* $\ln q$ *versus* β *and show that the results are consistent.*

2.3 Fluctuations Disappear in the Thermodynamic Limit

In the system of harmonic oscillators and in the ideal gas we have seen that the probability distribution over the states of individual oscillators or particles depends exponentially on the energy of the state. Naively one might think that the probability to find a group of particles, or even a system, with an energy E is proportional to $\exp[-\beta E]$. However, as we already know from the *Balls & Bucket* game, this is not correct.

Question 17 (Division into Subsystems)
Consider the system of question 4.

1. *Divide a system of* $N = 100$ *oscillators with a total energy* $E = 200$ *in groups with* m *oscillators within each group.* E_m *is the energy in the first* m *oscillators. Make energy distribution histograms* $P(E_m)$ *for* $m = 2, 5, 10, 20, 50$. *Explain the location of the maximum of this distribution.*
2. *From the histograms estimate the standard deviation* σ_{E_m} *and average* $\langle E_m \rangle$ *for each of the values of* m.
3. *Make a double-logarithmic plot of* $\sigma_{E_m} / \langle E_m \rangle$ *against* m *to find out whether the decay follows a power law* $\sigma_{E_m} / \langle E_m \rangle \propto m^{-\alpha}$ *and, if yes, estimate the exponent* α.

The reason that a peak appears in the distribution of the average particle energy in a group of m particles, and that this peak increases in height and decreases in width with increasing m, is a manifestation of a very general theorem in mathematics.

Question 18 (Central Limit Theorem)
Consider a large number of random numbers R *that are drawn from a uniform distribution between* 0 *and* 1.

1. *Make a frequency histogram* $p(R)$ *of these numbers and make sure that the shape of the histogram is consistent with what one should expect.*
2. *Draw a large number of averages* $a \equiv \left(\sum_{k=1}^{N} R_k\right)/N$ *of* N *subsequent random numbers. Make a frequency histogram* $p(a)$ *of these averages and check that this histogram has a peak near* $a \approx 1/2$, *which becomes narrower with increasing* N. *Fit* $p(a)$ *to a Gaussian shape,* $p(a) \propto \exp[-(a-\mu)^2/(2\sigma^2)]$, *explain the meaning of* μ *and* σ *and discuss how they do or do not depend on* N.
3. *Answer the same questions for numbers* R *that can take the value* 0 *with probability* p *and the value* 1 *with probability* $1 - p$. *First take* $p = 0.5$ *and next* $p = 0.1$. *Explain the difference.*

What we have seen in questions 17 and 18 is the so-called *Central Limit Theorem*. Let $x_1, x_2, \cdots, x_N$ be N independent stochastic variables, drawn from a distribution $p(x)$ with average μ and variance σ^2. Then the distribution $p(y)$ of the stochastic variable

$$y \equiv \frac{\sum_{i=1}^{N} x_i - N\mu}{\sigma\sqrt{N}} \tag{2.17}$$

will approach a standard normal distribution

$$p(y) = \frac{1}{\sqrt{2\pi}} \exp[-y^2/2] \tag{2.18}$$

for $N \to \infty$ for any $p(x)$. In parallel to the mathematical argument, there is also a thermodynamic argument to explain and interpret the decrease of the peak width with increasing number of particles m. The argument is based on a remarkable result, known as the *fluctuation dissipation theorem*. It states that the response of a variable to an external stimulus is proportional to the variance, as caused by thermal fluctuations, of that variable. In the present case the stimulus is a temperature variation and the energy change in response is proportional to the thermal energy fluctuation.

Question 19 (Energy Fluctuations)
By definition the variance of the energy is

$$\sigma_E^2 \equiv \left\langle (E - \langle E \rangle)^2 \right\rangle \tag{2.19}$$

were the brackets $\langle \cdots \rangle$ are used to denote an average.

1. *Show that Eq. 2.19 can alternatively be written as*

$$\sigma_E^2 = \left\langle E^2 \right\rangle - \langle E \rangle^2 \tag{2.20}$$

   for any probability distribution of the energy.

2. *Write out Eq. 2.16 to the form*

$$C_V = \frac{1}{k_B T^2} \left[\frac{1}{Q} \frac{\partial^2 Q}{\partial \beta^2} - \left(\frac{1}{Q} \frac{\partial Q}{\partial \beta} \right)^2 \right] \tag{2.21}$$

   and derive from this result the following explicit expression for the heat capacity

$$C_V = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2} \tag{2.22}$$

We see that the heat capacity measures not only the energy dissipation in a system but also the energy fluctuation. This result can also be used the other way around, to get an expression for the relative fluctuations of the system energy E around the average value $U = \langle E \rangle$

$$\frac{\sigma_E}{U} = \frac{\sqrt{C_V / k_B}}{\beta U} \propto \frac{1}{\sqrt{N}} \tag{2.23}$$

From a thermodynamic point of view it is obvious that both U and C_V are proportional to N (although the leading terms in both $\left\langle E^2 \right\rangle$ and $\langle E \rangle^2$ are of order N^2, their difference in Eq. 2.22 is proportional to N). Thus it follows from Eq. 2.23 that the energy fluctuations are proportional with $1/\sqrt{N}$, see Fig. 2.1. The effect that we find for the idealized systems of harmonic oscillators and ideal gases is very general. For macroscopic systems ($N \to \infty$) the energy fluctuations can be neglected and the energy of the system can be considered as constant. The same holds for pressure fluctuations in a system at constant volume, for volume fluctuations in a system at constant pressure, and for temperature fluctuations in an adiabatic system.

2.4 The Third Law

In thermodynamics the physical basis for the third law, stating that the entropy of any system is zero at zero temperature is difficult to understand. This is however straightforward in statistical mechanics. At zero temperature, i.e. $\beta \to \infty$, only the state or states with the lowest possible energy will be occupied. This is by definition the ground state. From quantum mechanics we

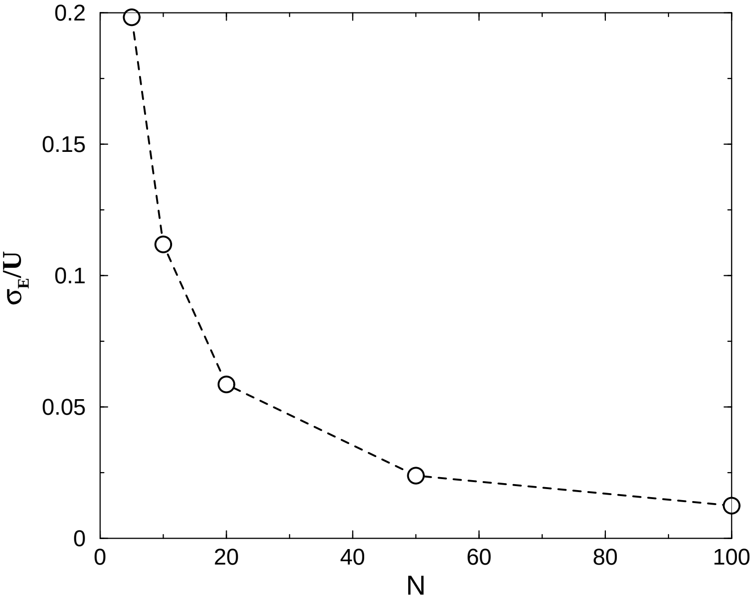

Figure 2.1: Relative energy fluctuations (Eq. 2.23) for a system of N harmonic oscillators with $U/N \approx 2$.

know that the ground state is non-degenerate. Therefore the only system distribution that has to be considered is $\mathcal{N} = (N, 0, 0, \cdots)$. Since $\mathcal{W}(\mathcal{N}) = 1$ for this system distribution, we get

$$S(T \to 0) = k_B \ln 1 = 0 \tag{2.24}$$

which is precisely the third law of thermodynamics. The same result can be derived from the partition function. At zero temperature the system energy U is the ground state energy E_0. The Boltzmann factor for the ground state is $\exp[-\beta E_0]$ and in the limit $\beta \to \infty$ the Boltzmann factor for all excited states is vanishingly small. Hence the partition function Q reduces to the first term $Q = \exp[-\beta E_0]$. Substituting this in Eq. 2.5 we find

$$S(T \to 0) = \lim_{T \to 0} \left(\frac{E_0}{T} + k_B \ln[\exp[-\beta E_0]] \right) = 0 \tag{2.25}$$

which is equivalent with Eq. 2.24.

Question 20 (Examples of the Third Law)
Consider the partition function for an ideal gas and an harmonic oscillator.

1. *Show that* $q(T \to 0) = 1$ *for the molecular partition function* q *of a harmonic oscillator (Eq. 1.5).*
2. *Show that* $q(T \to 0) = 1$ *for the molecular partition function* q *of an ideal gas (Eq. 1.9).*
3. *Show also that* $q(T \to 0) = 0$ *for the molecular partition function* q *of an ideal gas when the usually very accurate approximation Eq. 1.13 is used. This seems to imply* $S(T \to 0) = -\infty$ *for an ideal gas, violating the third law. Use question 9 to explain that Eq. 1.13 is essentially a high temperature approximation, even though it can be used at very low* T*. Argue that therefore the approximate result* $q(T \to 0) = 0$ *does* not *lead to the conclusion that the third law does not hold for an ideal gas.*

Chapter 3

Many Particle Systems

In general molecular systems may be very complicated. Each quantum state of the system may involve a very large number of quantum numbers. If we know nothing about the set of possible quantum numbers and the energy levels associated with them it is hopeless to obtain a reliable approximation for the partition function. Fortunately, there are often methods to reduce the complexity of this problem to a large extent. The first case is when the degrees of freedom influence each other hardly. In section 3.1 we shall discuss why and how the partition function factorizes in such cases. Complications arising from the indistinguishability of identical particles in quantum mechanics will be discussed shortly. The second case is when interactions are important, but they can be described by a relatively simple interaction model for the multiplicity of energy states can be approximated. This will be the subject of section 3.3.

3.1 Factorization for Independent Degrees of Freedom

In many cases it is appropriate to assume that different degrees of freedom in a system are independent. This means that the energy stored in one degree of freedom does not influence the other degrees of freedom. Consider an ideal gas classically. The ideal gas assumption, that molecules are not interacting, implies that the kinetic energy associated with the center of mass motion is independent of the rotations and internal vibrations of the molecule. Therefore, the energy of the system will be the sum of translational kinetic energy and internal (kinetic and potential) energy of the molecules. According to quantum mechanics, the eigenfunctions will factorize in center of mass coordinates and internal molecular coordinates, leading to the total energy being the sum of translational and internal molecular contributions.

For the moment, we restrict ourselves to an ideal gas consisting of N molecules. Each molecule is characterized by its own set of quantum numbers (the quantum mechanical indistinguishability of identical particles will be dealt with below). Let $\mathbf{k}_n = (k_{n,x}, k_{n,y}, k_{n,z})$ denote the translational quantum numbers of molecule n, corresponding to the *particle in a box* eigenfunction for that molecule (see Eq. 1.8). The translational state of the system is described by a set of $3N$ quantum numbers that we denote as $\mathbf{k} = (\mathbf{k}_1, \mathbf{k}_2, \cdots, \mathbf{k}_N)$. For an ideal gas of point particles these quantum numbers describe all possible system states. Real atoms and molecules however, have an internal structure. For atoms electronic excitations are possible and for molecules in addition we have rotations and internal vibrations. We write $\mathbf{l}_n$ for the quantum numbers that describe the internal excitations of particle n. They describe the electronic, rotational and vibrational eigenstates of molecule n. The internal states of the ideal gas system are described by the list $\mathbf{l} = (\mathbf{l}_1, \mathbf{l}_2, \cdots \mathbf{l}_N)$ of all $\mathbf{l}_n$. For the energy we write

$$E_{\mathbf{k},\mathbf{l}} = \sum_{n=1}^{N} E_{0,n} + \sum_{n=1}^{N} E_{\mathbf{k}_n}^{\text{trans}} + \sum_{n=1}^{N} E_{\mathbf{l}_n}^{\text{internal}} \tag{3.1}$$

The first term sums the ground state energies $E_{0,n}$ of the molecules n. In many cases the molecular ground state energy serves as an arbitrary zero of the energy scale, and can be omitted. However, in the presence of chemical reactions, the relative position of the energy levels in the reacting molecules is important as well (see section 4.2). Then the ground state energy can be chosen as zero for each of the elements of the periodic system, and this choice fixes the value of the ground state energy for molecules. Therefore, we can define the molecular partition function here as

$$q = \sum_{\mathbf{k},\mathbf{l}} \exp[-\beta(E_{\mathbf{k},\mathbf{l}} - E_0)] \tag{3.2}$$

which means that

$$\sum_{\mathbf{k},\mathbf{l}} \exp[-\beta E_{\mathbf{k},\mathbf{l}}] = q \times \exp[-\beta E_0] \tag{3.3}$$

In the sequel, for ideal gases and ideal gas mixtures, we shall only write the ground state energy explicitly when chemical reactions play a role (see chapter 4).

Question 21 (Factorization)
In general, if the energy of a system can be written as the sum of independent terms, the partition function of this system can be written as the product of partition functions corresponding to each term of the total energy. To illustrate this, show that

$$\sum_{i=0}^{3}\sum_{j=0}^{2} x^i y^j = \sum_{i=0}^{3}\left(\sum_{j=0}^{2} x^i y^j\right) = \left(\sum_{i=0}^{3} x^i\right) \times \left(\sum_{j=0}^{2} y^j\right) \tag{3.4}$$

The translational energy of molecule n is given by Eq. 1.10 and the internal energy $E_{\mathbf{l}_n}^{\text{internal}}$ of that molecule may, among others, include vibrational terms of the form of Eq. 1.6. If the quantum numbers $\mathbf{k}$ and $\mathbf{l}$ could be summed independently, then we would find for the summation in Eq. 3.1

$$\sum_{\mathbf{k}_1,\mathbf{l}_1} \cdots \sum_{\mathbf{k}_N,\mathbf{l}_N} \exp\left[-\beta \sum_{n=1}^{N} E_{\mathbf{k}_N,\mathbf{l}_N}\right] = \left(\sum_{\mathbf{k},\mathbf{l}} \exp[-\beta E_{\mathbf{k},\mathbf{l}}]\right)^N \tag{3.5}$$

This factorization however, is in general not valid. It is based on the tacit assumption that the particles are distinguishable. E.g. it is assumed that the system state with particle 1 in the ground state and particle 2 in the first excited state is different from the system state in which particle 2 is in the ground state and particle 1 is in the first excited state. From quantum mechanics we learn that identical particles can not be distinguished and that these two situations correspond to the same system state. Therefore, if we replace the summation in Eq. 2.2 by that in Eq. 3.5, we introduce an enormous over-counting of states when the particles are identical.

Fortunately, in most many particle systems, the over-counting can be repaired relatively easily. As we have seen in question 9, many translational states contribute to the partition function. Therefore, for almost all terms in the left hand side of Eq. 3.5 all N particles are in different molecular states. Interchanging particles when the system is in one of the states $(\mathbf{k}, \mathbf{l})$ is possible in $N!$ ways. All of these interchanges leave the system state unchanged, though they correspond to different terms in Eq. 3.5. Therefore we can correct for the over-counting by writing

$$Q = \frac{q^N}{N!} \tag{3.6}$$

where q is the molecular partition function (Eq. 3.2) *. For an ideal gas of molecules this amounts to

$$q^N = \left(\sum_{\mathbf{k}} \exp[-\beta E_{\mathbf{k}}^{\text{trans}}]\right)^N \times \left(\sum_{\mathbf{l}} \exp[-\beta E_{\mathbf{l}}^{\text{internal}}]\right)^N = (q^{\text{trans}})^N \times (q^{\text{internal}})^N \qquad (3.7)$$

These expressions form the basis of the statistical thermodynamics of systems of non-interacting particles. An ideal gas is an example of non-interacting molecules. Eq. 1.9 takes care of the translational degrees of freedom of the gas molecules. Internal degrees of freedom like rotations, other vibrational modes and electronic excitations can be treated in a similar way. As long as these degrees of freedom are (approximately) independent, each will give rise to a factor in the molecular partition function that is based on the eigenstates and energy levels of that degree of freedom.

The factorization of the partition function leads to the conclusion that the free energy can be written as a sum of contributions from different degrees of freedom. Indeed, combining Eq. 3.7 with the definition of the free energy (Eq. 2.6) gives

$$F = -Nk_BT\left[1 + \ln\frac{q^{\text{trans}}}{N}\right] - Nk_BT\ln q^{\text{internal}} \qquad (3.8)$$

for a system of non-interacting particles. Here some elementary properties of the logarithm and Stirling's approximation $\ln N! \approx N\ln N - N$ (Eq. C.48) have been used. Note that the denominator N which originates from the combinatorial factor N! appears only once in Eq. 3.6. This is because the internal degrees of freedom belong to the molecules whose indistinguishability was treated together with their translational motion. In systems of interacting particles the simple reduction in Eq. 3.8 of the canonical partition function Q to molecular partition functions q can not be used any more, and we shall need more elaborate techniques to obtain the partition function and the variables that can be derived from it. Also then the over counting of identical states should be properly treated. E.g. in the Monte Carlo simulations that we shall treat later in chapter 6, molecules are explicitly numbered, as otherwise they can not be addressed by the computer program. The over-counting thus induced can be taken into account again by factors $1/N!$ for all particle types that are included in the simulation.

3.2 The Ideal Gas

In section 2.2 we have seen that all thermodynamic variables can be derived from the canonical partition function. For an ideal gas we substitute Eq. 1.13 in Eq. 3.8 to find

$$\ln Q(N,V,T) = N\left[1 + \ln\frac{V}{N\Lambda^3}\right] + N\ln q^{\text{internal}}(T) \qquad (3.9)$$

where the thermal wavelength Λ is given by Eq. 1.14. The first term at the right hand side is the translational contribution, which depends on N, V and T and is the same for all types of molecules. The second term is due to the internal degrees of freedom of each molecule and this term depends on the type of molecule. It is proportional to N, but further it only depends on temperature. At very low temperature it may be that only the ground state of the molecule

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[*] In text books it is sometimes argued that in some systems the factor $1/N!$ in Eq. 3.6 should be omitted, notably in crystals, where the individual particles can be distinguished by the lattice position where they are situated. This argument however, can not be valid since even in crystals atoms and molecules may hop from one lattice site to another, though much slower than in gases or liquids.

is occupied and since $q^{\text{internal}}(T \to 0) = 1$ the internal structure of the molecules does not contribute to the partition function, neither to thermodynamic variables. To keep the expression transparent we shall drop the argument (T) of the internal molecular partition function, writing simply q^{internal} for $q^{\text{internal}}(T)$. The link with thermodynamics is via Eq. 2.6 for the Helmholtz free energy $F(N, V, T)$, where substituting Eq. 3.9 leads to

$$F(N, V, T) = -Nk_BT\left[1 + \ln\frac{V}{N\Lambda^3}\right] - Nk_BT\ln q^{\text{internal}} \tag{3.10}$$

In an analogous way the entropy can be found from $S = -\left(\partial F/\partial T\right)_{N,V}$, leading to the so-called *Sackur-Tetrode* equation for the entropy of a polyatomic ideal gas

$$S(N, V, T) = Nk_B\left[\frac{5}{2} + \ln\frac{V}{N\Lambda^3}\right] + Nk_B\left[\ln q^{\text{internal}} + T\frac{d\ln q^{\text{internal}}}{dT}\right] \tag{3.11}$$

The first term is the entropy of a mono-atomic ideal gas (with all atoms in their electronic ground state), the second term comprises the entropy associated with the internal degrees of freedom of a molecular ideal gas. This expression is very useful at all realistic temperatures, but it is in conflict with the third law (see question 20). For very low temperature the term with the thermal length Λ becomes dominating, leading to $S \approx Nk_B \ln T^{3/2}$, where $S(T \to 0) = -\infty$. For the energy we obtain

$$U(N, V, T) = \frac{3}{2}Nk_BT - N\frac{d\ln q^{\text{internal}}}{d\beta} \tag{3.12}$$

Here the first term is the kinetic energy of the center of mass of the molecules, the second term may comprise the kinetic energy of rotation, potential and kinetic vibrational energy and electronic energies. The specific heat is

$$C_V(N, V, T) = \frac{3}{2}Nk_B - \frac{N}{k_BT^2}\frac{d^2\ln q^{\text{internal}}}{d\beta^2} \tag{3.13}$$

Finally, we get the chemical potential from the definition $\mu = (\partial F/\partial N)_{T,V}$. As the chemical potential is especially useful in the context of chemical reactions, we have to take the molecular ground state energy E_0 explicitly into account. This amounts to replacing q by $q\exp[-\beta E_0]$ (Eq. 3.3). The final result is

$$\mu = E_0 - k_BT\ln\frac{V}{N\Lambda^3} - k_BT\ln q^{\text{internal}} \tag{3.14}$$

Question 22 (Chemical Potential of an Ideal Gas)
In thermodynamic applications the chemical potential of an ideal gas at temperature T *and pressure* P *is often written in the form*

$$\mu = \mu(P, T) = \mu^0(T) + k_BT\ln\left[P/P_0\right] \tag{3.15}$$

in which P_0 *is an arbitrary reference pressure (usually* $P_0 = 1$ *bar). Obviously an expression for* μ^0 *can be obtained by subtracting Eq. 3.15 from Eq. 3.14. Show that the resulting expression for* μ^0 *only depends on* T *and not on* N *and* V.

3.3 Multiplicity of Energy Levels

In question 8 we have seen that for a system consisting of many non-interacting particles there may be many different system (quantum-)states with the same energy. The number of system

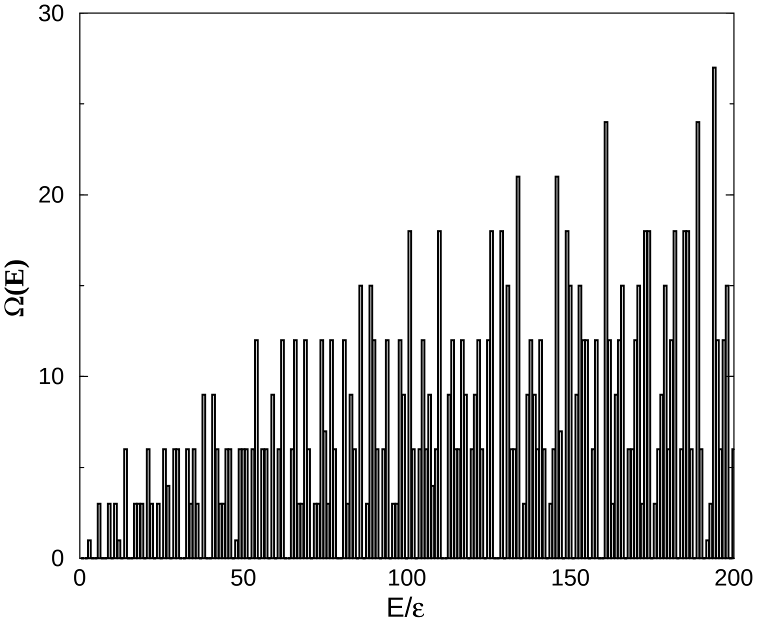


Figure 3.1: Multiplicity $\Omega(E)$ for $N = 1$ particle in a 3-dimensional box (question 8). The multiplicity $\Omega(E)$ is the number of system states with energy E. For the ground state E_{min} of this system, $k_x = k_y = k_z = 1$ so $E_{\text{min}} = 3\epsilon$ and $\Omega(E_{\text{min}}) = 1$. Note that $\Omega(E)$ increases with E. For systems of $N \gg 1$ particles the increase will be very sharp.

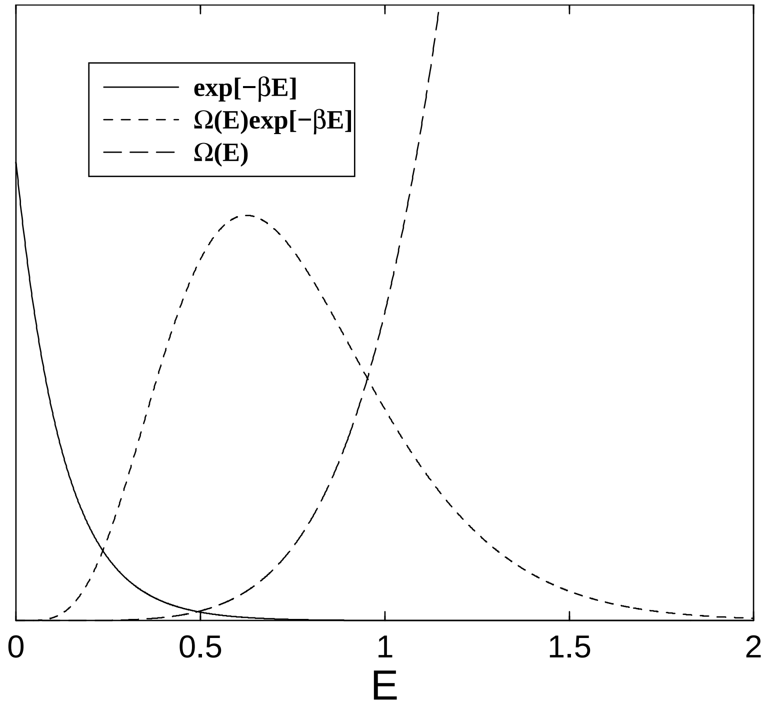


Figure 3.2: The product $\Omega(E)\exp[-\beta E]$ is often strongly peaked around the average energy $\langle E \rangle$. The position of this peak strongly depends on the temperature, its width decreases with the number of particles in the system.

states corresponding to the same energy E is called the *multiplicity* $\Omega(E)$ of that energy, see Fig. 3.1. Also for internal molecular degrees of freedom (e.g. rotations and vibrations) and for interacting systems multiplicities exist. Using these, the canonical probability distribution of states, Eq. 2.1, can be transformed into the canonical probability of energies

$$P(E) = \frac{\Omega(E)\exp[-\beta E]}{Q} \tag{3.16}$$

$$Q = \sum_{E} \Omega(E)\exp[-\beta E] \tag{3.17}$$

in which the summation is over all possible energies of the system and *not* over all system states. It is important to take into account the quantum mechanical indistinguishability of identical particles. One of the consequences is that the exact ground state (with energy E_{min}) of any physical system is non-degenerate, $\Omega(E_{\text{min}}) = 1$, whereas a classical description suggests that the *system* ground state, where all N molecules are in their *molecular* ground state, has a multiplicity of $N!$. For non-interacting molecules their indistinguishability is taken into account afterwords as in Eq. 3.6. In a classical description of interacting particles, the same factor $1/N!$ has to be included in Eq. 3.17.

Question 23 (Particle inside a Box)
For a particle in a 3-dimensional box most of the degeneracies are 1, 3 or 6. Let $\epsilon = h^2/\left(8mL^2\right)$ *denote the elementary energy scale for this particle. By finding out which combination(s) of* k_x, k_y *and* k_z *correspond to the requested particle energy, verify that* $\Omega(3\epsilon) = 1$, $\Omega(9\epsilon) = 3$ *and* $\Omega(14\epsilon) = 6$. *Also explain the exceptional value* $\Omega(38\epsilon) = 9$ *(hint: look at question 8).*

Usually $\Omega(E)$ strongly increases with energy (as suggested by Fig. 3.1) for large systems and $\exp[-\beta E]$ strongly decreases with energy. Therefore, the function $\Omega(E)\exp[-\beta E]$ is strongly peaked around the average energy $\langle E \rangle$, see Fig. 3.2. The value of $\langle E \rangle$ will therefore depend on the temperature. It depends on the temperature and on the location of the energy levels whether only a few, or many levels contribute to the molecular partition function in Eq. 3.17. We will come back to this in chapter 5.

Chapter 4

Mixtures of Ideal Gases

The applications of statistical thermodynamics that we have encountered so far were developed for molecules that do not interact. In reality, molecules have both physical and chemical interactions. With physical interactions we mean attraction and repulsion of molecules that do not essentially change the individual molecular properties. Such interactions are responsible for the phase behavior of systems. They will be the subject of the next chapters.

Chemical reactions are a form of interaction where molecules are formed or removed. During chemical reactions the number of molecules of one kind is not constant, but it approaches an average value, given by the equilibrium constants of the reactions. The equilibrium constant can, at least in principle, be calculated by statistical methods. The central problem in a statistical analysis is to compute the partition function of the system, *including the interactions*. This is a formidable task in general, and approximations have to be developed for almost all cases.

In the next chapter we shall develop the theory and the methods for treating systems of physically interacting subsystems. Here we shall treat the case where chemical reactions constitute the only molecular interactions, i.e. we restrict ourselves to chemically reactive ideal gas mixtures. In these systems the canonical partition function for each composition of the mixture can be computed directly from the molecular partition functions. Then the equilibrium situation can be analyzed by a proper averaging over the exact results for different compositions. In this way we shall already develop a feeling for the approximation methods that will be used later for physically interacting molecular systems. The essential point is that the distribution of $\Omega(E)\exp[-\beta E]$ (Eq. 3.17) is often sharply peaked around the average $\langle E \rangle$. Therefore, many important thermodynamic variables can be obtained from an analysis of the states with an energy close to the peak value $E \approx \langle E \rangle$. Methods that take into account only the states with the most probable energy $\langle E \rangle$ are referred to in literature as *mean field* or *random phase* approximations. They are often reliable, as long as one is not too close to a critical point (see chapter 5 and following). In general these methods reasonably estimate the system energy, but they underestimate the system entropy.

4.1 Non-Reactive Ideal Gas Mixtures

We start with an ideal gas mixture of gases A and B, first excluding chemical reactions. The canonical partition function for an ideal gas mixture of N_A molecules A and N_B molecules B is

$$Q(N_A, N_B, V, T) = \frac{q_A^{N_A} \exp[-\beta N_A E_{0,A}]}{N_A!} \times \frac{q_B^{N_B} \exp[-\beta N_B E_{0,B}]}{N_B!} \tag{4.1}$$

Note that we have explicitly written the ground state energy for both molecules according to Eq. 3.2 so here q_A and q_B are defined according to

$$q = \sum_{\mathbf{k}} \exp[-\beta(E_{\mathbf{k}} - E_0)] \tag{4.2}$$

This is necessary because below we need to take into account the energy change during chemical reactions. The free energy of the mixture is

$$F(N_A, N_B, V, T) = -k_B T \ln Q \tag{4.3}$$

When we apply the thermodynamic definition (Eq. B.28) for the molar free energy we get

$$\overline{F}_A = \left(\frac{\partial F}{\partial N_A}\right)_{P,T,N_B} = -k_B T \ln\left[\frac{q_A}{N_A}\right] + E_{0,A} - k_B T \tag{4.4}$$

The molar free energy $\overline{F}_B$ of molecules B is defined analogously. Using Eq. 3.14 we recover the thermodynamic relation $\overline{F} = \mu - k_B T$ for an ideal gas. We also see that

$$F = N_A \overline{F}_A + N_B \overline{F}_B \tag{4.5}$$

which is what one could expect for an ideal gas mixture.

Question 24 (Energy of an Ideal Gas Mixture)
Use the general relation between U and Q (Eq. 2.3) and Eq. 4.1 to show that the energy of this ideal gas mixture is given by

$$U(N_A, N_B, V, T) = N_A \overline{U}_A + N_B \overline{U}_B \tag{4.6}$$

where

$$\overline{U}_A = \left(\frac{\partial U}{\partial N_A}\right)_{P,T,N_B} = -\left(\frac{\partial \ln q_A}{\partial \beta}\right)_V + E_{0,A} \tag{4.7}$$

is the molar energy of A and the molar energy of B is defined analogously.

Question 25 (Probability Distribution of Energy in Mixtures)
Consider again an ideal gas for which the particles can exchange energy by collisions (see question 8). Set up simulations of N_A molecules A and N_B molecules B. Take a few different values for the respective ground state energies $E_{0,A}$ and $E_{0,B}$ and the total energy U. Measure the molecular energy distributions for A and B separately and fit them with $\ln P(E_{\mathbf{k}}) = -\beta(E - E_0) - \ln q$. Investigate whether they can be fitted with the same β and q for A and B. Explain your answer with physical arguments. Is your result influenced by the total energies or by the ground state energies of A and B molecules?

4.2 Isomerization Reaction in an Ideal Gas Mixture

In this section we discuss a simple first order reaction. We assume that the density of the mixture is sufficiently low that it can be treated as an ideal mixture. The reaction equation is

$$A \leftrightarrows B \tag{4.8}$$

Examples of such reactions are isomerization equilibria in organic chemistry, but also conformational changes in biomolecules fall in this class. The numbers N_A of isomers A and N_B of isomers B are not constant, but their sum $N = N_A + N_B$ is. The partition function of the reactive mixture is obtained by summing Eq. 4.1 over all possible values of N_A while substituting $N_B = N - N_A$

$$Q = \sum_{N_A=0}^{N} \frac{q_A^{N_A} \exp[-\beta N_A E_{0,A}]}{N_A!} \times \frac{q_B^{N-N_A} \exp[-\beta(N - N_A)E_{0,B}]}{(N - N_A)!} \tag{4.9}$$

Note that Eq. 4.9 has a very similar structure as Eq. 3.17. To see this, we use Eq. C.24 for the binomial coefficient $\binom{N}{N_A}$ to write Eq. 4.9 in the form

$$Q = \frac{1}{N!} \sum_{N_A=0}^{N} \binom{N}{N_A} \exp\left[-\beta\left[N_A(E_{0,A} - k_B T \ln q_A) + (N - N_A)(E_{0,B} - k_B T \ln q_B)\right]\right] \tag{4.10}$$

The summation over energy levels is replaced by a summation over N_A, the binomial coefficient gives the multiplicity and the energy in the Boltzmann factor is the sum of the zero-point energies and the internal free energy of the isomers. For the present isomerization reaction the summation in Eq. 4.10 can be done exactly using the binomial summation formula Eq. C.25:

$$\begin{aligned} Q &= \frac{1}{N!} \sum_{N_A=0}^{N} \binom{N}{N_A} (q_A \exp[-\beta E_{0,A}])^{N_A} \times (q_B \exp[-\beta E_{0,B}])^{(N-N_A)} \\ &= \frac{(q_A \exp[-\beta E_{0,A}] + q_B \exp[-\beta E_{0,B}])^N}{N!} \\ &= \frac{q^N}{N!} \end{aligned} \tag{4.11}$$

Here, we have introduced the average molecular partition function q

$$q = q_A \exp[-\beta E_{0,A}] + q_B \exp[-\beta E_{0,B}] \tag{4.12}$$

From this relation, the system energy of the reactive mixture is found as

$$U = U(N, V, T) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N} = N \times \frac{\overline{U}_A q_A \exp[-\beta E_{0,A}] + \overline{U}_B q_B \exp[-\beta E_{0,B}]}{q} \tag{4.13}$$

Applying the second binomial summation formula, Eq. C.26, we can calculate the average number of A isomers as well:

$$\begin{aligned} \langle N_A \rangle &= \frac{1}{Q}\frac{1}{N!} \sum_{N_A=0}^{N} N_A \binom{N}{N_A} (q_A \exp[-\beta E_{0,A}])^{N_A} \times (q_B \exp[-\beta E_{0,B}])^{(N-N_A)} \\ &= N \times \frac{q_A \exp[-\beta E_{0,A}]}{q} \end{aligned} \tag{4.14}$$

Question 26 (Exact Results for an Isomerization Reaction)
Consider the chemical reaction $A \leftrightarrows B$.

1. *Use Eq. 4.14 to obtain the following expression for the equilibrium constant of reaction Eq. 4.8:*

$$K = \frac{\langle N_B \rangle}{\langle N_A \rangle} = \frac{q_B \exp[-\beta E_{0,B}]}{q_A \exp[-\beta E_{0,A}]} \tag{4.15}$$

2. *Show that* K *depends only on temperature, as it should, and not on* V *or* N*, even though* Q *depends on these parameters. Hint: use Eq. 3.7 and the dependence of* q^{trans} *and* q^{internal} *on* N, V *and* T.

Question 27 (Simulation of an Isomerization Reaction)
Repeat the simulations that you carried out in question 25, but now with the additional possibility of the reaction $A \leftrightarrows B$.

1. *Determine* β *by fitting the energy distributions of the* A *and* B *isotherms. Is the result different from what you found in question 25?*

2. *Use the average numbers of* A *and* B *isomers in the simulation to measure the equilibrium constant* K *and check the validity of Eq. 4.15.*

3. *Discuss whether the measured values for* K *have the dependence on the zero-point energies of both isomers that one should expect.*

4. *Measure the instantaneous value of* $K(t) \equiv N_B/N_A$ *as a function of time. Explain why* $K(t)$ *fluctuates around* K.

5. *Make a histogram of the measured values for* K*. Repeat the simulations for twice as many particles and explain why the spread of* $K(t)$ *decreases.*

4.3 Mean Field Approximation

We can use the discussion in the previous section to illustrate the *mean field* or *random phase* approximation and to judge its reliability. Indeed we will see that for the simple example of a first order isomerization reaction Eq. 4.15 is also found by a mean field approximation.

Our starting point is the partition function Q (Eq. 4.9). Rather than taking all terms in the summation into account, we look for the largest term. Consider the situation that $q_A = q_B = q$ and $E_{0,A} = E_{0,B} = 0$ which means that

$$Q = q^N \sum_{N_A=0}^{N} \frac{1}{N_A!(N-N_A)!} \tag{4.16}$$

Anticipating that the largest term in this equation will appear for $N_A = N/2$, in Fig. 4.1 we have plotted the ratio

$$R = \frac{\dfrac{q^N}{N_A!(N-N_A)!}}{\dfrac{q^N}{(N/2)!(N/2)!}} = \frac{((N/2)!)^2}{N_A!(N-N_A)!} \tag{4.17}$$

as a function of N_A/N for various N. Clearly, for large N the terms with $N_A \approx N/2$ have the largest contribution to the summand of Eq. 4.16. In the mean field approximation, we assume that only a *single* value of N_A will be dominant in Eq. 4.16. For the general case, the largest term is easily found by differentiating the logarithm of the summand in Eq. 4.9 with respect to N_A and setting it to zero. The result is

$$\ln[q_A] - \beta E_{0,A} - \ln[N_A] - \ln[q_B] + \beta E_{0,B} + \ln[N-N_A] = 0 \tag{4.18}$$

With a little rewriting it follows that Eq. 4.15 and Eq. 4.18 are equivalent. We thus conclude that the average energy as well as the average composition of this isomeric system are the same as the energy and composition of the largest and therefore most important term of the canonical partition function, even though on the outset all terms could have their influence. In other words, here the mean field approximation leads to an *exact* result for the energy and the composition of our isomer mixture for any value of N.

Naively one might think that also the free energy and the entropy could be derived from the most important term only, i.e. that the mean field approximation is also exact for the free energy. This is *not* the case. These thermodynamic variables involve not only the *position* but also the *width* of the peak in the contributions to Q in Eq. 4.9. Consider again the situation that $q_A = q_B = q$ and $E_{0,A} = E_{0,B} = 0$. Eq. 4.16 can be rewritten as

$$Q = q^N \sum_{N_A=0}^{N} \frac{1}{N_A!(N-N_A)!} = \frac{q^N}{N!} \sum_{N_A=0}^{N} \binom{N}{N_A} = \frac{q^N}{N!} \times 2^N \tag{4.19}$$

where we have used Eq. C.25. This means that the free energy F equals

$$\begin{aligned} F &= -k_BT \ln Q \\ &= -Nk_BT\,[\ln q + \ln 2] + k_BT \ln N! \\ &\approx -Nk_BT\,[\ln q + \ln 2] + k_BT\left[N\ln N - N + \ln\sqrt{2\pi N}\right] \end{aligned} \tag{4.20}$$

where we have used Stirling's approximation for $\ln N!$ (Eq. C.53). By using only the largest term ($N_A = N/2$) in Eq. 4.16 we find

$$\begin{aligned} F_{\text{mean field}} &= -k_BT \ln Q_{\text{mean field}} \\ &= -k_BT \ln\left[\frac{q^N}{(N/2)!(N/2)!}\right] \\ &= -Nk_BT \ln q + 2k_BT \ln(N/2)! \\ &\approx -Nk_BT \ln q + Nk_BT \ln N - Nk_BT \ln 2 - Nk_BT + 2k_BT \ln\sqrt{\pi N} \end{aligned} \tag{4.21}$$

Clearly, the mean field result overestimates the free energy by

$$F_{\text{mean field}} - F = k_BT \ln\sqrt{\pi N/2} \tag{4.22}$$

4.4 Reactive Ideal Gas Mixtures

For the simple first order isomerization reaction discussed in the previous sections we have shown that for the calculation of chemical equilibrium it was not necessary to evaluate the complete sum that makes up the canonical partition function. Already from the largest and therefore most important term we could calculate the equilibrium constant and the average energy. That result could be proven exactly for any N, since analytical expressions existed for both the sum and the most important term. For general chemical reactions this is not the case, and the *mean field* approach, using the largest term only, may the only available route.

Question 28 (Equilibrium Constant of an Ideal Gas Reaction: Mean Field Approximation)
Consider a reaction of the form

$$A + B \leftrightarrows 2C \tag{4.23}$$

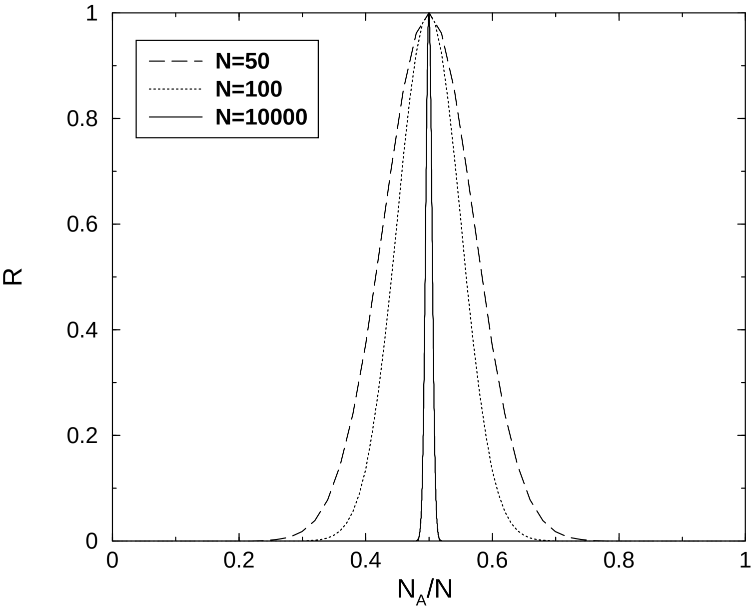


Figure 4.1: The ratio R (Eq. 4.17) as a function of N_A/N for various N.

1. *If we start with an initial ideal gas mixture of* $N/2$ *molecules A and B respectively and zero molecules C, explain why the partition function of the mixture equals*

$$Q = \sum_{N_A=0}^{N/2} \frac{q_A^{N_A} \exp[-\beta N_A E_{0,A}]}{N_A!} \times \frac{q_B^{N_A} \exp[-\beta N_A E_{0,B}]}{N_A!} \times \frac{q_C^{N-2N_A} \exp[-\beta (N-2N_A) E_{0,C}]}{(N-2N_A)!} \tag{4.24}$$

2. *Take the logarithm of one of the terms in Eq. 4.24 and differentiate it with respect to* N_A *using Eq. C.48. Show that the largest term in the sum corresponds to a value for* N_A *which satisfies*

$$\ln[q_A] - \beta E_{0,A} + \ln[q_B] - \beta E_{0,B} - 2\ln[N_A] - 2\ln[q_C] + 2\beta E_{0,C} + 2\ln[N-2N_A] = 0 \tag{4.25}$$

3. *Rewrite this result in the following form for the equilibrium constant of reaction Eq. 4.23:*

$$K_{\text{meanfield}} = \frac{\langle N_C \rangle^2}{\langle N_A \rangle \langle N_B \rangle} = \frac{q_C^2 \exp[-2\beta E_{0,C}]}{q_A q_B \exp[-\beta (E_{0,A} + E_{0,B})]} \tag{4.26}$$

4. *Show that the same result can be obtained by setting* $\mu_A + \mu_B = 2\mu_C$. *Hint: use Eq. 3.14 for the chemical potential* μ_A *and replace* N *by* N_A *and* E_0 *by* $E_{0,A}$. *Note that* $q_x \propto \Lambda_x^{-3}$. *The chemical potential for* B *and* C *can be derived in an analogous way.*

Question 29 (Equilibrium Constant of an Ideal Gas Reaction: Simulations)
Repeat the simulations that you carried out in question 25, but now with the additional possibility of the reaction $A + B \leftrightarrows 2C$. *Consider the situation that* $q_A = q_B = q_C = q$ *and* $E_{0,A} = E_{0,B} = E_{0,C} = 0$. *The simulation is started with* $N/2$ *molecules A and B respectively and zero molecules C. Compare the computed value of* K *with the mean field result (Eq. 4.26) for a various total number of molecules* ($N = N_A + N_B + N_C$)*. Make a plot of* $\ln(|K - K_{\text{meanfield}}|)$ *versus* N.

In summary, we have seen that the statistical thermodynamics of ideal gas mixtures is a straightforward generalization of a mono-component ideal gas. The equilibrium constant for ideal gas reactions can be directly computed from the partition functions of the components in the mixture. By definition, the equilibrium constant describes the *average* composition of the mixture, but in practice for macroscopic systems it is perfectly reliable to consider only the *most probable* composition. Therefore, for chemical equilibria in high temperature gases the mean field approximation is usually valid.

Chapter 5

Using Monte Carlo Simulations to Compute Ensemble Averages

5.1 Introduction

In the previous chapters, we have shown that once the partition function $Q(N, V, T)$ of a system is known, it is possible to compute all ensemble averages (e.g. the average energy $\langle E \rangle$ as a function of temperature). This suggests a simple recipe for computing thermodynamic properties: compute the partition function Q and everything else will follow from it. For several systems in the previous chapters this recipe works quite well. However, in this chapter we will show that for systems with interactions (e.g. a system of atoms in which the atoms interact with eachother), it is usually impossible to compute or approximate the partition function Q and therefore we have to rely on other methods to compute thermodynamic averages like the average energy $\langle E \rangle$. One of these methods is the so-called Monte Carlo method which will be introduced in this chapter. We will explain the Monte Carlo method using one of the simplest system with interactions, the Ising model. In the next chapters we will apply this method to systems of interacting atoms or molecules. For more information about the methodology, we refer the reader to more specialized textbooks [8–10].

5.2 The 1D Ising System

The 1D Ising system consists of N spins s_i arranged on a line, see Fig. 5.1. The value of each spin s_i can be either $+1$ or -1. Only neighboring spins s_i and s_{i+1} have an interaction energy that is proportional to the product $s_i * s_{i+1}$:

$$E(s_1, s_2, \cdots, s_N) = -\epsilon \sum_{i=1}^{N-1} s_i * s_{i+1} \tag{5.1}$$

The factor ϵ is a proportionality constant that describes the strength of the interaction.

Question 30 (Exact Partition Function for the 1D Ising Model)
Consider the 1D Ising model (Fig. 5.1). We write Q_N for the partition function of a system of N spins.

1. *Show that the partition function for $N = 2$ can be written as*

$$Q_2 = 2\exp[-\beta\epsilon] + 2\exp[\beta\epsilon] = 4\cosh(\beta\epsilon) \tag{5.2}$$

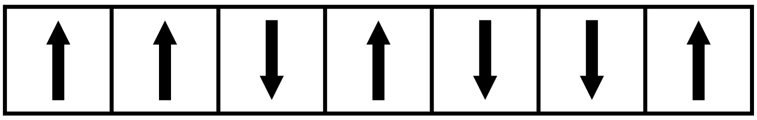


Figure 5.1: The 1D Ising system (here: $N = 7$ and $E = -2\epsilon$). The value of each spin s_i can be either $+1$ (spin up) or -1 (spin down) and each spin interacts only with its 2 neighbors. The interaction energy between two spins is proportional to the product of their spins.

in which

$$\cosh(x) = \frac{\exp[-x] + \exp[x]}{2} \tag{5.3}$$

2. *Show that*

$$Q_3 = Q_2 \times 2\cosh(\beta\epsilon) \tag{5.4}$$

3. *Explain that the following recursive relation*

$$Q_N = Q_{N-1} \times 2\cosh(\beta\epsilon) \tag{5.5}$$

is valid for all $N \geq 2$.

4. *Show that for large* N*, the partition function* Q_N *of the 1D Ising model can be written as*

$$Q_N = 2 * (2\cosh(\beta\epsilon))^{N-1} \tag{5.6}$$

5.3 The 2D Ising System

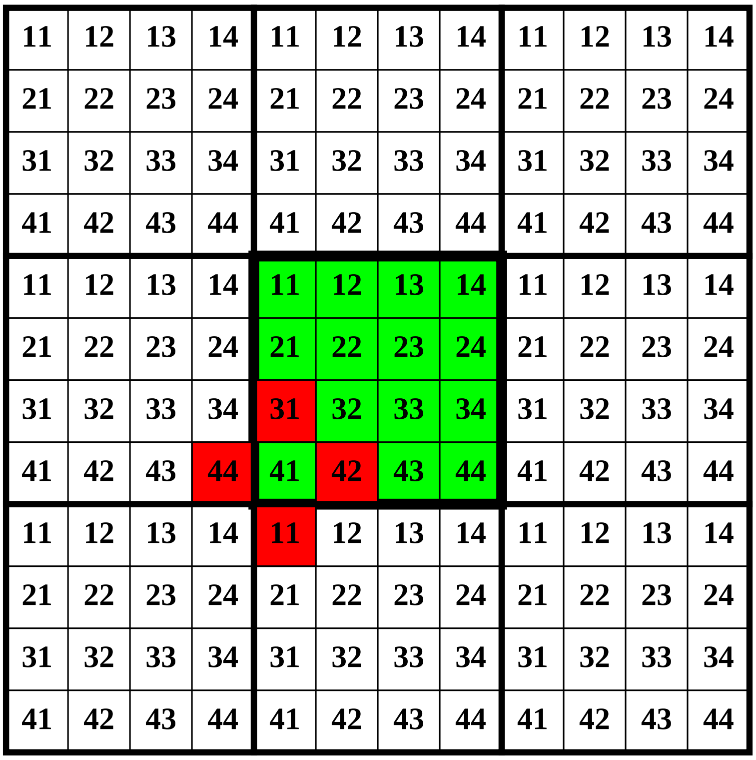
In the 2D Ising system, $N \times N$ spins s_{ij} are arranged on a two-dimensional lattice with periodic boundary conditions. This means that the system is surrounded by copies of itself, see Fig. 5.2. As the system is two-dimensional, we need in principle two indexes (i and j) for describing the location of a spin. For convenience however, we will often use a single index only so we will use s_i with $i = 1, 2, \cdots, N^2$ instead of s_{ij} (with $i = 1, 2, \cdots, N$ and $j = 1, 2, \cdots, N$) to identify a certain spin. The value of each spin s_i can be either $+1$ or -1. Each spin s_i has 4 neighbors (with $n(i,j)$ being the j-th neighbor of spin i) which interact with s_i. The interaction energy of spin s_i with neighbor $s_{n(i,j)}$ is proportional to the product $s_i * s_{n(i,j)}$. To handle spins at the boundaries, we apply the so-called periodic boundary conditions, see Fig. 5.2. The total energy of the system equals

$$E = -\frac{\epsilon}{2} \sum_{i=1}^{N^2} \sum_{j=1}^{4} s_i * s_{n(i,j)} \tag{5.7}$$

in which we have to consider the interactions of each spin i with each of its 4 neighbors $n(i,j)$. The factor 1/2 is present to ensure that interactions are not counted double (if i interacts with $n(i,j)$, then $n(i,j)$ also interacts with i, this interaction is counted only once).

An important parameter of the Ising model is the magnetization M, which is equal to the sum of all spins

$$M = \sum_{i=1}^{N^2} s_i \tag{5.8}$$



11	12	13	14	11	12	13	14	11	12	13	14
21	22	23	24	21	22	23	24	21	22	23	24
31	32	33	34	31	32	33	34	31	32	33	34
41	42	43	44	41	42	43	44	41	42	43	44
11	12	13	14	11	12	13	14	11	12	13	14
21	22	23	24	21	22	23	24	21	22	23	24
31	32	33	34	31	32	33	34	31	32	33	34
41	42	43	44	41	42	43	44	41	42	43	44
11	12	13	14	11	12	13	14	11	12	13	14
21	22	23	24	21	22	23	24	21	22	23	24
31	32	33	34	31	32	33	34	31	32	33	34
41	42	43	44	41	42	43	44	41	42	43	44

Figure 5.2: The 2D Ising system ($N^2 = 4 \times 4 = 16$ spins) with periodic boundary conditions. As the system is two-dimensional, we need two indexes (i and j) for the location of a spins, i.e. s_{34} means the spin for which $i = 3$ and $j = 4$. The central system is surrounded by copies of itself. The value of each spin s_{ij} can be either $+1$ or -1 and each spin only interacts with its 4 neighbors, the interaction energy between two spins is proportional to the product of their spins. As periodic boundaries are applied, spins 11, 31, 42 and 44 are the neighbors of spin 41. For convenience however, we often use a single index ($i = 1, 2, \cdots, N^2$) to identify each spin.

The 2D Ising model is almost 100 years old and it is one of the simplest interacting systems. During the second world war the behavior of this system was solved analytically by Onsager (note that his solution is highly non-trivial). It turns out that this system has a critical temperature at $k_B T_c / \epsilon = 2/\ln(1 + \sqrt{2}) \approx 2.269$ (so $\beta_c \epsilon = \epsilon/(k_B T_c) \approx 0.44$). Below the critical temperature large domains form in which nearly all spins have the same value (either $+1$ or -1) and there are small domains with opposite spins (Fig. 5.3 (left)). This phase coexists with a phase of opposite magnetization (all spins reversed). Above the critical point the system consists of a single phase only (Fig. 5.3 (right)).

Question 31 (2D Ising model for $N = 2$)
Consider the 2D Ising model for $N = 2$.

1. *Make a drawing similar to Fig. 5.2 and identify all neighbors of each spin.*
2. *Show that the total energy of the system (Eq. 5.7) equals*

$$U = -2\epsilon \left[s_{11}s_{12} + s_{11}s_{21} + s_{12}s_{22} + s_{21}s_{22} \right] \tag{5.9}$$

3. *Show that each product of spins in Eq. 5.9 can be either* $+1$ *or* -1.

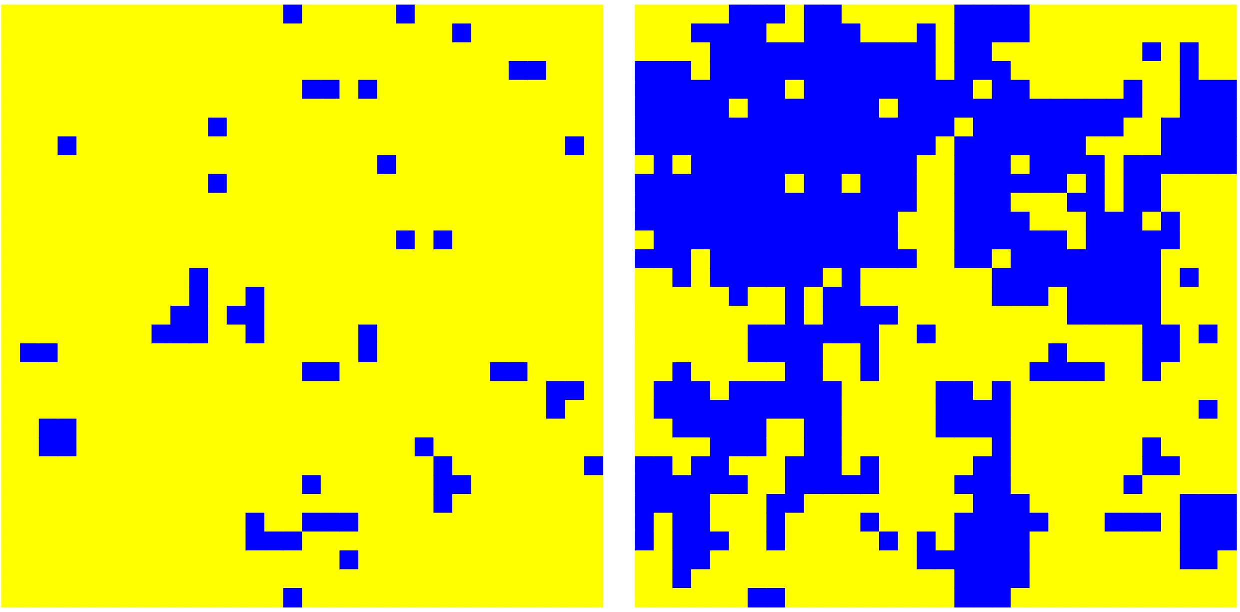


Figure 5.3: Typical snapshot of the 2D Ising model ($N = 32$) below the critical point (left) and above the critical point (right).

4. *How many system states are possible? Make a list of these system states and of their energy.*
5. *Show by evaluating all system states that the total energy* E *can be either* 8ϵ, -8ϵ *or* 0. *For each of these values determine the multiplicity* $\Omega(E)$, *i.e. the number of system states with energy* E.
6. *Use Eq. 3.17 to show that the partition function of this system equals*

$$Q = 2\exp[-8\beta\epsilon] + 2\exp[8\beta\epsilon] + 12 \tag{5.10}$$

7. *Derive the expression for the average system energy* $\langle E \rangle$ *by differentiation of Eq. 5.10.*
8. *Make a plot of the average energy of this system as a function of the temperature.*
9. *Explain why for this system,* $\langle M \rangle = 0$, *independent of the temperature.*
10. *Explain why for this system,* $\langle M^2 \rangle \neq 0$, *independent of the temperature.*

5.4 Computing the Partition Function of the 2D Ising Model

In question 31 we have seen that for a system of 2×2 spins, there are in principle $2^{2\times 2} = 16$ possible system states. Most of them (12) have energy 0, for 2 system states $U = 8\epsilon$ and for 2 system states $U = -8\epsilon$. This makes it convenient to express the partition function in the same way as in Eq. 3.17

$$Q = \sum_E \Omega(E) \exp\left[-\beta E\right] \tag{5.11}$$

in which the multiplicity $\Omega(E)$ counts how many system states have an energy equal to E (i.e. for the 2×2, system, $\Omega(8\epsilon) = \Omega(-8\epsilon) = 2$, $\Omega(0) = 12$ and $\Omega(E) = 0$ for other values of E). Note that the summation $\sum_E$ is over all possible energies of the system, and not over all system states.

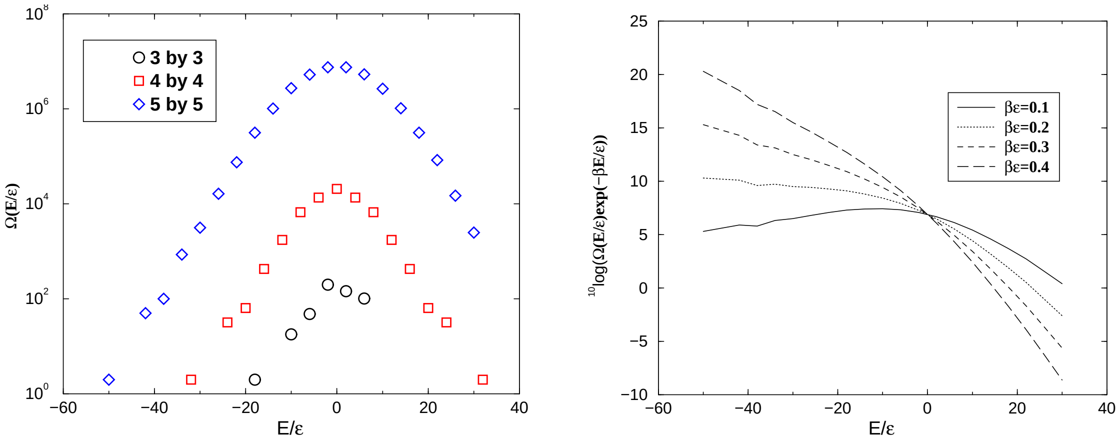


Figure 5.4: Left: Multiplicity $\Omega(E)$ for the 2D Ising model of various size (N). Note that the vertical axis is logarithmic. Right: ${}^{10}\log(\Omega(E)\exp[-\beta E])$ for $N = 5$ at various temperatures.

Question 32 (Multiplicity)
Consider the 2D Ising model with $N \times N$ *spins.*

1. *Show that the minimum energy of this system equals* $E_{\text{min}} = -2\epsilon N^2$ *with* $\Omega(E_{\text{min}}) = 2$. *Show that the next state has an energy* $-2\epsilon N^2 + 8\epsilon$ *and that there are* $2 \times N^2$ *realizations of this state.*
2. *Explain that the average energy of the system can be computed using*

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right) = \frac{\sum_E \Omega(E) E \exp[-\beta E]}{\sum_E \Omega(E) \exp[-\beta E]} = \frac{\sum_E \Omega(E) E \exp[-\beta E]}{Q} \tag{5.12}$$

3. *How many system states exist for* $N = 3$? *And for* $N = 4$ *or* $N = 100$?
4. *Explain that the computational effort to find all system states and to compute their energy is proportional to* $N^2 \times 2^{N \times N}$.
5. *On a somewhat older computer, it takes approximately* 5 *minutes to compute* $\Omega(E)$ *for* $N = 5$ *by counting all possible system states. Estimate how long it takes to compute* $\Omega(E)$ *for* $N = 6$ *and* $N = 10$.

In Fig. 5.4 (left), we have plotted $\Omega(E)$ for various N. Starting from the minimum energy $E_{\text{min}} = -2\epsilon N^2$, $\Omega(E)$ increases quite rapidly with E. For larger N, the number of energy levels "explodes" and it is no longer possible to evaluate all possible system states anymore, which means that we are unable to compute the partition function Q by evaluating all system states. This would suggest that it is no longer possible to evaluate thermodynamic properties like the average energy of these systems. Fortunately, this is not the case, even though it is not possible to compute Q.

5.5 The Monte Carlo Method

5.5.1 Random Sampling

In the previous section we have seen that we cannot compute Q exactly for large N as the total number of states is too large. A possible way to compute thermodynamic averages such as $\langle E \rangle$

would be to generate random system states and use the Boltzmann factor as the *statistical weight* for these configurations. After all, the average energy $\langle E \rangle$ equals

$$\langle E \rangle = \frac{\sum_{\text{spins}} E(s_1 \cdots s_{N^2}) \exp[-\beta E(s_1 \cdots s_{N^2})]}{\sum_{\text{spins}} \exp[-\beta E(s_1 \cdots s_{N^2})]} \tag{5.13}$$

in which $\sum_{\text{spins}}$ denotes a summation over all possible system states and $E(s_1 \cdots s_{N^2})$ is computed using Eq. 5.7. As for large N it is not possible to generate all system states, we can simply choose states at random. The relative "importance" or *statistical weight* of such a randomly chosen configuration is the Boltzmann factor. Suppose that we generate K random system states $\mathbf{s}_1 \cdots \mathbf{s}_K$ in which the vector $\mathbf{s} = \{s_1 \cdots s_{N^2}\}$ denotes the value of all spins in the system. The ensemble average of the energy can be approximated using

$$\langle E \rangle \approx \frac{\sum_{j=1}^{K} E(\mathbf{s}_j) \exp[-\beta E(\mathbf{s}_j)]}{\sum_{j=1}^{K} \exp[-\beta E(\mathbf{s}_j)]} \tag{5.14}$$

For a sufficiently large number of samples (K) this expression will be a good approximation. However, Fig. 5.4 (left) shows that although this approach is correct, it will be extremely inefficient. As $\Omega(E)$ has a maximum around $E = 0$, it will be most likely that a randomly generated configuration has an energy close to 0 (i.e. a configuration like in Fig. 5.3 (right)). However, at low temperatures those configurations have a very small statistical weight and do not contribute much to the average energy. Fig. 5.4 (right) shows that at $\beta\epsilon = 0.2$, the difference in $\Omega(E)\exp[-\beta E]$ between $E \approx 0$ and $E \approx E_{\text{min}}$ is already a factor 10^3 and at lower temperatures (larger β) this factor is even much larger (e.g. this factor equals approximately 10^{14} for $\beta\epsilon = 0.4$). In practice, this means that both the numerator and denominator of Eq. 5.14 will be zero and therefore it is not possible to calculate ensemble averages accurately using random sampling. Configurations with a larger statistical weight (energy around E_{min}, see Fig. 5.3 (left)) are never generated as $\Omega(E_{\text{min}})$ is extremely small compared to the maximum of $\Omega(E)$. However, usually only those configurations have a significant contribution to the summations in Eq. 5.14. This makes random sampling of most systems with interactions useless.

Question 33 (Random Sampling of the 2D Ising System)
Consider a series of simulations of the 2D Ising system at $k_B T/\epsilon = 1$ *(*$\beta\epsilon = 1$*) in which the system states are generated at random.*

1. *Assume that at this (low) temperature, only the ground state and the first excited state are occupied. Show that in this case, the average energy can be computed using*

$$\langle E \rangle = \frac{E_{\text{min}} + N^2 (E_{\text{min}} + 8\epsilon) \exp[-8\beta\epsilon]}{1 + N^2 \exp[-8\beta\epsilon]} \tag{5.15}$$

   with $E_{\text{min}} = -2\epsilon N^2$*. See also question 32.*

2. *Compute the average energy* $\langle E \rangle$ *for different lattice sizes (*N*) using the given computer code and compare your result with Eq. 5.15. Check how the estimate of* $\langle E \rangle$ *varies with the number of generated system states. Use these results to explain why random sampling is extremely inefficient for large* N.

5.5.2 Importance Sampling

In the previous section, we introduced random sampling in which K random system states are generated ($\mathbf{s}_1 \cdots \mathbf{s}_K$). The statistical weight of a randomly generated system state is the Boltzmann factor, so that ensemble averages like the average energy should be computed using Eq.

5.14. However, consider now the situation that the system states $\mathbf{s}_1 \cdots \mathbf{s}_K$ are *not generated randomly*, but instead *generated with a probability proportional to their Boltzmann factor* $\exp[-\beta E(\mathbf{s}_i)]$. How this can be achieved is explained to the interested reader in section 5.5.3. For now, we just assume that this is possible. In this particular case, the statistical weight of each system state is already taken into account in the generation of a certain configuration and therefore ensemble averages can be calculated as unweighted averages

$$\langle E \rangle = \frac{\sum_{j=1}^{K} E(\mathbf{s}_j)}{K} \tag{5.16}$$

This kind of sampling is called *importance sampling*; only system states that have a favorable Boltzmann weight are generated and therefore this scheme does not suffer from the problems of random sampling.

However, to use Eq. 5.16 we should be able to generate system states $\mathbf{s}_i$ with a probability proportional to $\exp[-\beta E(\mathbf{s}_i)]$. This can be achieved using the following *Monte Carlo* scheme (see also Fig. 5.5)

1. We start with an arbitrary system state $\mathbf{s}_1$. For example, we could choose all spins randomly.
2. We then generate a new system state $\mathbf{s}_n$ by flipping a single, randomly selected spin ($+1 \rightarrow -1$ or $-1 \rightarrow +1$). The generation of a new system state is often called *trial move*.
3. Calculate the energy $E(\mathbf{s}_n)$ of this new system state.
4. If $E(\mathbf{s}_n) < E(\mathbf{s}_1)$, we choose $\mathbf{s}_2 = \mathbf{s}_n$. Otherwise, we draw a uniformly distributed random number between 0 and 1 (this random number is denoted by `ranf()`). If `ranf()` $<$ $\exp[-\beta \times (E(\mathbf{s}_n) - E(\mathbf{s}_1))]$ we choose $\mathbf{s}_2 = \mathbf{s}_n$ and otherwise $\mathbf{s}_2 = \mathbf{s}_1$.
5. Update ensemble averages using Eq. 5.16.
6. Steps 2 till 5 are repeated $K - 1$ times until obtaining $\mathbf{s}_K$ (i.e. starting from $\mathbf{s}_2$, a new configuration is $\mathbf{s}_n$ generated and $\mathbf{s}_3$ is chosen as either $\mathbf{s}_2$ or $\mathbf{s}_n$ according to the rules outlined in step 4).

Basically, our *importance sampling Monte Carlo* algorithm ensures that system states with a very low Boltzmann factor are visited quite infrequently. There are many variations on this algorithm. Consider for example the situation that one is interested in the average price of a bottle of wine in a large shopping mall. Bottles of wine can only be found in one of the many liquor stores in the shopping mall, which means that only in the liquor stores the Boltzmann factor is non-zero. Outside the liquor stores (for example in shoe stores) the Boltzmann factor is zero as bottles of wine are not sold in shoe stores. In our Monte Carlo scheme, trial moves that take you to a place where there are no bottles of wine are therefore rejected, see Fig. 5.6. To calculate the average price of a bottle of wine in a large shopping mall the Monte Carlo scheme should be constructed in such a way that in principle it is possible to visit all bottles (or liquor stores) inside this shopping mall. This condition is called *ergodicity* and we will come back to this in chapter 10.

Note that it is not possible with this scheme to calculate the number of bottles of wine in the shopping mall (which corresponds to the partition function), unless one is able to *(1)* label the bottles of wine or *(2)* add a single bottle of wine with a known price to the shopping mall and compute the average price again.

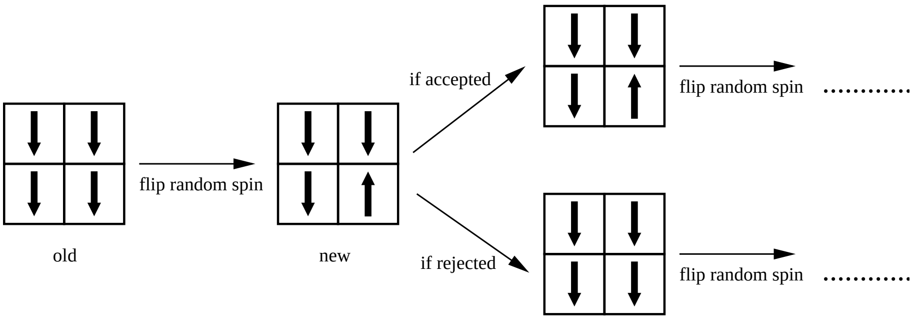


Figure 5.5: Schematic representation of the Monte Carlo algorithm. Starting from an old system state $\mathbf{s}_o$, a randomly selected spin is flipped. The energy of this new system $\mathbf{s}_n$ state is calculated. The new system state is either accepted (e.q. the simulation is continued with the new system state) or rejected (e.g. the simulation is continued with the old system state) depending on the energy difference $\Delta E = E(\mathbf{s}_n) - E(\mathbf{s}_o)$ and the temperature (Eq. 5.20).

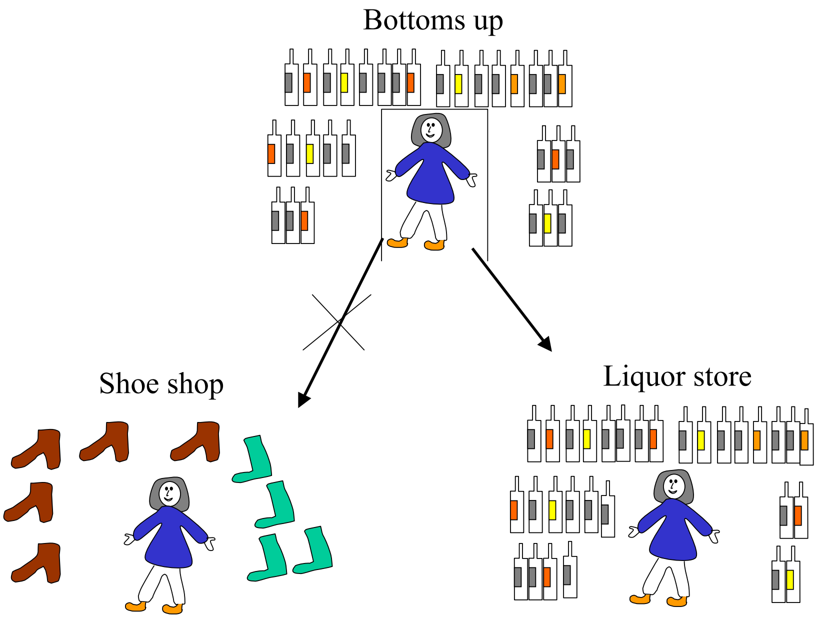


Figure 5.6: Only locations with a non-zero Boltzmann weight are visited.

5.5.3 Detailed Balance

In this subsection we will shown that the Monte Carlo scheme of section 5.5.2 samples configurations $\mathbf{s}_i$ with a probability proportional to $\exp[-\beta E(\mathbf{s}_i)]$. Readers who are not interested in this justification can safely skip this subsection.

To start, let us consider an old configuration $\mathbf{s}_o$. A randomly selected spin of this configuration is flipped leading to a new configuration $\mathbf{s}_n$. This process should not change the equilibrium distribution of system states $\mathbf{s}_i$. A sufficient condition for this is when during an infinitely long simulation the number of moves from $\mathbf{s}_o$ to $\mathbf{s}_n$ equals the number of moves from $\mathbf{s}_n$ to $\mathbf{s}_o$. This condition is called *detailed balance*. For the number of moves from $\mathbf{s}_o$ to $\mathbf{s}_n$ we can write

$$K(\mathbf{s}_o \to \mathbf{s}_n) = \exp[-\beta E(\mathbf{s}_o)] \times \alpha(\mathbf{s}_o \to \mathbf{s}_n) \times \mathrm{acc}(\mathbf{s}_o \to \mathbf{s}_n) \tag{5.17}$$

in which $\exp[-\beta E(\mathbf{s}_o)]$ is proportional to the probability to be in configuration $\mathbf{s}_o$, $\alpha(\mathbf{s}_o \to \mathbf{s}_n)$ is the probability to select a move in which configuration $\mathbf{s}_o$ changes into $\mathbf{s}_n$ and $\mathrm{acc}(\mathbf{s}_o \to \mathbf{s}_n)$ is the probability that we actually accept this move. Similarly, we can write for the number of moves from $\mathbf{s}_n$ to $\mathbf{s}_o$

$$K(\mathbf{s}_n \to \mathbf{s}_o) = \exp[-\beta E(\mathbf{s}_n)] \times \alpha(\mathbf{s}_n \to \mathbf{s}_o) \times \mathrm{acc}(\mathbf{s}_n \to \mathbf{s}_o) \tag{5.18}$$

Detailed balance requires that $K(\mathbf{s}_o \to \mathbf{s}_n) = K(\mathbf{s}_n \to \mathbf{s}_o)$. As $\alpha(\mathbf{s}_o \to \mathbf{s}_n) = \alpha(\mathbf{s}_n \to \mathbf{s}_o)$ we end up with

$$\frac{\mathrm{acc}(\mathbf{s}_o \to \mathbf{s}_n)}{\mathrm{acc}(\mathbf{s}_n \to \mathbf{s}_o)} = \exp[-\beta \times (E(\mathbf{s}_n) - E(\mathbf{s}_o))] = \exp[-\beta \Delta E] \tag{5.19}$$

Many choices for $\mathrm{acc}(\mathbf{s}_o \to \mathbf{s}_n)$ satisfy this condition, but a commonly used choice is that of Metropolis [13]

$$\mathrm{acc}(\mathbf{s}_o \to \mathbf{s}_n) = \begin{cases} \exp[-\beta \times (E(\mathbf{s}_n) - E(\mathbf{s}_o))] & \text{if } E(\mathbf{s}_n) > E(\mathbf{s}_o) \\ 1 & \text{if } E(\mathbf{s}_n) < E(\mathbf{s}_o) \end{cases} \tag{5.20}$$

More explicitly, to decide whether a trial move will be accepted or rejected we generate a random number, denoted by `ranf()`, from a uniform distribution in the interval between 0 and 1. If `ranf()` $<$ $\mathrm{acc}(\mathbf{s}_o \to \mathbf{s}_n)$ we accept the trial move and we reject it otherwise. This rule satisfies Eq. 5.19 and can be written as

$$\mathrm{acc}(\mathbf{s}_o \to \mathbf{s}_n) = \min(1, \exp[-\beta \times (E(\mathbf{s}_n) - E(\mathbf{s}_o))]) = \min(1, \exp[-\beta \Delta E]) \tag{5.21}$$

where $\Delta E = E(\mathbf{s}_n) - E(\mathbf{s}_o)$ and $\min(a, b) = a$ when $a < b$, and b otherwise. This means that new configurations that lower the energy are always accepted, and new configurations that increase the total energy are accepted with a certain probability that depends on the energy difference with the previous configuration and the temperature.

Question 34 (Generating the New Configuration)
Explain why $\alpha(\mathbf{s}_o \to \mathbf{s}_n) = \alpha(\mathbf{s}_n \to \mathbf{s}_o)$.

Question 35 (Symmetric Condition)
Show that the following acceptance rule

$$\mathrm{acc}(o \to n) = \frac{\exp[-\beta E(\mathbf{s}_n)]}{\exp[-\beta E(\mathbf{s}_n)] + \exp[-\beta E(\mathbf{s}_o)]} \tag{5.22}$$

also satisfies the condition for detailed balance $K(\mathbf{s}_o \to \mathbf{s}_n) = K(\mathbf{s}_n \to \mathbf{s}_o)$.

Question 36 (Updating Ensemble Averages)
Explain why it is necessary to also count rejected moves in Eq. 5.16. Hint: consider a Monte Carlo simulation of a quantum system with 2 energy levels with energy 0 *and* ϵ *respectively. What will be the value of* $\langle E \rangle$ *in this case?*

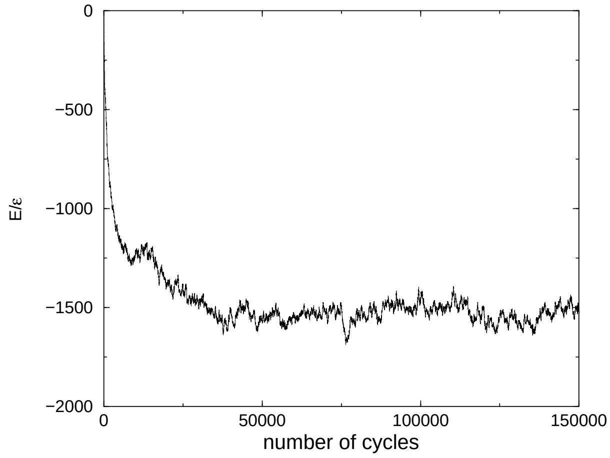


Figure 5.7: Evolution of the instantaneous energy E in a Monte Carlo simulation of the 2D Ising model at $\beta\epsilon = 0.5$ and $N = 32$. The initial configuration is chosen at random. In this simulation, only after approximately 50000 Monte Carlo moves we can sample ensemble averages using Eq. 5.16.

E/ϵ	$\Omega(E/\epsilon)$
-18	2
-10	18
-6	48
-2	198
2	144
6	102

Table 5.1: Multiplicity ($\Omega(E)$) for the 2D Ising system for $N = 3$. The total number of states equals $2^{3\times 3} = 512$.

5.5.4 Initialization and Length of the Simulation

In our simulation, we have to start with a certain initial configuration **s**. In principle, this could be any configuration. However, if the Boltzmann weight of this configuration is very small, our computed ensemble averages may be strongly influenced by our choice of initial configuration. The reason for this it that we can not average over infinitely long sequences of configurations (Eq. 5.16) so the number of elements in our sequence (K) is finite. Therefore, we should avoid preparing our system in a very unfavorable initial configuration, i.e., a configuration with a very low Boltzmann weight. It is therefore good practice to equilibrate the system first and throw away the first part of the sequence of configurations in Eq. 5.16. This is illustrated in Fig. 5.7.

In practice, we choose a certain number of trial moves and estimate the ensemble average $\langle A \rangle$ of a certain quantity A. Then we repeat the simulation using the final configuration of the previous simulation as our starting configuration. If $\langle A \rangle$ differs from the previous simulation, we repeat this step and increase the number of trial moves. A quick and dirty way to estimate the error in the computed ensemble averages is to perform the same simulation 5 times and to compute the standard deviation.

Question 37 (Monte Carlo Simulation of the 2D Ising Model)
Enclosed is a computer program to simulate the 2D Ising system with periodic boundary conditions. The program computes $\langle E\rangle$, $\left\langle M^2\right\rangle$, C_v *and the probability distribution of the magnetization* ($p(M)$)*. The simulation is performed in cycles, during each cycle an attempt is made to flip each of the spins in the system. The first 33% of the simulation is not used to compute ensemble averages. The evolution of the simulation can be followed by using* `display animation.gif`.

1. *Perform a simulation for* $N = 3$ *at different temperatures. For each simulation, you should check carefully whether or not the number of cycles is sufficient (i.e. comparing the results with a two times longer or shorter simulation). Compare the average energy* $\langle E\rangle$ *and heat capacity* C_v *with the results of an exact calculation using the multiplicity of Table 5.1.*

2. *For* $N = 32$*, make a plot of the average probability that a trial move (spin flip) is successful for a few temperatures. Explain your results.*

3. *In principle* $p(M)$=$p(-M)$. *For large* N *(i.e.* $N = 32$*) however, at low temperatures the observed values for* M *are either all positive or all negative. Confirm this with simulations. Explain why the observed values for* M *are either all positive or all negative. Why is this effect less clear for smaller* N*? What would you expect for very large* N*?*

4. *Perform simulations for* $N = 32$ *and investigate the effect of temperature on* $\langle E\rangle$, $\left\langle M^2\right\rangle$, C_v*, and* $p(M)$. *Explain your results. Estimate the critical temperature from your simulation results.*

5. *Investigate the effect of the system size* N *on* $\langle E\rangle$ *and* C_v *as a function of temperature. Explain your results.*

Part II

Molecular Simulation

Chapter 6

Monte Carlo Simulations of Interacting Particles

6.1 Introduction

In the previous chapter, we have shown that for systems with interactions, we can not compute the partition function Q exactly because the number of states is simply too large. Moreover, most states correspond to high energies, while the number of states at a low energy is many orders of magnitude smaller. This makes random sampling very inefficient at low temperature. However, using *importance sampling* we are able to visit only the relevant realizations of the system and in this way we are able to compute ensemble averages. In the previous chapter, this was demonstrated for the 2D Ising model. In this chapter, we will apply the methods of the previous chapter to a system of interacting atoms. Usually, those interactions strongly depend on the distance between atoms. We will first explain how the particles in our system interact and derive an expression for the partition function. This can be used to estimate deviations from the ideal gas law at very low densities. At larger densities, such estimations are no longer possible and we have to rely on Monte Carlo simulations. We will compare the results of these simulations with several equations of state (e.g. the van der Waals equation).

6.2 Computer Model

6.2.1 Periodic Boundary Conditions

We will consider a system of N interacting particles in a volume V at temperature T. Similar to the 2D Ising system, we will apply periodic boundary conditions which means that the system is surrounded by copies of itself, see Fig. 6.1. For a system of particles this also means that when a particle leaves the central box on one side, it enters the central box on the other side. In Fig. 6.1, particle 1 in the central box could interact in principle with many copies of particle 3 in different copies of the central box. However, it is more convenient to consider only a single interaction between particle 1 and 3, and the natural choice is to consider only the interaction for which the interatomic distance is minimum. This is called the *nearest image convention*.

Question 38 (Effect of Walls)
An important advantage of using periodic boundary conditions is that there are no walls in the system. As thermodynamic properties near walls usually differ from the corresponding bulk properties, it is important to minimize any wall-effect. For a system consisting of a small number of particles without periodic

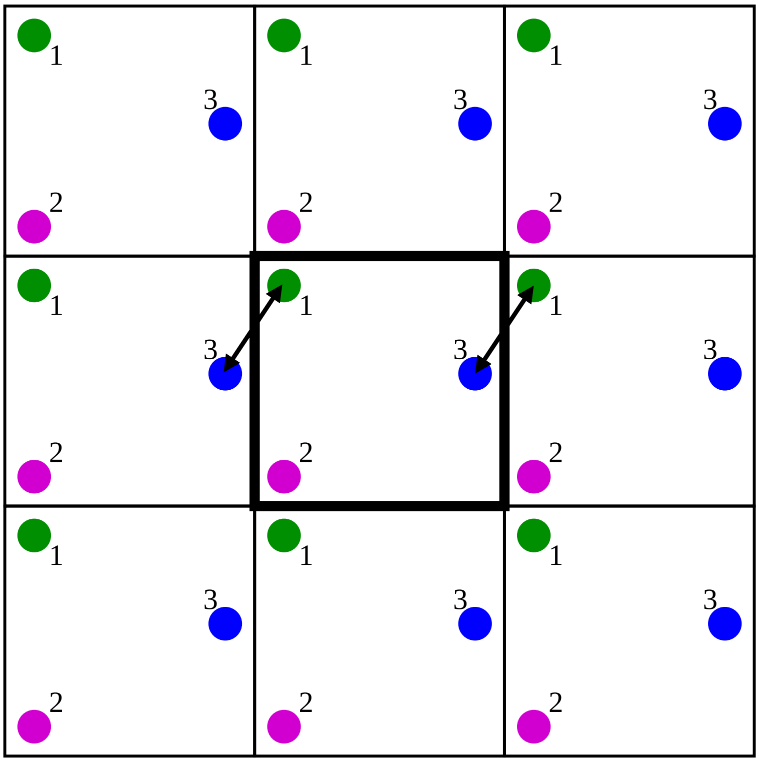


Figure 6.1: Periodic boundary conditions. A central box is surrounded by copies of itself. The arrows show the shortest distance between particles 1 and 3. This interaction is counted only once in Eq. 6.2.

boundary conditions, the fraction of particles at the wall is quite large. Consider a system of $n \times n \times n = n^3$ *particles arranged on a cubic lattice in 3 dimensions.*

1. *Explain that the number of "wall" particles equals* $n^3 - (n-2)^3$.
2. *Show that the fraction of "wall" particles is approximately equal to* $6/n$.
3. *How many particles are needed such that the fraction of "wall" particles is less than* 0.001*?*

6.2.2 Lennard-Jones Pair Potential

The Lennard-Jones potential is a popular pair potential to describe the interactions between atoms and molecules. In this model, the interaction energy of two atoms at distance $r_{ij} = |\mathbf{r}_{ij}| = |\mathbf{r}_i - \mathbf{r}_j|$ equals

$$\phi_{LJ}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] \tag{6.1}$$

where σ and ϵ are the so-called Lennard-Jones parameters, see Fig. 6.2. In this model two atoms attract each other at large distances as a result of attractive van der Waals forces, but at short distances two atoms repel each other. Reasonable values of the Lennard-Jones parameters are known for various atoms/molecules, see table 6.1.

compound	σ/Å	(ϵ/k_B)/K
Ar	3.41	120
Ne	2.75	36
Kr	3.83	164
Xe	4.06	229
CH_4	3.78	179
N_2	3.70	95
O_2	3.58	118

Table 6.1: Lennard-Jones parameters of various atoms/molecules.

Question 39 (Lennard-Jones Potential)
Answer the following questions:

1. *Two atoms repel each other at very small distances. Explain why.*
2. *Show that the Lennard-Jones potential has a minimum for* $r_{\text{min}} = 2^{1/6}\sigma$ *and that* $\phi(r_{\text{min}}) = -\epsilon$.
3. *Explain that the unit of* ϵ/k_B *is temperature.*
4. *Convert* ϵ *of argon (table 6.1) into units of kJ/mol and kJ/molecule respectively.*

As the Lennard-Jones pair potential describes the interaction energy between two particles, the total energy of a Lennard-Jones fluid should be computed by summing over all possible atom pairs, i.e.

$$E(\mathbf{r}^N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \phi(r_{ij}) = \sum_{i<j} \phi(r_{ij}) \tag{6.2}$$

in which the 3N dimensional vector $\mathbf{r}^N = (x_1, y_1, z_1, x_2, y_2, z_2, \cdots, x_N, y_N, z_N)$ denotes all particle positions. For a system consisting of N atoms, there are in principle $N(N-1)/2$ pairs which means that the computational cost of computing the energy of a system is of order N^2. The number of interactions that needs to be computed can be reduced by neglecting all interactions beyond a certain radius r_{cut}, which should not be too small (in practice, $r_{\text{cut}} = 2.5\sigma$ is often used). In any case, r_{cut} should always be smaller than half the boxsize L.

Question 40 (Nearest Image Convention)
Consider a system of particles in a rectangular box of dimensions $L \times L \times L$. *Show that the nearest image convention (section 6.2.1) is automatically satisfied when* $r_{\text{cut}} < L/2$.

Truncating the Lennard-Jones potential at r_{cut} results in the following potential

$$\phi(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] & r \leq r_{\text{cut}} \\ 0 & r > r_{\text{cut}} \end{cases} \tag{6.3}$$

which is a discontinuous function for $r = r_{\text{cut}}$. It is often convenient to remove this discontinuity. This results in the so-called truncated and shifted Lennard-Jones potential:

$$\phi(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] - \phi_{\text{cut}} & r \leq r_{\text{cut}} \\ 0 & r > r_{\text{cut}} \end{cases} \tag{6.4}$$

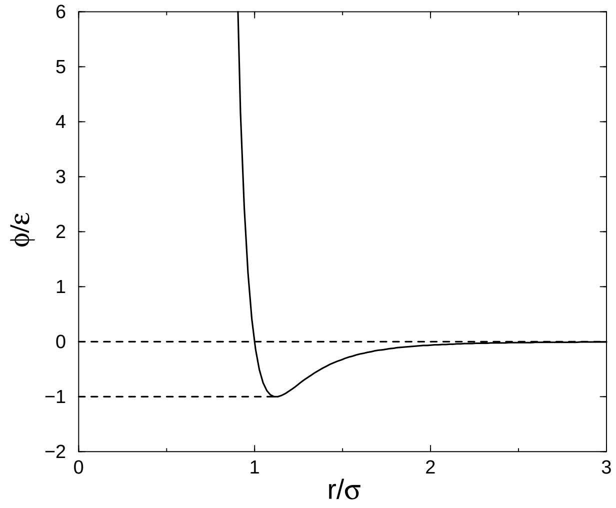


Figure 6.2: The Lennard-Jones potential. ϕ/ϵ is minimal (-1) for $r = 2^{1/6}\sigma \approx 1.12\sigma$.

in which

$$\phi_{\text{cut}} = 4\epsilon\left[\left(\frac{\sigma}{r_{\text{cut}}}\right)^{12} - \left(\frac{\sigma}{r_{\text{cut}}}\right)^{6}\right] \tag{6.5}$$

It is important to note that the result of a computer simulation may depend on r_{cut} and whether a truncated or truncated and shifted potential is used. Note that other truncation methods that remove discontinuities in higher order derivatives of $\phi(r)$ are also often used in simulations. For Coulombic interactions (for which $\phi(r) \propto r^{-1}$) simple truncation will result in artifacts and therefore other techniques are needed [8,14,15].

6.2.3 Partition Function

To compute the partition function $Q(N, V, T)$ of a system of N interacting particles in volume V at temperature T we have to consider all possible states of the system. For systems with discrete energy levels (e.g. harmonic oscillator, Ising model) we have to sum over the energy levels of the system, taking the multiplicity into account. However, a state of a system with particles consists of all possible positions and velocities of all particles in the system. It turns out that in this case we have to replace the summation by an integration over all particle positions ($\mathbf{r}^N$) and velocities ($\mathbf{v}^N$) in the system

$$Q(N, V, T) \propto \int d\mathbf{v}^N \int d\mathbf{r}^N \exp[-\beta E_{\text{kin}}(\mathbf{v}^N) + E(\mathbf{r}^N)] \tag{6.6}$$

in which E_{kin} is the total kinetic energy of all particles in the system. As the integration over particle velocities appears to be exactly executable, the partition function is therefore

$$Q(N, V, T) = c \times \int d\mathbf{r}^N \exp[-\beta E(\mathbf{r}^N)] \tag{6.7}$$

in which $E(\mathbf{r}^N)$ is given by Eq. 6.2. The prefactor c follows from the requirement that for an ideal gas Eq. 6.7 should lead to the exact result (Eqs. 1.9 and 3.6). The result is

$$c = \frac{1}{N!\Lambda^{3N}} \tag{6.8}$$

so

$$Q(N, V, T) = \frac{1}{N!\Lambda^{3N}} \int d\mathbf{r}^N \exp[-\beta E(\mathbf{r}^N)] \tag{6.9}$$

The factor $1/N!$ is originating from the fact that particles are indistinguishable, which means that we have to divide by the number of permutations of our N particles (see section C.6). The thermal wavelength Λ depends on the temperature and the mass of the particle (Eq. 1.14).

Question 41 (Partition Function)

1. *Show that* $\int d\mathbf{r}^N = V^N$.
2. *Show that* $Q(N, V, T)$ *(Eq. 6.9) is dimensionless.*
3. *Explain that for an ideal gas*

$$\int d\mathbf{r}^N \exp[-\beta E(\mathbf{r}^N)] = V^N \tag{6.10}$$

For an ideal gas we are able to obtain an exact expression for $Q(N, V, T)$. However, for systems *with* interactions ($E(\mathbf{r}^N) \neq 0$) this is in general not possible. One might think that $Q(N, V, T)$ can be evaluated by conventional numerical integration techniques such as numerical quadrature. However, evaluating the integrand on a grid in the high-dimensional phase space is impossible as the number of gridpoints becomes more than astronomically large. For instance, $N = 100$ particles in $D = 3$ dimensions using a very rough grid of only $m = 5$ gridpoints already leads to $m^{DN} = 5^{300}$ gridpoints at which this integrand has to be evaluated. This is impossible within the lifetime of our universe. In addition, suppose that we would somehow be able to perform the integration of Eq. 6.9. Our claim is that the numerical error will then be so large that the result is not meaningful anyway. The reason is that when two particles overlap the potential energy is extremely large and therefore the Boltzmann factor equals almost zero. In fact, it turns out that for a typical liquid this is the case for almost all configurations $\mathbf{r}^N$ and only an extremely small part of the phase space $\mathbf{r}^N$ will have a significant contribution to $Q(N, V, T)$.

6.3 Reduced Units

In physics and chemistry, it is common practice to use standard SI units (kilogram, meter, second). However, on the scale of a single molecule, this results in very small numbers. For example, the mass of a typical atom is of the order of 10^{-25}kg. Therefore, for molecular systems, it is more natural to use a single molecule as a unit. For example, consider a system consisting of argon atoms that interact via a Lennard-Jones potential. A convenient set of units would be

- unit of energy: ϵ
- unit of length: σ
- unit of mass: m (the mass of a single argon atom)

All other units follow directly from these basic units. For example, a reduced distance l^* equals l/σ, in which l is the real distance and σ the basic unit of length. For the reduced energy, temperature, pressure and number density we find respectively $U^\star = U/\epsilon$, $T^\star = k_B T/\epsilon$, $P^\star = P\sigma^3/\epsilon$, $\rho^\star = \rho\sigma^3$. Using reduced units has several important advantages:

- Very small and very large numbers are avoided. If the outcome of a computer simulation is an extremely large number, it is quite likely that this is because of a programming error. Also, we avoid a numerical underflow or overflow on the computer.
- For different systems characterized by the same functional form of the interaction potential, only a single calculation is required. For example, from the equation of state of a Lennard-Jones potential in reduced units, we are able to calculate the equation of state for argon and neon, provided that their Lennard-Jones parameters are available.

Question 42 (Reduced Units)
Show that the reduced unit of time equals $\sigma\sqrt{m/\epsilon}$*.*

Question 43 (Conversion between simulations)
Suppose that we simulate argon at a temperature of 500 *K and a pressure of* 1 *bar using a Lennard-Jones potential. For which conditions of neon can we use the same simulation? The Lennard-Jones parameters are:* $\sigma_{Ar} = 3.41Å$, $\sigma_{Ne} = 2.75Å$, $\epsilon_{Ar}/k_B = 120K$, $\epsilon_{Ne}/k_B = 36K$.

6.4 Calculating the Pressure

It is possible to compute the ensemble average of the pressure in a Monte Carlo simulation. Our starting point is Eq. 2.10,

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \tag{6.11}$$

that relates the pressure to a partial derivative of the free energy. Using Eq. 2.6 we find

$$\begin{aligned} P &= k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} \\ &= \frac{k_B T}{Q}\left(\frac{\partial Q}{\partial V}\right)_{T,N} \\ &= \frac{k_B T}{V^N \int d\mathbf{s}^N \exp[-\beta E(\mathbf{r}^N)]}\left(\frac{\partial \left(V^N \int d\mathbf{s}^N \exp[-\beta E(\mathbf{r}^N)]\right)}{\partial V}\right)_{T,N} \end{aligned} \tag{6.12}$$

where we have assumed a rectangular box of dimension $L = V^{1/3}$ and $\mathbf{s}^N = L \times \mathbf{r}^N$. As we are allowed to switch the differentiation of Q and the integration over $\mathbf{s}^N$, we can express the pressure as an ensemble average

$$\langle P \rangle = \rho k_B T - \frac{1}{3V}\left\langle \sum_{i<j} r_{ij} \times \left(\frac{dU}{dr}\right)_{r_{ij}} \right\rangle \tag{6.13}$$

that can be measured in a simulation. In chapter 9 we will show that all partial derivatives of the free energy can be expressed as ensemble averages.

6.5 Radial Distribution Function

The radial distribution function $g(r)$ measures the ratio between the average number density $\rho(r)$ at a distance r from any given particle and the density at a distance r from a particle in an ideal gas at the same overall density (Fig. 6.3):

$$g(r) = \frac{V}{N}\left\langle \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i) \times \sum_{j=1}^{N} \delta(\mathbf{r}-\mathbf{r}_j) \right\rangle \tag{6.14}$$

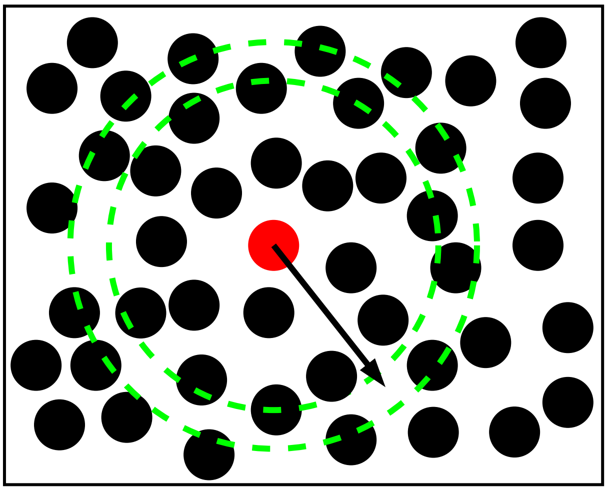


Figure 6.3: The radial distribution function $g(r)$ describes the local density at distance r from a central particle.

in which $\delta(x)$ is Dirac's δ function (see section C.11). By definition, $g(r) = 1$ for an ideal gas. The radial distribution function (or its Fourier transform) can be measured in (scattering) experiments. Moreover, the $g(r)$ plays a key role in many liquid state theories [16].

Question 44 (Radial Distribution Function)
Show that the average energy of a system can be computed using

$$\langle E \rangle = 2\pi\rho N \int_0^{r_{\text{cut}}} dr r^2 g(r)\phi(r) \tag{6.15}$$

6.6 Deviation from the Ideal Gas Law

6.6.1 Virial Expansion

Experimentally, we know that the pressure of a real gas does not satisfy the ideal-gas relation

$$\frac{PV}{Nk_BT} = 1 \tag{6.16}$$

Rather, we find that, as the number density $\rho = N/V$ is increased, deviations from this relation occur

$$\frac{PV}{Nk_BT} = 1 + B_2\rho + B_3\rho^2 + \cdots \tag{6.17}$$

where B_2, B_3 etc. are called the second, third etc. *virial coefficients*. The virial coefficients depend on the intermolecular interactions and are a function of temperature. Here we shall derive an expression for B_2. First, we can write the general expression for the partition function in the following way:

$$\begin{aligned}
Q(N,V,T) &= \frac{1}{N!\Lambda^{3N}}\int d\mathbf{r}^N \exp[-\beta E(\mathbf{r}^N)] \\
&= \frac{V^N}{N!\Lambda^{3N}}\frac{\int d\mathbf{r}^N \exp[-\beta E(\mathbf{r}^N)]}{V^N} \\
&= \frac{V^N}{N!\Lambda^{3N}}\frac{\int d\mathbf{r}^N \exp[-\beta E(\mathbf{r}^N)]}{\int d\mathbf{r}^N} \\
&= \frac{V^N}{N!\Lambda^{3N}}\left\langle \exp[-\beta E(\mathbf{r}^N)]\right\rangle
\end{aligned} \tag{6.18}$$

where the angular brackets denote the average of the Boltzmann factor $\exp[-\beta E(\mathbf{r}^N)]$ over all possible positions $\mathbf{r}^N$ within the volume V. At extremely low densities, the molecules are almost always too far apart to interact and hence the average Boltzmann factor is simply equal to one, resulting in the ideal gas law. At higher densities, we shall notice the effect of interactions between molecules. Let us assume that the interactions between molecules are such that a molecule must be within a certain distance r_{cut} in order to experience the potential of the other molecules. Or, phrased in another way, if there are no molecules within a volume $v_{\text{cut}} = (4\pi/3)r_{\text{cut}}^3$ of a given molecule, then that molecule does not contribute to the interaction energy. Let us denote by P_0 the probability that there are no two molecules within a distance r_{cut}. At very low densities, we can write the average of the Boltzmann factor as

$$\left\langle \exp[-\beta E(\mathbf{r}^N)]\right\rangle = P_0 + P_1\left\langle \exp[-\beta E(\mathbf{r}^N)]\right\rangle_{\text{pair}} \tag{6.19}$$

where P_1 denotes the probability that there is exactly one pair of molecules at a distance less than r_{cut} (see Fig. 6.4). Because the density is very low, we can ignore the probability that there will be more than two molecules at a distance less than r_{cut}. At higher density the probability to find two or more particles within r_{cut} becomes larger and then it will become extremely difficult to find a good approximation for the average Boltzmann factor. In other words, we have either *no* molecules that are interacting (probability P_0) or just *one pair* (probability P_1). Clearly, $P_0+P_1 = 1$ and hence $P_0 = 1 - P_1$. Now we should still compute the average Boltzmann factor for a pair of molecules at a distance less than r_{cut}. It is

$$\langle \exp[-\beta E]\rangle_{\text{pair}} = \frac{\int_0^{r_{\text{cut}}} dr 4\pi r^2 \exp[-\beta\phi(r)]}{\int_0^{r_{\text{cut}}} dr 4\pi r^2} \tag{6.20}$$

where $\phi(r)$ is the potential energy of interaction of a *pair* of molecules at a distance r (i.e. Eq. 6.4). We can now write

$$\begin{aligned}
\left\langle \exp[-\beta E(\mathbf{r}^N)]\right\rangle &= P_0 + P_1\left\langle \exp[-\beta E(\mathbf{r}^N)]\right\rangle_{\text{pair}} \\
&= 1 + P_1\left[\frac{\int_0^{r_{\text{cut}}} dr 4\pi r^2 \exp[-\beta\phi(r)]}{\int_0^{r_{\text{cut}}} dr 4\pi r^2} - 1\right] \\
&= 1 + P_1\left[\frac{\int_0^{r_{\text{cut}}} dr 4\pi r^2 \exp[-\beta\phi(r)]}{\int_0^{r_{\text{cut}}} dr 4\pi r^2} - \frac{\int_0^{r_{\text{cut}}} dr 4\pi r^2}{\int_0^{r_{\text{cut}}} dr 4\pi r^2}\right] \\
&= 1 + P_1\left[\frac{\int_0^{r_{\text{cut}}} dr 4\pi r^2 \left(\exp[-\beta\phi(r)] - 1\right)}{\int_0^{r_{\text{cut}}} dr 4\pi r^2}\right]
\end{aligned} \tag{6.21}$$

Now we should still compute P_1, the probability that there is a single pair of (randomly distributed) molecules within the same volume v_{cut}. At low densities, the probability that there is another molecule in a volume around a *given* molecule is simply equal to ρv_{cut} (where $\rho = N/V$ is the number density of the molecules). As there are N molecules in the system, and we could have taken any of these molecules as our "central" molecules, the probability to find a pair is N/2 times larger (the factor 1/2 comes in to avoid double counting). Hence, at low densities, $P_1 = N\rho v_{\mathrm{cut}}/2$ and therefore

$$\left\langle \exp[-\beta E(\mathbf{r}^N)] \right\rangle = 1 + \frac{N\rho}{2} \int_o^{r_{\mathrm{cut}}} dr 4\pi r^2 \left(\exp[-\beta\phi(r)] - 1\right) \tag{6.22}$$

With this result, we can write

$$Q \approx \frac{V^N}{N!\Lambda^{3N}} \left(1 + \frac{N\rho}{2} \int_o^{r_{\mathrm{cut}}} dr 4\pi r^2 \left(\exp[-\beta\phi(r)] - 1\right)\right) \tag{6.23}$$

The pressure P is given by

$$\begin{aligned} P &= k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} \\ &\approx \frac{N k_B T}{V} - \frac{\frac{\rho^2}{2} \int_0^{r_{\mathrm{cut}}} dr 4\pi r^2 \left(\exp[-\beta\phi(r)] - 1\right)}{1 + \frac{N\rho}{2} \int_0^{r_{\mathrm{cut}}} dr 4\pi r^2 \left(\exp[-\beta\phi(r)] - 1\right)} \\ &\approx \rho k_B T + \frac{\rho^2}{2} \int_0^{r_{\mathrm{cut}}} dr 4\pi r^2 \left(1 - \exp[-\beta\phi(r)]\right) \end{aligned} \tag{6.24}$$

where, in the third line, we have used the fact that, at sufficiently low densities,

$$\frac{N\rho}{2} \int_0^{r_{\mathrm{cut}}} dr 4\pi r^2 \exp[-\beta\phi(r)] - 1] \ll 1 \tag{6.25}$$

If we compare this expression with the virial series (Eq. 6.17), we find that the second virial coefficient is equal to

$$B_2 = \frac{1}{2} \int_0^{r_{\mathrm{cut}}} dr 4\pi r^2 \left(1 - \exp[-\beta\phi(r)]\right) = 2\pi \int_0^{r_{\mathrm{cut}}} dr r^2 \left(1 - \exp[-\beta\phi(r)]\right) \tag{6.26}$$

Again, this is a very important result because it shows that a measurement of the second virial coefficient provides information about the intermolecular interactions. To give a specific example: assume that molecules are hard spheres with a diameter σ. Hard spheres interact according to

$$\phi(r) = \begin{cases} \infty & r \le \sigma \\ 0 & r > \sigma \end{cases} \tag{6.27}$$

For $r > \sigma$, $\phi(r) = 0$ and hence $\exp[-\beta\phi(r)] = 1$. For $r < \sigma$, $\phi(r) = \infty$ and hence $\exp[-\beta\phi(r)] = 0$, see Fig. 6.5. Therefore,

$$B_2^{HS} = \frac{1}{2} \int_0^{\sigma} dr 4\pi r^2 = \frac{2\pi\sigma^3}{3} \tag{6.28}$$

Question 45 (Square-Well Potential)
Unlike hard spheres, real molecules do not only repel each other at short distances, they also attract at larger distances. A very simple model potential that exhibits both features is the so-called square-well potential. *The square-well potential is equal to the hard-sphere potential for* $r < \sigma$. *But for* $\sigma < r < \lambda\sigma$ *(with* $\lambda > 1$*), the square well potential is attractive:*

$$\phi(r) = \begin{cases} \infty & r \le \sigma \\ -\epsilon & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases} \tag{6.29}$$

see Fig. 6.5.

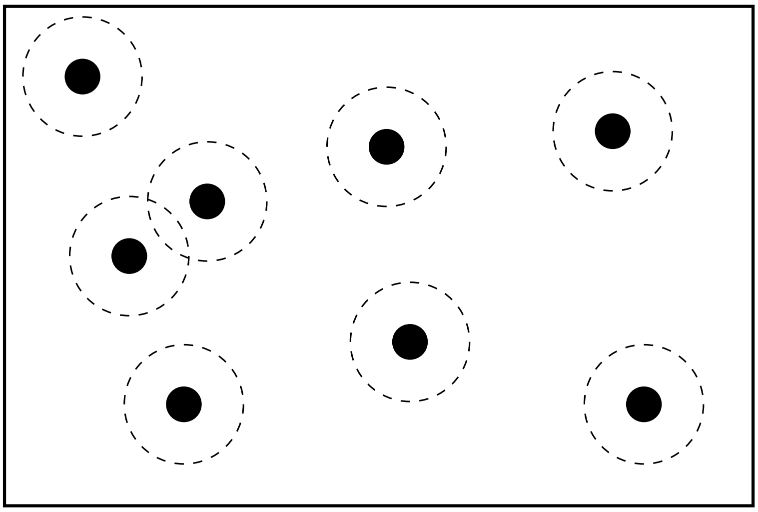


Figure 6.4: At low densities, a non-ideal gas can be approximated by assuming that there is either a single pair of interacting molecules or no interacting molecules at all. The dotted lines show the interaction volumes around the particles. Here, there is only a single pair of interacting molecules.

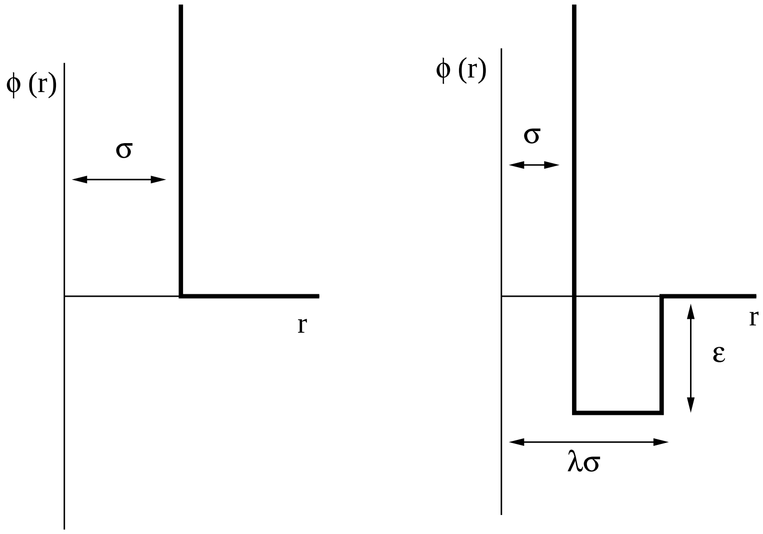


Figure 6.5: Left: the hard-sphere potential. Right: the square-well potential.

1. *Derive that the second virial coefficient of this interaction can be written as*

$$B_2^{SW} = \frac{2\pi\sigma^3}{3}\left(1 + (1 - \exp[\beta\epsilon]) \times (\lambda^3 - 1)\right) \tag{6.30}$$

2. *Show that at very high temperatures ($\beta \to 0$), B_2^{SW} is equal to the hard-sphere second virial coefficient (Eq. 6.28).*

At low temperatures, the term with $\exp[\beta\epsilon]$ *dominates, and* B_2^{SW} *becomes large and negative. The point where* B_2 *changes sign is called the Boyle temperature. At that temperature* $B_2 = 0$ *and the gas behaves almost ideal.*

3. *Show that the Boyle temperature of the square-well potential follows from*

$$\frac{k_BT}{\epsilon} = \frac{1}{\ln[\lambda^3/(\lambda^3 - 1)]} \tag{6.31}$$

6.6.2 Equation of State

In the previous subsection, we described deviations from the ideal gas law with the virial expansion. For sufficiently low densities, only the second virial coefficient $B_2(T)$ is needed to describe the pressure as a function of the density. At higher densities, more terms are needed. An alternative approach which requires less parameters is the use of an appropriate *equation of state* such as the van der Waals equation. To see how this works, consider again the ideal gas law

$$P\overline{V} = k_BT \tag{6.32}$$

in which we used $\overline{V} = V/N = 1/\rho$ for the volume per particle. The term $\overline{V}$ in the ideal gas law reflects the volume that is available for a particle. For an ideal gas, particles do not interact so the accessible volume for a particle is $\overline{V}$. However, as real atoms and molecules have a certain size and cannot overlap, the accessible volume is less then $\overline{V}$, i.e. $\overline{V} - b$. This would suggest the following equation of state ($P = P(\rho, T)$)

$$P\left(\overline{V} - b\right) = k_BT \tag{6.33}$$

that we have already seen in Eq. 2.14 as an approximation for the equation of state of a system of hard spheres. In this equation, the parameter b is related to the size of a molecule and therefore it can be expected that b does not depend on the temperature. An effect that is not yet taken into account in Eq. 6.33 is the attraction between molecules or atoms. As we have seen before, the strength of these attractions depends on the average distance between particles, and this is related to the density. In general, attractive interactions will lower the pressure and therefore it seems logical to replace P in Eq. 6.33 by $P + c(\overline{V})$, in which c is a positive function of the volume per particle. It turns out that we can write $c(\overline{V}) \propto \rho^2$ [17], leading to the following equation of state

$$\left(P + \frac{a}{\overline{V}^2}\right) \times \left(\overline{V} - b\right) = k_BT \tag{6.34}$$

which is the famous van der Waals equation. The parameter a is a measure of the strength of the interactions between molecules. In the van der Waals equation of state, a does not depend on the temperature. Other equations of state in which the strength of the attractive interactions does depend on the temperature (e.g. the Redlich-Kwong equation of state, Eq. 7.21) are usually better in describing experimental and simulation data.

Question 46 (van der Waals Equation of State)
Show that the van der Waals equation of state can be written as (see also section C.5)

$$\begin{aligned} P &= \frac{k_B T}{\overline{V} - b} - \frac{a}{\overline{V}^2} \\ &= \frac{k_B T}{\overline{V}} \times \frac{1}{1 - \frac{b}{\overline{V}}} - \frac{a}{\overline{V}^2} \\ &= \frac{k_B T}{\overline{V}} \times \left[1 + \frac{b}{\overline{V}} + \frac{b^2}{\overline{V}^2} + \frac{b^3}{\overline{V}^3} + \cdots \right] - \frac{a}{\overline{V}^2} \end{aligned} \tag{6.35}$$

and that

$$B_2 = b - \frac{a}{k_B T} \tag{6.36}$$

Question 47 (Energy as a Function of Volume)
For an ideal gas, the energy U is only a function of temperature (see Eq. B.2). However, for non-ideal gasses this is often not the case.

1. *Show that for any system we may write*

$$\left(\frac{\partial U}{\partial V}\right)_{T,N} = \left(\frac{\partial F}{\partial V}\right)_{T,N} + T \left(\frac{\partial S}{\partial V}\right)_{T,N} = -P + T \left(\frac{\partial P}{\partial T}\right)_{V,N} \tag{6.37}$$

2. *Calculate $(\partial U/\partial V)_{T,N}$ for an ideal gas and compare your result with Eq. B.2.*

3. *Calculate $(\partial U/\partial V)_{T,N}$ for a van der Waals gas and compare your result with Eq. B.2.*

6.7 Simulation Technique

Essentially, the Monte Carlo technique to compute ensemble averages for a system of N interacting particles in volume V at temperature T does not significantly differ from the scheme for the Ising model described in the previous chapter (section 5.5). The main difference is the way in which a trial move is performed; instead of flipping a randomly selected spin, a randomly selected particle is given a random displacement. Basically, the scheme is as follows:

1. Generate an initial configuration.

2. Start with an old configuration o, and calculate its energy $E(o)$.

3. Select a particle at random.

4. Give the selected particle a random displacement $x(n) = x(o) + \Delta$ in which Δ is a uniformly distributed random number from $[-\Delta x, \Delta x]$. Periodic boundary conditions are used (Eq. 6.1), so if a particle moves out of the central box, it enters on the other side.

5. Calculate the energy $E(n)$ of the new configuration n.

6. Accept the trial move with a probability

$$\text{acc}(o \to n) = \min(1, \exp[-\beta \times (E(n) - E(o))]) = \min(1, \exp[-\beta \Delta E]) \tag{6.38}$$

7. Update ensemble averages, also after a rejected trial move.

Question 48 (Trial Moves)
Show that for this scheme $\alpha(o \to n) = \alpha(n \to o)$.

A pseudo computer code of this algorithm is listed in table 6.2. A few more subtle differences between Monte Carlo simulation of the Ising model and a system of interacting atoms/molecules are described below.

6.7.1 Initial Configuration

In principle, the initial configuration $\mathbf{r}^N$ can be chosen by placing all particles at random positions in the simulation box. However, this leads to particle overlaps and therefore the initial energy would be extremely large. A Monte Carlo algorithm can be used to remove these overlaps. Alternatively, the particles could be placed initially on a lattice (i.e. a face centered cubic lattice).

6.7.2 Trial Moves

In each trial move, a randomly selected particle is given a random displacement. This means that the displacement of a particle is chosen randomly from the interval $[-\Delta x, \Delta x]$, in which Δx is the maximum particle displacement. In principle, our algorithm should work for any value of Δx. However, a very small or very large value of Δx makes our simulation very inefficient. If $\Delta x \approx 0$, particles hardly move and as a consequence $E(n) \approx E(o)$ which means that nearly all moves are accepted. However, these moves are meaningless since the system makes only very small steps in phase space. On the other hand, a very large value of Δx nearly always results in an overlap with another particle, so $\beta \Delta E \gg 1$ and no trial moves are accepted. Therefore, in practice we need to find an optimum and as a rule of thumb we should tune Δx in such a way that on average 50% of all trial moves are accepted. However, at very low densities usually more than 50% of all trial moves are accepted, independent of the maximum displacement. In this case, one should limit the maximum displacement to half the boxsize ($L/2$).

Question 49 (Maximum Displacement)
Explain why at very low densities the fraction of accepted displacements will always be close to 100%.

Question 50 (Hard-core potential)
Colloidal particles are often modeled as hard spheres (Eq. 6.27). For the same density, it is more efficient to use a larger maximum displacement Δx *for the hard sphere potential than for the Lennard-Jones potential. Explain why.*

Question 51 (Equation of State of the Lennard-Jones System)
In this question, we will perform Monte Carlo simulations for N *interacting particles in a volume* V *and temperature* T. *The particles interact via a truncated and shifted Lennard-Jones potential with* $r_{\text{cut}} = 2.5\sigma$. *During the simulation, the trajectory of all particle positions is saved (*`Traject.xyz`*). This trajectory can be visualized using the* `vmd` *program.*

1. *At* $T^\star = 2.0$, $N = 256$ *and maximum particle displacement* $\Delta x^\star = 1.0$, *make a plot of the fraction of accepted trial moves as a function of the density. Explain your results.*
2. *Fit the simulation data for* $P(\rho)$ *of Lennard-Jones particles at* $T^\star = 2.0$ *to a virial expansion*

$$P(\rho) = \rho k_B T + B_2 \rho^2 + B_3 \rho^3 + B_4 \rho^4 + \cdots \tag{6.39}$$

```
 program mc                               basic Monte Carlo algorithm

 do icycle=1,ncycle                       number of MC cycles
    call move                             displace randomly selected particle
    if(mod(icycle,nsample).eq.0)          each nsample MC cycles
+      call sample                        sample the ensemble averages
 enddo
 end



 subroutine move                          subroutine to displace a particle

 i=int(ranf()*npart)+1                    select particle i at random
 call energy(x(i),eold,i)                 calculate energy of old configuration
 xnew=x(i)+(2*ranf()-1)*Δx                random displacement of particle i
 call energy(xnew,enew,i)                 calculate energy of new configuration
 if(ranf().lt.exp(-beta*(enew-eold))      acceptance rule
+   x(i)=xnew                             accept new position of particle i
 return
 end



 subroutine energy(xi,e,i)                subroutine to calculate the energy

 e=0.0
 do j=1,npart                             loop over all particles
    if(j.ne.i) then                       if particle j is not i
       dx=x(j)-xi                         calculate distance between particle i and j
       dx=dx-box*nint(dx/box)             apply periodic boundary conditions
       eij=4*(1.0/(dx**12)-1.0/(dx**6))   calculate Lennard-Jones potential energy
       e=e+eij
    endif
 enddo
 return
 end
```

Table 6.2: Pseudo-computer code of the Monte Carlo algorithm described in the text. The program consists of three parts. The main program `mc` controls the simulation. The subroutine `move` displaces a randomly selected particle, and the subroutine `energy` computes the energy of a particle. The function `ranf()` generates a uniformly distributed random number between 0 and 1. The function `int` truncates a real number to its integer value, while the function `nint` converts a real number to its nearest integer value (i.e. `int(5.9)=5` and `nint(5.9)=6`).

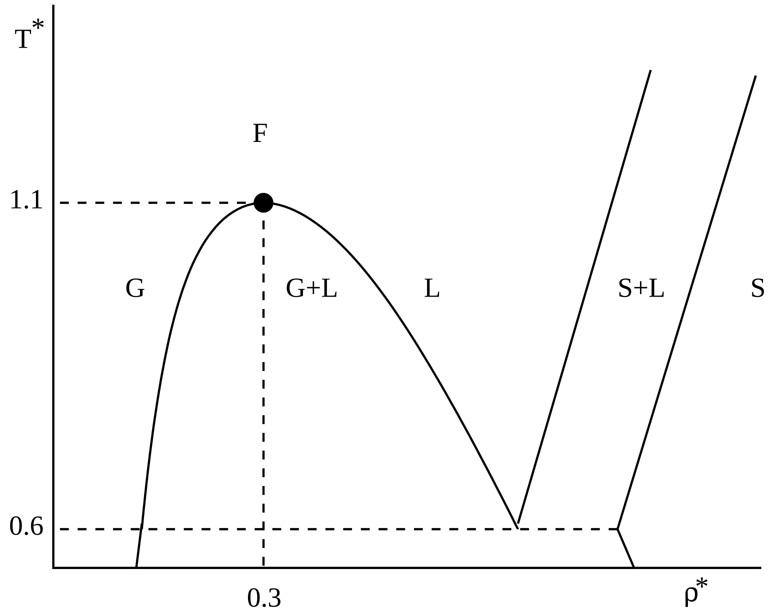


Figure 6.6: Schematic representation of the phase diagram of the Lennard-Jones system. The different phases are solid (S), liquid (L), and gas (G). Above the critical temperature ($T_c^\star \approx 1.1$) there is no gas/liquid coexistence possible anymore; the resulting phase is called a fluid (F). The solid/liquid coexistence does not have a critical point. At the so-called triple point ($T^\star \approx 0.6$), three phases (gas, liquid, solid) coexist.

For each simulation, you should carefully check that the simulation is long enough and that the maximum displacement is set correctly (i.e. according to the guidelines described in section 6.7.2). Explain why $B_2 < 0$ *at this temperature. How many terms in the virial expansion (Eq. 6.17) are needed to fit* $P(\rho)$ *up to* $\rho^\star = 1.0$ *?*

3. *At constant temperature and density, check how the heat capacity per particle (*C_v/N*) and the average energy per particle (*$\langle E \rangle / N$*) scale with the number of particles* N.

4. *How does the radial distribution function* $g(r)$ *change with the density?*

5. *Try to fit the pressure as a function of density at* $T^\star = 2.0$ *using the van der Waals equation of state (Eq. 6.34).*

Question 52 (Boyle Temperature of the Lennard-Jones Potential)
Calculate the second virial coefficient of the Lennard-Jones potential as a function of temperature using Eq. 6.26 and estimate the Boyle temperature. Check your results with Monte Carlo simulations. Hint: in general, the integral of a function $f(x)$ *can be approximated using [18]*

$$\int_a^b dx f(x) \approx h \left[\frac{1}{2} f(x_0) + f(x_1) + f(x_2) + \cdots + f(x_{n-1}) + \frac{1}{2} f(x_n) \right] \qquad (6.40)$$

in which $h = (b - a)/n$ *and* $x_i = a + h \times i$. *Note that* n *should be chosen sufficiently large.*

6.8 Gas/Liquid Equilibrium

In this chapter, we introduced Monte Carlo simulations of a system of interacting atoms or molecules. One of the most important results was that these simulations can be used to study deviations from the ideal gas law and that the simulation data of the Lennard-Jones system can be well described with an appropriate equation of state (i.e. the van der Waals equation). It is well known that this equation of state is not only used for gases, but also predicts the existence of a liquid phase. This suggests that at a certain density and temperature, a system of Lennard-Jones particles should separate into a liquid phase in coexistence with a gas. It turns out that this suggestion is indeed correct. Fig. 6.6 shows a schematic representation of the phase diagram of the Lennard-Jones system. At temperatures below the critical point ($T_c^\star \approx 1.1$), there is a stable region in which the gas and liquid phase can coexist. The equilibrium densities of the gas and liquid phase as a function of temperature are drawn by solid lines that end in the critical point ($T_c^\star \approx 1.1$, $\rho_c^\star \approx 0.3$). Note that the critical temperature strongly depends on the details of the truncation scheme of the pair potential [19].

The most obvious approach to calculate coexistence densities would be to simulate a system with a density ρ_s, somewhere in between the gas (ρ_g) and liquid density (ρ_l). If simulated long enough, the system will separate into a gas phase and a liquid phase.

Question 53 (Direct Estimation of Coexistence Densities)
In this question we will simulate a system at a density in between the gas (ρ_g) and liquid density (ρ_l).

1. *Using the given simulation code, perform a long simulation for $N = 256$ particles at density $\rho^\star = 0.3$ at temperature $T^\star = 0.65$. Investigate the trajectory using the* `vmd` *program. Is it possible to estimate the coexistence densities?*
2. *Using the final configuration (*`Coordnew`*) of the previous simulation at $T^\star = 0.65$ as starting configuration (*`Coordold`*), perform various short simulations at increasing temperatures (up to $T^\star = 1.5$) and analyze the trajectories. Up to which temperature seems the gas/liquid interface stable?*

In chapter 8 we will describe a more suitable method to compute coexistence densities of the gas and the liquid.

Chapter 7

Monte Carlo Simulations in the NPT and μVT Ensemble

7.1 Introduction

In the previous chapter, we have described the Metropolis Monte Carlo algorithm in the canonical (NVT) ensemble and calculated the average pressure P. In the canonical ensemble the number of particles (N), the volume (V) and the temperature (T) are fixed. However, this is not the only ensemble used in molecular simulations. Often, we would like to specify the pressure P instead of the volume V. The reason is that in experiments it is usually much easier to specify a pressure than to specify a density. Therefore, most experiments in a laboratory are performed at a constant pressure of 1 bar rather than at a certain (constant) volume. The ensemble of systems at a given temperature, pressure an number of particles is called the isothermal-isobaric (or NPT) ensemble.

Another important ensemble is the so-called grand-canonical (μVT) ensemble in which the number of particles in the system (N) is fluctuating and the chemical potential of the particles (μ) is specified instead. This corresponds for example to the experimental situation where a gas is in contact with a porous medium. The pressure of the gas is directly related to the chemical potential, which controls the amount of gas adsorbed in the pores of the porous medium, see for example Ref. [20–22].

Question 54 (μPT ensemble)
Is the μPT *ensemble useful? Explain your answer.*

To derive Monte Carlo schemes for the NPT and μVT ensembles, let us consider a system (volume V, number of particles N, temperature T) that is coupled to a reservoir at the same temperature. This reservoir consists of $M - N$ particles and has a volume $V_0 - V$. See Fig. 7.1. We consider the following cases in which the total number of particles ($N + M - N = M$) and the total volume ($V + V_0 - V = V_0$) of the ensemble are fixed:

- The system and the reservoir can exchange volume, but no particles. This corresponds to the Isobaric-Isothermal (NPT) ensemble and it is discussed in section 7.2. In this ensemble, the pressure P is specified and the volume V fluctuates. The number of particles (N) is constant.

- The system and the reservoir can exchange particles, but no volume. This corresponds to the grand-canonical (μVT) ensemble and it is discussed in section 7.3. In this ensemble, the chemical potential μ is specified and the number of particles N fluctuates. The volume V is constant.

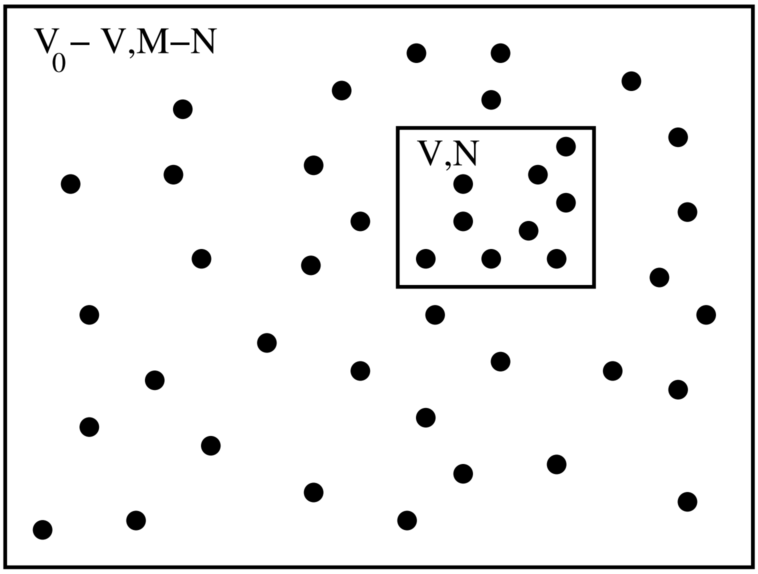


Figure 7.1: A system (N particles, volume V) in contact with a reservoir (M−N particles, volume $V_0 - V$).

- The system and the reservoir can exchange both particles and volume. This corresponds to the so-called Gibbs ensemble and this ensemble will be discussed in chapter 8.

7.2 Isobaric-Isothermal (NPT) Ensemble

Below we derive the acceptance rules of constant-pressure Monte Carlo simulations using the classical ensemble theory. The canonical partition function for a system consisting of N particles, in a volume V, and at a temperature T is given by

$$Q(N, V, T) = \frac{1}{N!\Lambda^{3N}} \int d\mathbf{r}^N \exp[-\beta E(\mathbf{r}^N)], \tag{7.1}$$

As we did in section 6.4 we use scaled coordinates $\mathbf{s}^N$ defined by

$$\mathbf{r}_i = L\mathbf{s}_i \quad i = 1, \dots N \tag{7.2}$$

where we assume a cubic box of volume $V = L^3$. The canonical partition function in scaled coordinates equals

$$Q(N, V, T) = \frac{V^N}{N!\Lambda^{3N}} \int_0^1 d\mathbf{s}^N \exp[-\beta E(\mathbf{s}^N; V)] \tag{7.3}$$

The next step is to couple our system of N particles and volume V to the reservoir (Fig. 7.1). Assume that the two systems are separated by a piston from each other. Thus we allow fluctuations in the system volume V (the total volume V_0 is constant) at constant N. In addition, we impose that the particles in the reservoir do not interact and therefore the reservoir is an ideal gas. The total volume of the system and the reservoir is V_0, while the total number of particles is M. The total partition function of the coupled system is the product of the partition functions of the two subsystems:

$$\begin{aligned} Q(N,M,V,V_0,T) &= \left[\frac{(V_0-V)^{M-N}}{(M-N)!\Lambda^{3(M-N)}}\int d\mathbf{s}^{M-N}\right]\times\left[\frac{V^N}{N!\Lambda^{3N}}\int d\mathbf{s}^N\exp[-\beta E(\mathbf{s}^N;V)]\right] \\ &= \frac{V^N(V_0-V)^{M-N}}{N!(M-N)!\Lambda^{3M}}\int d\mathbf{s}^{M-N}\int d\mathbf{s}^N\exp[-\beta E(\mathbf{s}^N;V)] \\ &= \frac{V^N(V_0-V)^{M-N}}{N!(M-N)!\Lambda^{3M}}\int d\mathbf{s}^N\exp[-\beta E(\mathbf{s}^N;V)] \end{aligned} \tag{7.4}$$

where we performed the integral over the $\mathbf{s}^{M-N}$ scaled coordinates of the ideal gas reservoir. The probability density $W(V)$ that our system of N particles has a volume V is given by

$$W(V)=\frac{V^N(V_0-V)^{M-N}\int d\mathbf{s}^N\exp[-\beta E(\mathbf{s}^N;V)]}{\int_0^{V_0}dV'V'^N(V_0-V')^{M-N}\int d\mathbf{s}^N\exp[-\beta E(\mathbf{s}^N;V')]} \tag{7.5}$$

We now consider the limit that the reservoir tends to infinity, i.e. $V_0\to\infty, M\to\infty$, while $(M-N)/(V_0-V)\to M/V_0=\rho$. In that limit, a small volume change of the small system does not change the pressure P of the reservoir and the reservoir acts as a manostat for our system of interest.

Question 55 (Infinite reservoir)
Show that in that limit, we can write

$$(V_0-V)^{M-N}\approx V_0^{M-N}\exp[-\rho V]=V_0^{M-N}\exp[-\beta PV] \tag{7.6}$$

in which P *is the pressure of the ideal gas reservoir. Hint: use Eq. C.10 and the ideal gas law* $\rho=\beta P$.

This results in the following expression for $W(V)$:

$$W(V)=\frac{V^N\exp[-\beta PV]\int d\mathbf{s}^N\exp[-\beta E(\mathbf{s}^N;V)]}{\int_0^{V_0}dV'V'^N\exp[-\beta PV']\int d\mathbf{s}^N\exp[-\beta E(\mathbf{s}^N;V')]} \tag{7.7}$$

where we used Eq. 7.6. The probability density to find our system in a configuration $\{\mathbf{s}^N\}$ and with a volume V is:

$$\begin{aligned} W(V;\mathbf{s}^N) &\propto V^N\exp[-\beta PV]\exp[-\beta E(\mathbf{s}^N;V)] \\ &\propto \exp[-\beta(E(\mathbf{s}^N;V)+PV-N\beta^{-1}\ln V)] \end{aligned} \tag{7.8}$$

In constant-pressure Monte Carlo simulations, Metropolis sampling is performed on the reduced coordinates $\{\mathbf{s}^N\}$ and on the volume V. The volume V is treated as an additional coordinate for which we should perform trial moves which will be accepted according to the same rules as trial moves in $\{\mathbf{s}^N\}$. To be more specific, we perform trial moves that consist of an attempted change of the volume V to $V'=V+\Delta V$, where ΔV is a random number uniformly distributed over the interval $[-\Delta V_{\max},\Delta V_{\max}]$. This trial move in the volume will be accepted with a probability ratio

$$\begin{aligned} \frac{\mathrm{acc}(o\to n)}{\mathrm{acc}(n\to o)} &= \frac{\exp[-\beta(E(\mathbf{s}^N;V')+PV'-N\beta^{-1}\ln V')]}{\exp[-\beta(E(\mathbf{s}^N;V)+PV-N\beta^{-1}\ln V)]} \\ &= \exp[-\beta(E(\mathbf{s}^N;V')-E(\mathbf{s}^N;L)+P(V'-V)-N\beta^{-1}\ln(V'/V))] \end{aligned} \tag{7.9}$$

so

$$\mathrm{acc}(o \to n) = \min(1, \exp[-\beta(E(\mathbf{s}^N; V') - E(\mathbf{s}^N; L) + P(V' - V) - N\beta^{-1}\ln(V'/V))]) \tag{7.10}$$

It is important to note that in this trial move, the reduced coordinates of the particles do not change. A schematic overview of the algorithm is presented in table 7.1. It can be shown that the applied pressure P (in Eq. 7.10) is identical to the average pressure computed using Eq. 6.13 [8].

Question 56 (Random walk in $\ln V$)
In the algorithm described in table 7.1, a random walk is performed in volume V. However, it is also possible to perform a random walk in the logarithm of the volume by using

$$V_{\mathrm{new}} = \exp\left[\ln(V_{\mathrm{old}}) + (2 * \mathtt{ranf}() - 1) \times \Delta V\right] \tag{7.11}$$

Derive the correct acceptance rule for this trial move.

Question 57 (Scaling)
Suppose that the cut-off radius r_{cut} is always exactly equal to half the box length. Show that for particles with an interaction potential of the form $u(r) \propto r^{-n}$, the total energy of the system after a change in volume equals

$$E_{\mathrm{new}} = E_{\mathrm{old}} \times \left(\frac{V_{\mathrm{new}}}{V_{\mathrm{old}}}\right)^{-n/3} \tag{7.12}$$

Question 58 (NPT simulation of an ideal gas)
Show using Eq. 7.7 that the ensemble average of the volume $\langle V \rangle$ in an NPT simulation of an ideal gas equals $n/(\beta P)$. Hint: see Eq. C.40.

7.3 Grand-Canonical (μVT) Ensemble

Below we derive the acceptance rules of grand-canonical Monte Carlo simulations, i.e. the chemical potential μ, the volume V, and the temperature T are fixed. To this end, we couple our system of N particles and volume V to an ideal gas reservoir (Fig. 7.1). The two systems can only exchange particles and thus, we allow for particle number fluctuations. The volume of the reservoir ($V_0 - V$) and our system (V) are fixed, while the total number of particles is M ($M - N$ in the reservoir). The total partition function of the coupled system is the product of the partition functions of the two subsystems:

$$\begin{aligned} Q(M, V, V_0, T) &= \sum_{N=0}^{M} \left[\frac{(V_0 - V)^{M-N}}{(M-N)!\Lambda^{3(M-N)}} \int d\mathbf{s}^{M-N}\right] \times \left[\frac{V^N}{N!\Lambda^{3N}} \int d\mathbf{s}^N \exp[-\beta E(\mathbf{s}^N)]\right] \\ &= \sum_{N=0}^{M} \frac{V^N (V_0 - V)^{M-N}}{N!(M-N)!\Lambda^{3M}} \int d\mathbf{s}^{M-N} \int d\mathbf{s}^N \exp[-\beta E(\mathbf{s}^N)] \\ &= \sum_{N=0}^{M} \frac{V^N (V_0 - V)^{M-N}}{N!(M-N)!\Lambda^{3M}} \int d\mathbf{s}^N \exp[-\beta E(\mathbf{s}^N)] \end{aligned} \tag{7.13}$$

where we performed the integral over the $\mathbf{s}^{M-N}$ scaled coordinates of the ideal gas reservoir. The probability density $W(\mathbf{s}^M; N)$ that our system has N particles at coordinates $\mathbf{s}^N$ in volume

```
 program npt-mc                          basic NPT Monte Carlo algorithm

 do icycle=1,ncycle                      number of MC cycles
    if(ranf().lt.pvol) then              select trial move at random
       call volumechange                 perform a volume change
    else
       call move                         move a particle
    endif
    if(mod(icycle,nsample).eq.0)         sample the ensemble averages
+      call sample
 enddo
 end


 subroutine volumechange                 perform a volume change

 call energy(eold)                       compute the old energy
 vold=box**3                             compute old volume
 vnew=vold+(2*ranf()-1)*ΔV               compute new volume
 if(vnew.lt.0) return                    reject negative volume
 boxn=vnew**(1/3)                        compute new boxsize
 do i=1,npart                            scale all coordinates
   x(i)=x(i)*boxn/box
   y(i)=y(i)*boxn/box
   z(i)=z(i)*boxn/box
 enddo
 call energy(enew)                       compute new energy
 arg=-beta*(enew-eold +                  acceptance rule
+  p*(vnew-vold)-N×ln(vnew/vold)/beta
 if(ranf().gt.exp(arg)) then             accept or reject?
   do i=1,npart                          reject, restore coordinates
     x(i)=x(i)*box/boxn
     y(i)=y(i)*box/boxn
     z(i)=z(i)*box/boxn
   enddo
 else
   box=boxn                              accept, update boxsize
 endif
 return
 end
```

Table 7.1: Pseudo computer code of Metropolis Monte Carlo in the NPT ensemble. It is selected at random with a fixed probability `pvol` to perform either a particle displacement or a volume change. The subroutine `energy` computes the total energy of the system. `a**b` means a^b. The subroutine `move` is identical to the one in table 6.2.

V and that the reservoir consists of $M-N$ particles at coordinates $\mathbf{s}^{M-N}$ in volume $V_0 - V$ is given by

$$W(\mathbf{s}^M;N) \propto \frac{V^N(V_0-V)^{M-N}\exp[-\beta E(\mathbf{s}^N)]}{\Lambda^{3M}N!(M-N)!} \tag{7.14}$$

The probability of acceptance of a trial move in which a particle is transferred from the ideal reservoir to our system is given by the ratio of the probability densities

$$\begin{aligned}\frac{\mathrm{acc}(N\to N+1)}{\mathrm{acc}(N+1\to N)} &= \frac{V^{N+1}(V_0-V)^{M-N-1}\exp[-\beta E(\mathbf{s}^{N+1})]}{(N+1)!(M-N-1)!} \\ &\quad\times\frac{(N)!(M-N)!}{V^N(V_0-V)^{M-N}\exp[-\beta E(\mathbf{s}^N)]} \\ &= \frac{V(M-N)}{(V_0-V)(N+1)}\exp[-\beta(E(\mathbf{s}^{N+1})-E(\mathbf{s}^N))] \\ &= \frac{V}{\Lambda^3(N+1)}\exp[\beta(\mu-E(\mathbf{s}^{N+1})+E(\mathbf{s}^N))] \end{aligned} \tag{7.15}$$

so

$$\mathrm{acc}(N\to N+1) = \min\left(1,\frac{V}{\Lambda^3(N+1)}\exp[\beta(\mu-E(\mathbf{s}^{N+1})+E(\mathbf{s}^N))]\right) \tag{7.16}$$

where we have used that the ideal gas reservoir is much larger than our system of interest, i.e. $M \gg N$, $V_0 \gg V$, and $(M-N)/(V_0-V) \approx M/V_0 = \rho$. In addition, we used $\rho = \exp[\beta\mu]/\Lambda^3$ in which μ is the chemical potential of the ideal gas reservoir. Similarly, we can derive that the removal of a particle is given by the ratio of the probability densities

$$\begin{aligned}\frac{\mathrm{acc}(N\to N-1)}{\mathrm{acc}(N-1\to N)} &= \frac{V^{N-1}(V_0-V)^{M-N+1}\exp[-\beta E(\mathbf{s}^{N-1})]}{(N-1)!(M-N+1)!} \\ &\quad\times\frac{(N)!(M-N)!}{V^N(V_0-V)^{M-N}\exp[-\beta E(\mathbf{s}^N)]} \\ &= \frac{(V_0-V)N}{V(M-N+1)}\exp[-\beta(E(\mathbf{s}^{N-1})-E(\mathbf{s}^N))] \\ &= \frac{N\Lambda^3}{V}\exp[-\beta(\mu+E(\mathbf{s}^{N-1})-E(\mathbf{s}^N))] \end{aligned} \tag{7.17}$$

so

$$\mathrm{acc}(N\to N-1) = \min\left(1,\frac{N\Lambda^3}{V}\exp[-\beta(\mu+E(\mathbf{s}^{N-1})-E(\mathbf{s}^N))]\right) \tag{7.18}$$

Often, instead of the chemical potential μ the fugacity f is specified. The fucagity of a system is defined as the pressure that the system would have if it would be an ideal gas, at exactly the same chemical potential. As for an ideal gas $\mu = k_BT\ln\rho\Lambda^3$ it follows directly that

$$f = \frac{\exp[\beta\mu]}{\beta\Lambda^3} \tag{7.19}$$

It can be shown that the pressure P and the fugacity f are related according to [23]

$$\ln\frac{f}{P} = \int_0^P dP'\frac{Z(P')-1}{P'} \tag{7.20}$$

in which Z is the compressibility factor $Z = P\overline{V}/k_BT$ and $\overline{V} = V/N$ is the volume per molecule.

It is important to note that the grand-canonical ensemble replies on the insertion and removal of molecules from/to the system. For molecules that consist of a single interaction site, *random insertion* usually works quite well (unless the density is too high). For chain molecules, random insertion will usually fail as this nearly always results in an overlap with another atom, leading to an extremely low acceptance probability (Eqs. 7.16, 7.18). The solutions for this problem is to *bias* the insertion/removal of chain molecules [24, 25]. For more details, we refer the reader to Refs. [26–32].

Question 59 (Fugacity)
Use Eq. 7.20 to show that for an ideal gas $f = P$. *Derive an expression for the fugacity as a function of pressure for a gas that obeys the equation of state of Eq. 2.14.*

Question 60 (Grand-canonical ensemble)
Answer the following questions:

- *Does the grand-canonical ensemble work well for solids?*
- *In principle, one could omit particle displacements in simulations in the* μVT *ensemble. Explain why.*
- *Derive the correct acceptance rules for particle exchange if the probability to select a particle removal is twice as large as selecting a particle addition.*

Question 61 (Comparison between Different Ensembles)
In this question, we will compare Monte Carlo simulations in the NVT, NPT, *and* μVT *ensemble. We will use the Lennard-Jones potential which is truncated and shifted at* $r_{\text{cut}} = 2.5\sigma$ *(Eq. 6.4). For the* μVT *ensemble, the fugacity* (f) *of the reservoir is needed as input for the program (Eq. 7.19).*

1. *Check whether* NVT *and* NPT *simulations result in the same equation of state (Eq. 6.39) at* $T^\star = 2.0$.
2. *In the* NVT *and* NPT *ensemble, the chemical potential is calculated using the method outlined in section 9.4. Check that at the same value for* μ, *the average density of a* μVT *simulation is identical to the density in an* NVT *or* NPT *simulation. Note that the program requires the fugacity and not the chemical potential as input, see Eq. 7.19.*
3. *Try to fit the pressure as a function of density at* $T^\star = 2.0$ *using the Redlich-Kwong equation of state in reduced units*
$$P^\star = \frac{T^\star}{\overline{V}^\star - b^\star} - \frac{a^\star}{\overline{V}^\star(\overline{V}^\star + b^\star)\sqrt{T^\star}} \tag{7.21}$$
in which $a^\star$ *and* $b^\star$ *are positive constants and* $\overline{V}^\star = 1/\rho^\star$ *is the volume per particle. Use only simulation data for* $\rho^\star < 0.5$.
4. *It can be shown that the critical temperature* $T^\star_c$, *the critical molar volume* $\overline{V}^\star_c$ *and the critical pressure* $P^\star_c$ *of the Redlich-Kwong equation are related according to*
$$\overline{V}^\star_c = 3.8473 \times b^\star \tag{7.22}$$
$$P^\star_c = 0.02989 \frac{(a^\star)^{2/3}}{(b^\star)^{5/3}} \tag{7.23}$$
$$T^\star_c = 0.34504 \times \left(\frac{a^\star}{b^\star}\right)^{2/3} \tag{7.24}$$
in which $a^\star$ *and* $b^\star$ *are the Redlich-Kwong parameters (Eq. 7.21). Calculate* $T^\star_c$, $\overline{V}^\star_c$ *and* $P^\star_c$ *from the fitted parameters* $a^\star$ *and* $b^\star$.

5. *For argon, experiments show that* $T_c = 151$ *K and* $P_c = 4.9 \times 10^6$ *Pa. Use the result from the previous question to compute* ϵ / k_B *(in units of* K*) and* σ *(in units of Å) for argon and compare your result with table 6.1.*

```
 program gcmc                                 basic μVT Monte Carlo algorithm

 do icycle=1,ncycle                           number of MC cycles
    if(ranf().lt.pexch) then                  select trial move at random
       call exchange                          perform a particle exchange
    else
       call move                              move a particle
    endif
    if(mod(icycle,nsample).eq.0)              sample the ensemble averages
+      call sample
 enddo
 end


 subroutine exchange                          exchange particle
                                              with reservoir
 if(ranf().lt.0.5) then
   if(npart.eq.0) return                      remove a particle
   i=1+int(npart*ranf())                      select random particle
   call ener(x(i),eold,i)                     compute the energy
   arg=npart*exp(beta*eold)/(chem*vol)        acceptance rule
   if(ranf().lt.arg) then                     accept or reject
     x(i)=x(npart)                            accept
     npart=npart-1                            remove the particle
   endif
 else                                         insert new particle
   xnew=ranf()*box                            at random position
   call ener(xn,enew,0)                       compute energy
   arg=chem*vol*exp(-beta*enew)/(npart+1)     acceptance rule
   if(ranf().lt.exp(arg)) then                accept or reject
     npart=npart+1                            accept
     x(npart)=xnew                            add the new particle
   endif
 endif
 return
 end
```

Table 7.2: Pseudo computer code of Metropolis Monte Carlo in the grand-canonical ensemble. We have defined `chem` $= \exp[\beta\mu]/(\beta\Lambda^3)$. The subroutine `move` is defined in table 6.2. The probability for a particle exchange trial move is constant during the simulation and equals `pexch`. The probabilities of attempting a particle addition or removal are equal. If no particle is present, a particle removal is always rejected.

Chapter 8

The Gibbs Ensemble

8.1 Phase Behavior

In simulations, we are often interested in predictions for the phase behavior of a substance. Naively, one can study the phase behavior by performing a simulation at a given statepoint (a given N, V and T or a given N, P and T) and investigate what happens when one changes the statepoint. For instance, one can perform canonical Monte Carlo simulations, i.e. fix N, V, and T, and measure P or one can perform Isothermal-Isobaric Monte Carlo simulations, i.e. fix N, P, T, and measure V. To be more specific, one can study a system consisting of hard sphere colloids and compress the system until it freezes. However, this method is very inaccurate for precisely determining the transition density as large hysteresis will be found when one compresses or expands the system. The hysteresis found for first-order phase transitions is a result of the presence of a large free energy barrier that separates the two coexisting phases. The height of the free energy barrier is determined by the interfacial free energy and increases when the area of the interface between the two coexisting phases increases. In chapter 6 it was shown that a considerable fraction of the particles of typical systems belongs to the interface. It is therefore, difficult to simulate two coexisting phases simultaneously in a single box as the interfacial free energy is much too high. There are several solutions to this problem, which will be described in the next section.

8.2 Gibbs Ensemble Monte Carlo Simulation

One way to determine phase coexistence is the Gibbs ensemble Monte Carlo method, which was proposed by Panagiotopoulos in 1987 [33, 34]. He proposed a method in which the two coexisting phases are simulated simultaneously in two separate boxes and hence, it avoids the interface between the two phases. The thermodynamic conditions for phase equilibria are equal chemical potential (μ), equal pressure (P), and equal temperature (T), i.e. chemical, mechanical, and thermal equilibrium. One might think that the μPT ensemble would be the ideal ensemble to study phase coexistence. However, as already mentioned in question 54, such an ensemble does not exist, as μ, P, and T are intensive variables, and the extensive variables are unbounded in this ensemble. We have to fix at least one extensive variable to get a well-defined ensemble. It may come therefore as a surprise that we can determine phase coexistence in the Gibbs ensemble method. The reason why this method works is that we fix the difference in chemical potentials between the two coexisting phases, i.e., $\Delta\mu = \mu_I - \mu_{II} = 0$, and the difference in pressure $\Delta P = P_I - P_{II} = 0$, while the absolute values (P_I, P_{II}, μ_I, μ_{II}) are still undetermined. More precisely, the temperature, the total number of particles in the two boxes, and the total volume of the two boxes are kept fixed. In addition, the two systems can exchange particles *and* volume to ensure equal chemical potential and pressure between the two phases. A Gibbs ensemble Monte Carlo simulation consists of three different trial moves (see table 8.1 and Fig. 8.1): *(1)* a trial move to displace a randomly selected particle in one of the boxes, *(2)* a trial move to exchange volume in such a way that the total volume of the two boxes remains fixed, *(3)* a trial move to transfer a particle from one box to the other. The derivation of the acceptance rules for the trial moves is similar to the ones described in chapter 7 for the various ensembles and will be described below.

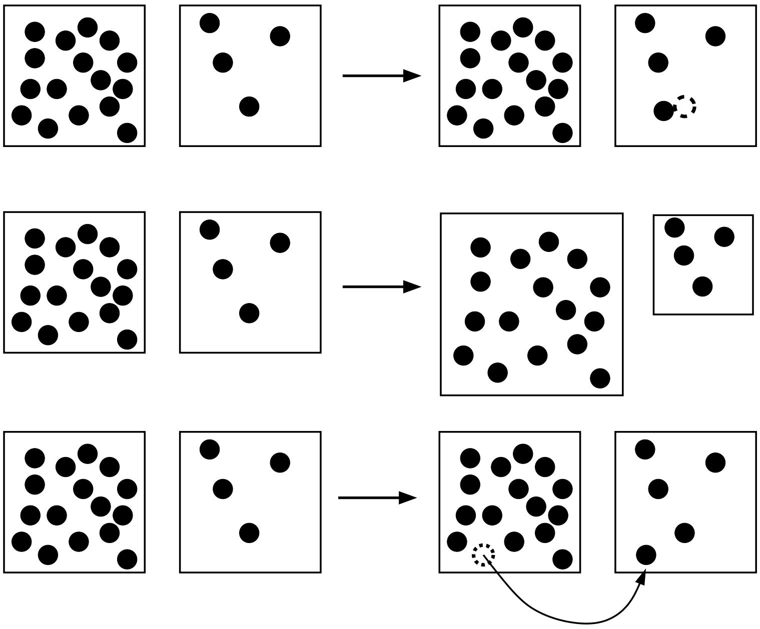


Figure 8.1: A Gibbs ensemble simulation consists of the following trial moves: *(1)* particle displacement, *(2)* exchange of volume and *(3)* exchange of particles.

8.3 The Partition Function

Consider a system of N particles distributed over two volumes V_1 (with N_1 particles) and $V_2 = V - V_1$ (with $N_2 = N - N_1$ particles), where the particles interact with each other in both volumes with the same intermolecular interactions. The volumes V_1 and V_2 can change in such a way that the total volume $V = V_1 + V_2$ remains fixed. The partition function for the total system reads:

$$\begin{aligned} Q(N,V,T) &= \sum_{N_1=0}^{N} \frac{1}{V\Lambda^{3N} N_1!(N-N_1)!} \int_0^V dV_1 V_1^{N_1} (V-V_1)^{N-N_1} \\ &\times \int d\mathbf{s}_1^{N_1} \exp\left[-\beta E(\mathbf{s}_1^{N_1}; V_1)\right] \int d\mathbf{s}_2^{N-N_1} \exp\left[-\beta E(\mathbf{s}_2^{N-N_1}; V-V_1)\right] \end{aligned} \tag{8.1}$$

The probability of finding a configuration with N_1 particles in box 1 with volume V_1 and positions $\mathbf{s}_1^{N_1}$ and $N - N_1$ particles in box 2 with volume $V - V_1$ and positions $\mathbf{s}_2^{N-N_1}$ is given by

$$W(N_1, V_1, \mathbf{s}_1^{N_1}, \mathbf{s}_2^{N-N_1}, T) \propto \frac{V_1^{N_1}(V - V_1)^{N-N_1}}{N_1!(N - N_1)!} \exp\left[-\beta E(\mathbf{s}_1^{N_1}) + E(\mathbf{s}_2^{N-N_1})\right] \tag{8.2}$$

Using this equation we can derive the acceptance rules for the trial moves in the Gibbs ensemble Monte Carlo method.

8.3.1 Particle Displacement

One of the trial moves in Gibbs ensemble Monte Carlo simulations is particle displacement. To be more specific, a new configuration is generated by selecting randomly one of the particles in box $i = 1, 2$ and by displacing it randomly. The probability of acceptance of a particle displacement is given by the ratio of the statistical weights of the new and old configurations

$$\frac{W(n)}{W(o)} = \frac{\exp\left[-\beta E(\mathbf{s}_i^{N_i}(n))\right]}{\exp\left[-\beta E(\mathbf{s}_i^{N_i}(o))\right]} = \exp[-\beta \Delta E] \tag{8.3}$$

This acceptance rule is identical to the one used in a conventional NVT ensemble simulations (Eq. 6.38).

Question 62 (Particle displacements)
Consider the following ways to select a particle displacement in the Gibbs ensemble:

- *Pick a particle at random, irrespective of which box it is in.*
- *Pick a box at random, and then pick a particle at random in this box.*

Are the acceptance rules identical?

8.3.2 Volume Exchange

In addition, we perform trial moves that consist of an attempted change of the old volume $V_1(o)$ of box 1 to a new volume $V_1(n) = V_1(o) + \Delta V$, while the volume of box 2 changes from $V_2(o)$ to $V_2(n) = V_2(o) - \Delta V$. ΔV is a random number uniformly distributed over the interval $[-\Delta V_{\text{max}}, \Delta V_{\text{max}}]$. This trial move will be accepted with a probability ratio equal to the ratio of the statistical weights of the new and old configuration

$$\frac{W(n)}{W(o)} = \frac{(V_1(n))^{N_1}(V - V_1(n))^{N-N_1}}{(V_1(o))^{N_1}(V - V_1(o))^{N-N_1}} \exp\left[-\beta\left(E(\mathbf{s}^N(n)) - E(\mathbf{s}^N(o))\right)\right] \tag{8.4}$$

resulting in

$$\text{acc}(o \to n) = \min\left(1, \left(\frac{V_1(n)}{V_1(o)}\right)^{N_1}\left(\frac{V_2(n)}{V_2(o)}\right)^{N_2} \exp\left[-\beta(E(\mathbf{s}^N(n)) - E(\mathbf{s}^N(o)))\right]\right) \tag{8.5}$$

A schematic overview of this trial move is presented in table 8.2.

Question 63 (Random walk in $\ln(V_1/V_2)$)
It is also possible to perform a random walk in $\ln[V_1/V_2]$ *instead of in* V_1*. Derive the correct acceptance rule for this trial move.*

```
 program Gibbs                      basic Gibbs ensemble Monte Carlo algorithm

 do icycle=1,ncycle                 number of MC cycles
    ran=ranf()*(npart+nvol+nswap)   select trial move at random
    if(ran.le.npart) then
       call move                    move a particle
    elseif(ran.le.(npart+nvol))
       call volumechange            perform a volume change
    else
       call swap                    swap a particle
    endif
    if(mod(icycle,nsample).eq.0)    sample the ensemble averages
+      call sample
 enddo
 end
```

Table 8.1: Pseudo computer code of a Gibbs ensemble Monte Carlo simulation. Each cycle consists of on average `npart` attempts to displace a particle, `nvol` attempts to change the volume and `nswap` attempts to transfer a particle from one to the other box. The subroutine `move` is identical to the one in table 6.2. See also tables 8.2 and 8.3.

8.3.3 Particle Exchange

The third trial move that is used in a Gibbs ensemble Monte Carlo simulation is the exchange of particles. A new configuration is generated from the old configuration by removing a particle from box 1 and inserting this particle in box 2 (50%) or by removing a particle from box 2 and inserting this particle in box 1 (50%). For the transfer of a particle from box 1 to box 2, the ratio of statistical weights of the new and old configuration is given by

$$\frac{W(n)}{W(o)} = \frac{N_1!(N-N_1)!V_1^{N_1-1}(V-V_1)^{N-(N_1-1)}}{(N_1-1)!(N-(N_1-1))!V_1^{N_1}(V-V_1)^{N-N_1}} \exp\left[-\beta(E(\mathbf{s}^N(n))-E(\mathbf{s}^N(o)))\right] \tag{8.6}$$

The acceptance rule is therefore

$$\mathrm{acc}(o \rightarrow n) = \min\left(1, \frac{N_1 V_2}{(N_2+1)V_1} \exp\left[-\beta(E(\mathbf{s}^N(n))-E(\mathbf{s}^N(o)))\right]\right) \tag{8.7}$$

In a similar way, it can be derived that the acceptance rule for the transfer of a particle from box 2 to box 1 is

$$\mathrm{acc}(o \rightarrow n) = \min\left(1, \frac{N_2 V_1}{(N_1+1)V_2} \exp\left[-\beta(E(\mathbf{s}^N(n))-E(\mathbf{s}^N(o)))\right]\right) \tag{8.8}$$

A schematic overview of this trial move is presented in table 8.3. For the efficient insertion/removal of chain molecules, we refer the reader to Refs. [26–32].

Question 64 (Gibbs ensemble)
When one of the boxes in the Gibbs ensemble is infinitely large, the acceptance rules for particle swaps become identical to the acceptance rules for particle swaps in a grand-canonical ensemble (Eqs. 7.15 and 7.17). Derive this result.

```
 subroutine volumechange                  perform a volume change

 call energy_tot(box(1),e1old)            compute the old energy of box 1
 call energy_tot(box(2),e2old)            compute the old energy of box 2
 vo1=box(1)**3                            compute old volume box 1
 vo2=box(2)**3                            compute old volume box 2
 vn1=vo1+(2*ranf()-1)*$\Delta V$                 compute new volume box 1
 if(vn1.lt.0) return                      reject negative volume
 vn2=v-vn1                                compute new volume box 2
 boxn(1)=vn1**(1/3)                       compute new boxsize box 1
 boxn(2)=vn2**(1/3)                       compute new boxsize box 2
 do i=1,npart                             scale all coordinates
    if(ibox(i).eq.1) then                 check in which box particle i is
       fact=boxn(1)/box(1)
    else
       fact=boxn(2)/box(2)
    endif
   x(i)=x(i)*fact
   y(i)=y(i)*fact
   z(i)=z(i)*fact
 enddo
 call energy_tot(boxn(1),e1new)           compute new energy box 1
 call energy_tot(boxn(2),e2new)           compute new energy box 2
 arg=-beta*(e1new+e2new-e1old-e2old -     acceptance rule
+   (npbox(1)*ln(vn1/vo1)+
+    npbox(2)*ln(vn2/vo2))/beta)
 if(ranf().gt.exp(arg)) then              accept or reject?
   do i=1,npart                           reject, restore coordinates
      if(ibox(i).eq.1) then               check in which box particle i is
         fact=box(1)/boxn(1)
      else
         fact=box(2)/boxn(2)
      endif
      x(i)=x(i)*fact
      y(i)=y(i)*fact
      z(i)=z(i)*fact
   enddo
 else
   box(1)=boxn(1)                         accept, update boxsize
   box(2)=boxn(2)
 endif
 return
 end
```

Table 8.2: Pseudo computer code for a volume change in a Gibbs ensemble Monte Carlo simulation. The subroutine `energy_tot` computes the total energy of the system. `a**b` means a^b.

```
 subroutine swap                  attempt to swap a particle

 if (ranf().lt.0.5) then          select boxes at random
    in=1                          transfer from box out to box in
    out=2
 else
    in=2
    out=1
 endif
 xn=box(in)*ranf()                add a particle to box in
 yn=box(in)*ranf()                at a random position
 zn=box(in)*ranf()
 call ener(xn,yn,zn,enn,in)       calculate energy of new particle in box in
 if(npbox(out).eq.0) return       delete particle from box out, if box empty return
 ido=0                            find a particle to be removed
 do while (ido.ne.out)
    ipart=int(npart*ranf())+1
    ido=ibox(ipart)
 enddo
 xo=x(ipart)                      old configuration
 yo=y(ipart)
 zo=z(ipart)
 call ener(xo,yo,zo,eno,out)      calculate energy particle o in box out
 arg=exp(-beta*(enn-eno +
+ log(vol(out)*npbox(in)+1)/      acceptance rule
+ (vol(in)*npbox(out)))/beta))
 if(ranf().lt.arg) then
   x(ipart)=xn
   y(ipart)=yn                    add new particle to box in
   z(ipart)=zn
   ibox(ipart)=in
   npbox(out)=npbox(out)-1
   npbox(in)=npbox(in)+1
 endif
 return
 end
```

Table 8.3: Pseudo computer code for an attempt to swap a particle between the two boxes in a Gibbs ensemble Monte Carlo simulation. The subroutine `ener` computes the energy of a particle at a given position in a certain box.

8.4 Analyzing the Results

In a Gibbs ensemble simulation, the densities of the coexisting phases can be obtained simply by sampling the densities of both boxes during the simulation. Of course, in estimating the standard deviations of the results, one should be careful since the two coexisting densities are not independent. Moreover, close to the critical point (see Fig. 9.3), it is possible that the systems change identity during a simulation. Therefore, the measured density will tend to the overall density N/V in both systems. In this case, it is more useful to determine the probability density $p(\rho)$ to observe a density ρ. The two maxima of $p(\rho)$ correspond to the coexisting densities. However, close to the critical point the Gibbs ensemble method will not work well as the free energy associated with creating a phase separation will become very small. Instead, we can estimate the location of the critical point by using the following scaling relations [8]

$$\frac{\rho_g + \rho_l}{2} = \rho_c + A \times (T_c - T) \tag{8.9}$$

$$\rho_l - \rho_g = B \times (T_c - T)^{\alpha} \tag{8.10}$$

in which $\alpha \approx 0.32$ for three-dimensional systems, A and B are fit parameters and the subscripts g, l, and c are used to denote the gas, liquid, and critical phases respectively.

Question 65 (Gibbs Ensemble Simulation)
Perform a Gibbs ensemble simulation of Lennard-Jones particles at $T^\star = 0.8$ *using the given computer program. Make sure that enough particle exchanges are accepted. In the Gibbs ensemble, the chemical potential of box* i *is equal to*

$$\beta\mu_i = -\ln \Lambda^3 - \ln \left\langle \frac{V_i}{N_i + 1} \exp\left[-\beta \Delta E_i^+\right] \right\rangle \tag{8.11}$$

where N_i *is the number of particles in box* i, V_i *is the volume of box* i, *and* ΔE_i^+ *is the energy change of box* i *when a particle is transferred from the other box [35]. See also section 9.4. It is important to note that this expression is only correct when the boxes do not change their identity.*

1. *Check that at coexistence* $\Delta\mu = \mu_I - \mu_{II} = 0$ *and* $\Delta P = P_I - P_{II} = 0$ *in which* μ_i *is the chemical potential of box* i *and* P_i *is the pressure of box* i.

2. *Check that at coexistence, the average densities are identical to the ones obtained in* μVT *and* NPT *simulations (using the values of* μ *and* P *at coexistence, obtained from Gibbs ensemble simulations).*

A zero pressure simulation is a quick and dirty way to obtain an estimate of the liquid coexistence density. If we perform a NPT *simulation at zero pressure and start with a density larger than the liquid density, the averaged density obtained from a simulation will be close to the coexistence density of the liquid phase.*

3. *Perform* NPT *simulations at* $T^\star = 0.6, 0.7, 0.8$ *and* 0.9 *and zero pressure and compare the results with Gibbs ensemble simulations.*

4. *Use the results from the Gibbs ensemble simulations to estimate the critical point using Eqs. 8.9 and 8.10. Compare your result with the result obtained from the Redlich-Kwong equation (question 61). The Lennard-Jones parameters of argon are* $\sigma_{Ar} = 3.41\text{Å}$, $\epsilon_{Ar}/k_B = 120K$. *Compare the simulation results with the experimental critical temperature and density of argon (*$T_c = 151\text{K}$, $\rho_c = 537.7\text{kg}/\text{m}^3$*). The molar mass of argon is* $39.95 \times 10^{-3}\text{kg}/\text{mol}$.

Chapter 9

Free Energy Calculations

In the previous chapter, we have used the Gibbs ensemble Monte Carlo method to calculate the vapor-liquid coexistence of a Lennard-Jones system. It was verified numerically that the pressure difference ΔP and chemical potential difference $\Delta\mu$ between the coexisting phases was zero. A disadvantage of the Gibbs ensemble Monte Carlo method is that it can only be used for the determination of fluid equilibria as it involves the insertion and removal of particles, which is impossible for solid phases and dense fluids. To determine phase equilibria for dense fluids or solids, we have to *compute* chemical potentials and free energies and choose the conditions of the phases such that $\Delta\mu = 0$ and $\Delta P = 0$. Only in a few cases the free energy is known explicitly. A method that can often be used to calculate free energies from simulations is a generalization of what is done in real systems to obtain free energies. One starts with a system whose free energy is known. Next one changes the system slowly, e.g. by heating it up, or by compressing it, until the system is brought to the state where the free energy was not yet known. By taking properly the exchange of heat, mass and work into account during the process one finds the new free energy. This *thermodynamic integration* method does not work conveniently if phase transitions are passed. To compute the free energy of a dense fluid, one can construct a reversible path to a system for which the free energy is known, e.g. the ideal gas. However, for a solid, a direct path to the ideal gas without crossing a phase transition is not possible as the solid-liquid coexistence does not have a critical point (Fig. 6.6). Therefore, we will use another reference state, the so-called Einstein crystal. The free energy difference of a real crystal and the Einstein crystal can be computed using an auxiliary Hamiltonian, which depends on a coupling parameter λ. Note that the thermodynamic integration from an ideal gas to a liquid has an equivalent in the real world, but the integration from an Einstein crystal to a real crystal has not.

9.1 Free Energy and Partition Function

In principle, the free energy $F(N,V,T)$ can be computed by integrating the Boltzmann factor over the positions of all N particles in the system

$$F(N,V,T) = -k_B T \ln Q(N,V,T) = -k_B T \ln \left(\frac{\int d\mathbf{r}^N \exp\left[-\beta E\left(\mathbf{r}^N\right)\right]}{N!\Lambda^{3N}} \right) \tag{9.1}$$

in which $\beta = 1/k_B T$ and $\mathbf{r}^N$ is a $3N$ dimensional vector containing the positions of all particles. In section 6.2.3 we have shown that for most systems we cannot compute this integral directly, except for a few trivial cases such as the ideal gas. This suggests that we are not able to compute the free energy of a system of interacting particles. However, it turns out that we are able to compute free energy differences between systems by thermodynamic integration.

Directly related to the free energy is the chemical potential of component i, which is defined as the partial derivative of the free energy with respect to N_i while keeping V, T, and N_j ($j \neq i$) fixed

$$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_j\,(j\neq i)} \tag{9.2}$$

If two phases are in thermodynamic equilibrium, the temperatures, pressures, and chemical potentials of the coexisting phases must be equal. For a single component system (only one type of particles), there is a direct relation between the free energy F and the chemical potential μ:

$$F = -PV + \mu N \tag{9.3}$$

in which V is the volume of the system and N is the number of particles. Alternatively, we can examine the Gibbs free energy G

$$G = U - TS + PV = F + PV \tag{9.4}$$

which for a single component is directly related to the chemical potential μ

$$G = \mu N \tag{9.5}$$

As the chemical potentials of the coexisting phases are equal, the Gibbs free energy per particle

$$\bar{G} = \frac{G}{N} = \mu \tag{9.6}$$

must be equal for both phases. The chemical potential can either be computed from the free energy (Eq. 9.3), or by Widom test particle method (see section 9.4).

9.2 Derivatives of the Free Energy

In a computer simulation, one can measure derivatives of the free energy such as the derivatives with respect to volume or temperature

$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = -P \tag{9.7}$$

$$\left(\frac{\partial (F/T)}{\partial T}\right)_{N,V} = -\frac{U}{T^2} \tag{9.8}$$

in which P is the pressure and U is the total energy of the system (see section B.6). If the free energy is known for a given state, we can compute the free energy at another temperature or volume by thermodynamic integration of Eqs. 9.7 and 9.8. For example, to compute the free energy at temperature T_2 when the free energy at temperature T_1 is known, we can use:

$$\frac{F(V,T_2)}{T_2} - \frac{F(V,T_1)}{T_1} = \int_{T_1}^{T_2} dT \left(\frac{\partial (F/T)}{\partial T}\right)_{N,V} = -\int_{T_1}^{T_2} dT \frac{U(V,T)}{T^2} \tag{9.9}$$

where $U(V,T)$ can be obtained from simulations.

Question 66 (Free energy of an ideal gas)
Show that the free energy of an ideal gas equals (N *particles in volume* V, $\rho = N/V$*)*

$$\frac{F_{IG}}{Nk_BT} = \ln \Lambda^3 \rho - 1 \tag{9.10}$$

were we have used Eq. C.48 for $\ln N!$.

Question 67 (Maxwell relation)
Show that Eq. 9.7 can be rewritten as

$$\left(\frac{\partial F/N}{\partial \rho}\right)_T = \frac{P(\rho)}{\rho^2} \tag{9.11}$$

Question 68 (Excess free energy)
An important property is the so-called excess free energy F_{ex} *of a system, which equals the free energy of the system* F *minus the free energy if the system would be an ideal gas* F_{IG}*:*

$$F_{\text{ex}} = F - F_{\text{IG}} \tag{9.12}$$

Show that at constant temperature T *we can write*

$$\frac{F_{\text{ex}}(\rho)}{Nk_BT} = \frac{F(\rho) - F_{\text{IG}}(\rho)}{Nk_BT} = \frac{1}{k_BT}\int_0^\rho d\rho' \frac{P(\rho') - \rho' k_BT}{\rho'^2} \tag{9.13}$$

in which $P(\rho)$ *is the equation of state of the system. Show that for a gas with the following equation of state*

$$P(\rho) = \rho k_BT + B_2\rho^2 + B_3\rho^3 + B_4\rho^4 + \cdots \tag{9.14}$$

the excess free energy equals

$$F_{\text{ex}}(\rho) = N \times \left[B_2\rho + \frac{B_3\rho^2}{2} + \frac{B_4\rho^3}{3} + \cdots\right] \tag{9.15}$$

9.3 Using an Arbitrary Order Parameter

Not only are we able to compute changes in the free energy when T or ρ is changed, but we can also compute the free energy change when an arbitrary coupling parameter λ in the potential energy function is changed at constant N, V, and T. To this end, we consider a system of N particles in a volume V interacting with a potential energy function $E\left(\mathbf{r}^N, \lambda\right)$ that depends on a coupling parameter λ in a way that we leave for this moment unspecified. The derivative of the free energy with respect to λ reads

$$\begin{aligned}
\left(\frac{\partial F}{\partial \lambda}\right)_{N,V,T} &= -\frac{1}{\beta}\frac{\partial}{\partial \lambda}\ln Q\left(N,V,T,\lambda\right) \\
&= -\frac{1}{\beta Q}\frac{\partial Q\left(N,V,T,\lambda\right)}{\partial \lambda} \\
&= \frac{\int d\mathbf{r}^N \left(\frac{\partial E(\mathbf{r}^N,\lambda)}{\partial \lambda}\right) \exp\left[-\beta E\left(\mathbf{r}^N,\lambda\right)\right]}{\int d\mathbf{r}^N \exp\left[-\beta E\left(\mathbf{r}^N,\lambda\right)\right]} = \left\langle \frac{\partial E\left(\mathbf{r}^N,\lambda\right)}{\partial \lambda}\right\rangle_\lambda
\end{aligned} \tag{9.16}$$

The brackets $\langle \cdots \rangle_\lambda$ denote an ensemble average at a fixed value of λ. This ensemble average

$$\left\langle \frac{\partial E\left(\mathbf{r}^N,\lambda\right)}{\partial \lambda}\right\rangle_\lambda \tag{9.17}$$

can be measured in a simulation. Therefore, the free energy difference between $\lambda = 0$ and $\lambda = 1$ equals

$$\Delta F = F(\lambda = 1) - F(\lambda = 0) = \int_0^1 d\lambda \left(\frac{\partial F}{\partial \lambda}\right)_{N,V,T} = \int_0^1 d\lambda \left\langle \frac{\partial E\left(\mathbf{r}^N,\lambda\right)}{\partial \lambda}\right\rangle_\lambda \tag{9.18}$$

In practice, we need of the order of 10 simulations at different values of λ to evaluate this integral numerically. In section 9.6, we will use this method to compute the free energy of a solid.

Question 69 (Gibbs-Bogoliubov inequality)
Suppose that we would like to compute the free energy difference between a system for which $\lambda = 0$ *and a system for which* $\lambda = 1$*. In addition, it is chosen that the energy depends linearly on the coupling parameter* λ*:*

$$E(\mathbf{r}^N, \lambda) = (1-\lambda) \times E_{I}(\mathbf{r}^N) + \lambda \times E_{II}(\mathbf{r}^N) \tag{9.19}$$

Show that in this case

$$\left(\frac{\partial^2 F}{\partial \lambda^2}\right)_{N,V,T} \leq 0 \tag{9.20}$$

9.4 Widom test particle method

A simple method to compute the chemical potential is Widom test particle method [17], which estimates the derivative of Eq. 9.2:

$$\mu \approx \frac{F(N+1,V,T) - F(N,V,T)}{N+1-N} = -k_B T \ln \frac{Q(N+1,V,T)}{Q(N,V,T)} \tag{9.21}$$

where $Q(N, V, T)$ is the partition function of a system of N interacting particles in a volume V at a temperature T. Using Eq. 6.9 and reduced coordinates ($s_i = r_i/L$; $V = L^3$) leads to

$$\begin{aligned}
\mu &= -k_B T \ln\left(\frac{V\Lambda^{-3}}{N+1}\right) - k_B T \ln\left(\frac{\int d\mathbf{s}^{N+1} \exp\left[-\beta E(\mathbf{s}^{N+1})\right]}{\int d\mathbf{s}^{N} \exp\left[-\beta E(\mathbf{s}^{N})\right]}\right) \\
&= -k_B T \ln\left(\frac{V\Lambda^{-3}}{N+1}\right) - k_B T \ln\left(\frac{\int d\mathbf{s}^{N+1} \exp\left[-\beta E(\mathbf{s}^{N})\right] \exp\left[-\beta \Delta E^{+}\right]}{\int d\mathbf{s}^{N} \exp\left[-\beta E(\mathbf{s}^{N})\right]}\right) \\
&\approx k_B T \ln(\rho\Lambda^3) - k_B T \ln\left\langle \exp\left[-\beta \Delta E^{+}\right]\right\rangle_{N,V,T} \\
&= \mu_{\mathrm{IG}} + \mu_{\mathrm{ex}}
\end{aligned} \tag{9.22}$$

in which $\Delta E^{+} = E(\mathbf{s}^{N+1}) - E(\mathbf{s}^{N})$ is the energy change when a test particle is inserted at a certain position in the system and $\mu_{\mathrm{IG}} = k_B T \ln(\rho\Lambda^3)$ is the chemical potential of an ideal gas. We should keep in mind that the ensemble average

$$\left\langle \exp\left[-\beta \Delta E^{+}\right]\right\rangle_{N,V,T} \tag{9.23}$$

is an *unbiased average* over all possible positions of the test particle *and* a *Boltzmann average* for our system of N particles at volume $V = L^3$ and temperature T, see Fig. 9.1. In practice, we simulate a system of N particles in volume V at temperature T using the conventional Monte Carlo algorithm. During this simulation, we keep track of the ensemble average of $\exp\left[-\beta \Delta E^{+}\right]$, in which ΔE^{+} is the energy change when an additional particle is inserted into the system at a random position (without ever accepting such an insertion).

Widom test particle method is not only possible in the NVT ensemble, but also in the Gibbs ensemble (see Eq. 8.11) and the NPT ensemble. The resulting expression for the NPT ensemble is [36,37]

$$\mu(P) = k_B T \ln(\beta P \Lambda^3) - k_B T \ln\left\langle \frac{PV}{k_B T (N+1)} \exp[-\beta \Delta E^{+}]\right\rangle_{N,P,T} \tag{9.24}$$

Question 70 (Widom Test Particle Method)
Consider a system of N *Lennard-Jones particles in a volume* V *at* $T^\star = 2.0$*.*

1. *Explain why Widom test particle method does not work well at high densities.*

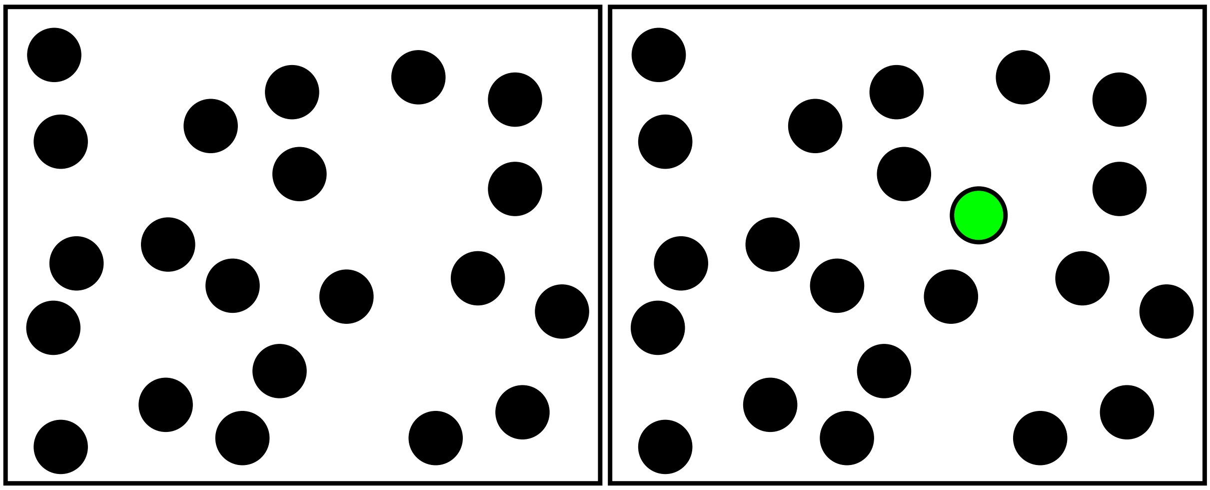


Figure 9.1: Widom test particle method. A test particle is placed at a random position in the system and the energy change ΔE^{+} is calculated. The excess chemical potential is related to the average value of $\exp[-\beta\Delta E^{+}]$.

2. *Compute the chemical potential as a function of the density for* $\rho^{\star} \leq 0.8$ *using Widom test particle method in the* NVT *ensemble using the given computer program.*

3. *Check that a simulation in the grand-canonical ensemble at the chemical potential that you measured in the previous question results in the same density.*

4. *Compute the excess free energy as a function of the density* $\rho^{\star}$ *by integrating* $P^{\star}(\rho^{\star})$ *(see questions 51 and 68). Use this result and Eqs. 9.12, 9.10 and 9.3 to calculate the chemical potential as a function of the density. Compare this result with the chemical potential obtained using Widom test particle method in the* NVT *ensemble.*

Question 71 (Particle removal)
Instead of Eq. 9.21, we could also compute the chemical potential by computing the energy change when a randomly selected particle is removed from the system

$$\mu = k_B T \ln \frac{Q(N,V,T)}{Q(N+1,V,T)} \approx \mu_{IG} + k_B T \ln \left\langle \exp\left[\beta \Delta E^{+}\right] \right\rangle_{N+1,V,T} \tag{9.25}$$

in which $\Delta E^{+} = E(\mathbf{s}^{N+1}) - E(\mathbf{s}^{N})$*. This requires a simulation of a system of* $N+1$ *particles. Explain why this method is not practical to compute the chemical potential of a system consisting of Lennard-Jones particles, although it is in principle correct.*

9.5 Umbrella Sampling

In a Monte Carlo simulation in the canonical ensemble, we compute averages by sampling configurations with a probability proportional to the Boltzmann factor

$$\langle A \rangle = \frac{\int d\mathbf{r}^N A(\mathbf{r}^N) \exp\left[-\beta E(\mathbf{r}^N)\right]}{\int d\mathbf{r}^N \exp\left[-\beta E(\mathbf{r}^N)\right]} \tag{9.26}$$

However, it is straightforward to perform a simulation in a slightly different ensemble π, in which configurations are sampled with a probability proportional to

$$\pi(\mathbf{r}^N) = \exp[-\beta E(\mathbf{r}^N) + W(\mathbf{r}^N)] \tag{9.27}$$

in which $W(\mathbf{r}^N)$ is a weight function (sometimes called biasing function) that only depends on $\mathbf{r}^N$. The ensemble average $\langle A \rangle$ in the canonical ensemble can be computed using [38]

$$\begin{aligned}
\langle A \rangle &= \frac{\int d\mathbf{r}^N A(\mathbf{r}^N) \exp\left[-\beta E(\mathbf{r}^N)\right]}{\int d\mathbf{r}^N \exp\left[-\beta E(\mathbf{r}^N)\right]} \\
&= \frac{\int d\mathbf{r}^N A(\mathbf{r}^N) \exp\left[-W(\mathbf{r}^N)\right] \exp\left[-\beta E(\mathbf{r}^N) + W(\mathbf{r}^N)\right]}{\int d\mathbf{r}^N \exp\left[-W(\mathbf{r}^N)\right] \exp\left[-\beta E(\mathbf{r}^N) + W(\mathbf{r}^N)\right]} \\
&= \frac{\dfrac{\int d\mathbf{r}^N A(\mathbf{r}^N) \exp\left[-W(\mathbf{r}^N)\right] \exp\left[-\beta E(\mathbf{r}^N) + W(\mathbf{r}^N)\right]}{\int d\mathbf{r}^N \exp\left[-\beta E(\mathbf{r}^N) + W(\mathbf{r}^N)\right]}}{\dfrac{\int d\mathbf{r}^N \exp\left[-W(\mathbf{r}^N)\right] \exp\left[-\beta E(\mathbf{r}^N) + W(\mathbf{r}^N)\right]}{\int d\mathbf{r}^N \exp\left[-\beta E(\mathbf{r}^N) + W(\mathbf{r}^N)\right]}} \\
&= \frac{\langle A \exp[-W] \rangle_\pi}{\langle \exp[-W] \rangle_\pi}
\end{aligned} \tag{9.28}$$

in which $\langle \cdots \rangle_\pi$ denotes an ensemble average in the ensemble π (Eq. 9.27). Applying a biasing potential can be useful when we wish to confine our system into a certain region of the phase space. Moreover, it is sometimes useful to split a simulation into a number of different simulations, each with a slightly different window potential $W(\mathbf{r}^N)$, and combine all the simulations afterward using Eq. 9.28.

Question 72 (Ensemble averages at different temperatures)
Suppose that we perform a Monte Carlo simulation at a certain temperature T. *Using Eq. 9.28, we could in principle compute ensemble averages at any other temperature* T^* *different from* T. *Explain how this can be done. However, it turns out that in practice, this method only works well when* $|T - T^*|$ *is small. Explain this.*

Question 73 (Weight Function)
Explain why it usually not a good idea to set $W(\mathbf{r}^N) = \beta E(\mathbf{r}^N)$.

Question 74 (Umbrella Sampling of a 2D Ising Model)
In this question we consider the Monte Carlo simulation of a 2D Ising model, see section 5.3.

1. *Calculate the distribution of the magnetisation* M *for* $N = 32 \times 32$ *and* $T^\star = 2$ *in the canonical ensemble (*$W(M) = 0$ *in Eq. 9.27) using the given computer program. In principle, this distribution should be symmetrical:*

$$p(M) = p(-M) \tag{9.29}$$

   Why does this not seem to be the case?

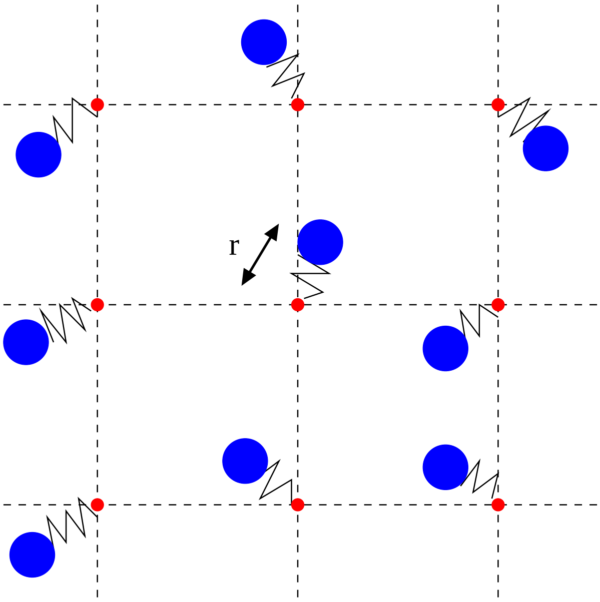


Figure 9.2: Schematic representation of an Einstein crystal. Atoms are bound to their lattice positions by harmonic springs and do not interact.

Instead of a simulation in the canonical ensemble, one can perform the simulation in a different ensemble, see Eq. 9.27.

2. *Perform simulations with some given distributions* $W(M)$ *(*`w.type1.dat`*,* `w.type2.dat`*, and* `w.type3.dat`*). Explain your results.*

9.6 Free energy of Solids: Einstein Integration

Rather than the ideal gas phase, a more useful reference system for a crystal is the so-called Einstein lattice, for which there is an exact expression for the free energy. In this system, particles are bound to grid positions by harmonic springs while the particles themselves do not interact with each other (Fig. 9.2). Each particle has a different equilibrium position in such a way that these grid positions resemble the real crystal as much as possible.

Consider a single particle that is bound with a spring to a grid position. The energy of this particle equals

$$\phi(r) = \frac{\alpha}{2} \times r^2 \tag{9.30}$$

in which r is the distance to the fixed grid position and α is a spring constant. In three dimensions, we can compute the partition sum by using spherical coordinates

$$Q = \int_0^\infty dr 4\pi r^2 \exp\left[-\beta\phi(r)\right] = \int_0^\infty dr 4\pi r^2 \exp\left[-\frac{1}{2}\alpha\beta r^2\right]. \tag{9.31}$$

Using this so-called Einstein crystal as a reference state for the free energy, the next step in computing the free energy of a real crystal is to construct a reversible path from the real crystal to the Einstein crystal. This can be done by introducing an order parameter λ with $0 \leq \lambda \leq 1$. In a computer simulation, we can simulate a crystal with the following potential:

$$E(\mathbf{r}^N, \lambda) = \lambda E_{ein}(\mathbf{r}^N) + (1-\lambda)E_{cr}(\mathbf{r}^N) \tag{9.32}$$

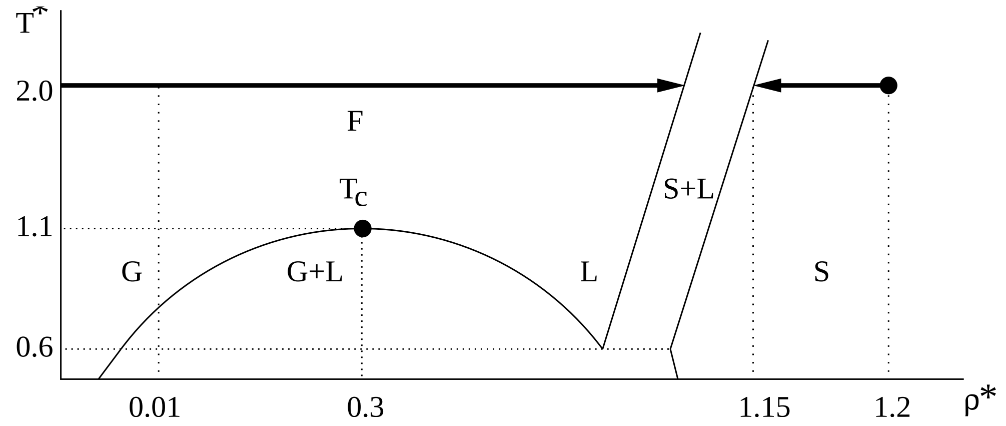


Figure 9.3: Schematic representation of the phase diagram of the Lennard-Jones system. The bold lines show the thermodynamic integration path to estimate the solid-liquid coexistence at $T^\star = 2$. For the liquid, the ideal gas is used as a reference state for the free energy. For the solid, the Einstein crystal is used instead.

in which E_{ein} is the potential energy that the system would have if it would be an Einstein crystal and E_{cr} is the potential energy if the system would be a real crystal. Thus, for $\lambda = 0$ we recover the real system and for $\lambda = 1$ we have the Einstein crystal for which we have an exact expression for the free energy. The free energy difference of the real crystal and the Einstein crystal is (Eq. 9.16)

$$\Delta F = F_{\text{ein}} - F_{\text{cr}} = \int_0^1 d\lambda \left(\frac{\partial F}{\partial \lambda}\right)_{N,V,T,\lambda} = \int_0^1 d\lambda \left\langle \frac{\partial E}{\partial \lambda} \right\rangle_\lambda = \int_0^1 d\lambda \left\langle E_{\text{ein}} - E_{\text{cr}} \right\rangle_\lambda . \tag{9.33}$$

However, there is a subtle difficulty. The problem is that fluctuations in E_{ein} become very large when $\lambda \to 0$. The reason for this is that for $\lambda = 0$ the particles are no longer bound to their lattice position and can in principle move freely. Therefore, $\langle r^2 \rangle$ will be of the order of the square of the system size which may be quite large. This problem is solved by performing the integration of Eq. 9.33 using a fixed center of mass resulting in ΔF^{CM}

$$\Delta F^{\text{CM}} = F^{\text{CM}}_{\text{ein}} - F^{\text{CM}}_{\text{cr}} = \int_0^1 d\lambda \left\langle E_{\text{ein}} - E_{\text{cr}} \right\rangle_{\lambda,\text{CM}} \tag{9.34}$$

in which the brackets $\langle \cdots \rangle_{\lambda,\text{CM}}$ denote an ensemble at a fixed value of λ and at a fixed center of mass. It is important to note that ensemble averages with and without a fixed center of mass are different, i.e.

$$\int_0^1 d\lambda \left\langle E_{\text{ein}} - E_{\text{cr}} \right\rangle_{\lambda,\text{CM}} \neq \int_0^1 d\lambda \left\langle E_{\text{ein}} - E_{\text{cr}} \right\rangle_\lambda . \tag{9.35}$$

However, we would like to compute the free energy of a system in which the center of mass is not fixed because this corresponds to the "real" system. The resulting expression for the free energy of the unconstrained system is derived in the paper by Polson *et al.* [39]. Most important is Eq. 17 of this paper to compute the excess free energy F_{ex}, which is the free energy of the system (F) minus the free energy of the system if it would be an ideal gas (F_{IG}),

$$F_{\text{ex}}(N,V,T) = F(N,V,T) - F_{\text{IG}}(N,V,T) \tag{9.36}$$

$$\frac{\beta F_{\text{ex}}}{N} = -\frac{3}{2}\ln\frac{2\pi}{\alpha\beta} - \frac{3}{2N}\ln\frac{\alpha\beta}{2\pi} + \frac{\ln\rho}{N} - \frac{2\ln N}{N} - \ln\rho + 1 - \frac{\ln 2\pi}{2N} - \frac{\beta}{N}\Delta F^{\text{CM}} \tag{9.37}$$

in which ΔF^{CM} is given by Eq. 9.34 and F_{IG} by Eq. 9.10.

Question 75 (Free energy of an Einstein crystal)
Derive that the free energy of a crystal containing N *particles that are all bound to different lattice positions with equal spring constants* α*, equals*

$$F = -k_B T \ln Q = -\frac{3N}{2\beta} \ln \frac{2\pi}{\alpha\beta}. \tag{9.38}$$

See also Eq. C.46. If $\alpha \to 0$*,* F *diverges. Provide a physical explanation for this.*

Question 76 (Mean-squared displacement)
Show that the mean-squared particle displacement of an Einstein crystal equals

$$\left\langle r^2 \right\rangle = \frac{3}{\alpha\beta} \tag{9.39}$$

See also Eq. C.47.

Question 77 (Hard sphere solid)
Suppose we would like to study the solid/liquid coexistence of particles interacting with a hard-core potential (Eq. 6.27). Explain why the reversible path of Eq. 9.32 will not work in this case.

Question 78 (Melting of a Lennard-Jones Crystal)
We will compute a single point of the solid/liquid coexistence curve of a Lennard-Jones system at $T^\star = 2.0$*. For this, we need to compute the free energy of the solid as well as the liquid. The free energy of the liquid phase can be computed by constructing a path from the liquid density all the way up to the ideal gas limit (see Fig. 9.3 and Eq. 9.13). For the solid phase, we use the Einstein integration method using a fixed center of mass. The equilibrium crystal structure of the solid is* fcc *(face centered cubic). This means that the equilibrium grid positions for the Einstein integration are also organized on an* fcc *lattice. Before you start, answer the following questions:*

1. *What happens with the accuracy of the thermodynamic integration when* α *has a very low or very high value?*
2. *We can compute the free energy of the liquid phase at* $T^\star = 2.0$ *by constructing a direct path to the ideal gas, see Fig. 9.3. If we would like to compute the phase equilibrium at* $T^\star = 0.8$*, this direct approach will not work. Explain why.*

Use the following steps to compute the coexistence densities:

3. *Compute the excess free energy of the liquid as a function of* $\rho^\star$ *by thermodynamic integration to the ideal gas limit, see also questions 68 and 70.*
4. *Compute the excess free energy of the solid by performing an Einstein integration for* $\rho^\star = 1.2$*. You will have to play a little bit with* α *to get reasonable results. Hint: try* $\alpha^\star = 100$ *and* $\alpha^\star = 500$ *for* $\lambda = 0$*,* $\lambda = 0.5$*, and* $\lambda = 1$ *just to get a feeling which value of* α *is the best.*
5. *To compute the coexistence pressure, construct a plot of the chemical potential as a function of the pressure for both the solid and liquid phase. You will have to use*

   $$\left(\frac{\partial \mu}{\partial P}\right)_{T,N} = \frac{1}{\rho(P)} \tag{9.40}$$

   for both phases. For the solid phase at $T^\star = 2.0$*, the following equation of state can be used:* $P^\star(\rho^\star) = 276.47 - 554.051\rho^\star + 290.756(\rho^\star)^2$.
6. *Use the coexistence pressure to compute the coexistence densities.*
7. *Estimate the coexistence density of the liquid and pressure at* $T^\star = 2.1$ *using Eq. B.46.*

Chapter 10

Introduction to Molecular Dynamics

10.1 Molecular Dynamics

In Molecular Dynamics simulations, Newton's equations of motion are integrated numerically for typically $N = 100 - 10000$ particles, starting from an initial configuration Γ (representing all particle positions and velocities in the system). After equilibration, we can measure time averages $\overline{\mathcal{A}}$ of a corresponding microscopic function $\mathcal{A}(\Gamma)$ over a certain time interval $t_0 \leq t \leq t_0 + \tau$ of a phase trajectory:

$$\overline{\mathcal{A}} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t_0}^{t_0+\tau} dt \mathcal{A}(\Gamma(t)) \tag{10.1}$$

In contrast to Monte Carlo simulations, which only yield thermodynamic ensemble averages, Molecular Dynamics simulations can provide us not only equilibrium properties, but also transport properties of the system. A Molecular Dynamics simulation is performed as follows (see table 10.1):

1. Start with a configuration Γ_o, i.e., select initial positions and velocities for all particles.
2. Calculate the forces on all particles. For a given pair of particles the α-component of the force ($\alpha = x, y, z$) is given by

   $$f_\alpha(r) = -\frac{\partial \phi(r)}{\partial r_\alpha} = -\frac{r_\alpha}{r} \times \frac{\partial \phi(r)}{\partial r} \tag{10.2}$$

   with $\phi(r)$ the pair potential and $r = |\mathbf{r}| = \sqrt{r_x^2 + r_y^2 + r_z^2}$ is the distance between two particles. The total force on a particle i can be calculated by considering interactions with all particles j ($j \neq i$).
3. Integrate Newton's equations of motion to obtain the new positions and velocities:

   $$\begin{aligned} F_i &= m_i \times \frac{dv_i}{dt} \\ v_i &= \frac{dr_i}{dt} \end{aligned} \tag{10.3}$$

   in which F_i, m_i, v_i are r_i are the total force, mass, velocity and position of particle i respectively.
4. Repeat step 2 and 3

Question 79 (Force for a Lennard-Jones system)
Derive an expression for the x-component of the force for a Lennard-Jones system.

```
program md                    Molecular Dynamics algorithm

call init                     select initial positions and velocities
t=0.0                         time t = 0
do while (t.lt.tmax)          for t < tmax
   call force(f,en)           calculate the forces on all particles
   call integrate(f,en)       integrate equations of motion
   t=t+deltat                 update the time
   call sample                sample the time averages
enddo
end
```

Table 10.1: Pseudo computer code for a Molecular Dynamics simulation.

10.2 Initialization

A Molecular Dynamics simulation is started from an initial configuration of N particles in a fixed volume V. We select first initial positions and velocities for every particle in our system. The positions of the particles are chosen such that the associated Boltzmann weight is non-zero, i.e., no hard-core particle overlaps. For Lennard-Jones interactions, it is a good idea to ensure that all particle-particle distances are at least equal to σ. The particles can be placed at random in the simulation box, or they can be placed on lattice sites. Alternatively, particle positions can be taken from an equilibrated Monte Carlo simulation. We then assign a velocity to each particle, which can either be picked randomly in an interval $[-1;1]$ for each component v_α, where α denotes the x, y, and z-direction, or can be taken from a Maxwell-Boltzmann velocity distribution (Eq. 10.41). Subsequently, the velocities are shifted such that the total momentum of all the particles is zero and the velocities are scaled such that the mean kinetic energy E_{kin} matches the desired temperature T:

$$E_{kin} = \sum_{i=1}^{N} \frac{m\mathbf{v}_i^2}{2} = \frac{3Nk_BT}{2} \tag{10.4}$$

where $\mathbf{v}_i^2 = v_{x,i}^2 + v_{y,i}^2 + v_{z,i}^2$. As $T \propto \sum_{i=1}^{N} \mathbf{v}_i^2$, the instantaneous temperature $T(t)$ can be adjusted to match the desired temperature T by scaling all velocities with a factor $\sqrt{T/T(t)}$.

10.3 Force Calculation

In the next step of a Molecular Dynamics simulation, we determine the force acting on every particle. If we assume a system interacting with pairwise additive interactions, we calculate the contribution to the force on particle i due to the presence of all the other particles. If we consider only the interaction between a particle and the nearest image of another particle (just as we did for the Monte Carlo method in chapter 6), we must evaluate $N(N-1)/2$ pairs of particles, where N is the number of particles in our simulation box. Hence, we first compute the distance between each pair of particles i and j. We use periodic boundary conditions and compute the nearest image distance. Moreover, it is often convenient to use a cut-off at a distance r_{cut}, where r_{cut} is less than half the diameter of the periodic box. We then calculate the force for a given pair between particle i and j as a result of the corresponding pair interaction.

```
subroutine init              Initialization of MD program

sumv=0
sumv2=0
do i=1,npart
   x(i)=latticepos(i)        place the particle on a lattice position
   v(i)=2×(ranf()-0.5)       give random velocity
   sumv=sumv+v(i)            total momentum
   sumv2=sumv2+v(i)**2       kinetic energy
enddo
sumv=sumv/npart
sumv2=sumv2/npart
fs=sqrt(3*temp/sumv2)        we assume a three-dimensional system
do i=1,npart                 scale velocities to desired temperature
   v(i)=(v(i)-sumv)*fs       set total momentum to zero
enddo
return
end
```

Table 10.2: Pseudo computer code for an initialization of a Molecular Dynamics simulation. Function `latticepos` gives the coordinates of lattice position i and `ranf()` gives a random number uniformly distributed between $[0 : 1]$. We do not start with a Maxwell-Boltzmann velocity distribution (Eq. 10.41), but after equilibration this distribution will be reached very quickly.

10.4 Integration of the Equations of Motion

For the integration of Newton's equations of motion (Eq. 10.3), we employ the Verlet algorithm, which is based on a Taylor expansion (Eq. C.13) of the coordinate of a particle at time $t + \Delta t$ and $t - \Delta t$ about time t:

$$r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 + \frac{\partial^3 r}{\partial t^3}\frac{\Delta t^3}{3!} + \mathcal{O}(\Delta t^4). \tag{10.5}$$

and

$$r(t - \Delta t) = r(t) - v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 - \frac{\partial^3 r}{\partial t^3}\frac{\Delta t^3}{3!} + \mathcal{O}(\Delta t^4). \tag{10.6}$$

Adding these two equations and subtracting $r(t - \Delta t)$ on both sides gives us

$$r(t + \Delta t) = 2r(t) - r(t - \Delta t) + \frac{f(t)}{m}\Delta t^2 + \mathcal{O}(\Delta t^4). \tag{10.7}$$

Note that the new position is accurate to order Δt^4. The Verlet algorithm does not use the velocity to compute the new position, but the velocity can be derived from the trajectory, which is only accurate to order Δt^2:

$$v(t) = \frac{r(t + \Delta t) - r(t - \Delta t)}{2\Delta t} + \mathcal{O}(\Delta t^2) \tag{10.8}$$

The velocities can be used to compute the kinetic energy and, thereby, the instantaneous temperature calculated by Eq. 10.4. It is important to note that Eqs. 10.7 and 10.8 conserve:

```
subroutine force(f,en)               calculation of the forces

en=0                                 set total energy to zero
do i=1,npart
   f(i)=0                            set forces to zero
enddo
do i=1,npart-1                       consider all particle pairs
   do j=i+1,npart
      xr=x(i)-x(j)                   distance between i and j
      xr=xr-box*nint(xr/box)         periodic boundary conditions
      r2=xr**2
      if(r2.lt.rc2) then             rc2=rc*rc, where rc is the cut-off distance
        r2i=1/r2
        r6i=r2i**3
        ff=48*r2i*r6i(r6i-0.5)
        f(i)=f(i)+ff*xr              update force for particle i
        f(j)=f(j)-ff*xr              update force for particle j
        en=en+4*r6i*(r6i-1)-ecut     update total potential energy
      endif
   enddo
enddo
return
end
```

Table 10.3: Pseudo computer code for the calculation of the forces in a Molecular Dynamics simulation. `ecut` denotes the value of the potential at $r = r_{\text{cut}}$. For the Lennard-Jones potential `ecut` is given by Eq. 6.5.

- the total linear momentum of the system, i.e.

$$\frac{d}{dt}\sum_{i=1}^{N} m_i v_i(t) = 0 \tag{10.9}$$

- the *total* energy of the system, which is the sum of the potential energy

$$E_{\text{pot}} = \sum_{i<j} \phi_{ij}(\mathbf{r}_{ij}) \tag{10.10}$$

  and the kinetic energy E_{kin} (Eq. 10.4).

If these quantities are not conserved in an actual simulation there must be an error in the simulation program.

10.5 Other Integration Algorithms

In a Molecular Dynamics simulation it is essential to have a good algorithm to integrate Newton's equation of motions. Different integration algorithms exist and a good algorithm should satisfy several criteria. First, the algorithm should be fast, and require little memory. Second, it should be sufficient accurate for large time steps as larger time steps results in fewer evaluations

```
subroutine integrate(f,en)          Integration of equations of motion

sumv=0
sumv2=0
do i=1,npart
   xx=2*x(i)-xm(i)+delt**2*f(i)     Verlet algorithm (Eq. 10.7)
   vi=(xx-xm(i))/(2*delt)
   sumv2=sumv2+vi**2
   xm(i)=x(i)                       update positions
   x(i)=xx
enddo
temp=sumv2/(3*npart)                temperature
etot=(en+0.5*sumv2)/npart           total energy per particle
return
end
```

Table 10.4: Pseudo computer code for the integration of the equations of motion in a Molecular Dynamics simulation.

of the force and a speed up of the simulation. Third, it should satisfy energy and momentum conservation, and it should be time reversible. It is important to note that time-reversibility is much more important than accuracy (e.g. predicting positions and velocities as accurately as possible) and therefore Molecular Dynamics of a system of interacting particles is fundamentally different from predicting the trajectory of a satellite that is send into space. For a more in-depth discussion about why this is we would like to refer the reader to Ref. [8].

The Verlet algorithm satisfies the criteria of a good integration algorithm. Below, we discuss a few alternatives for this algorithm. The Euler algorithm is simply based on a Taylor expansion of the particle coordinates truncated beyond the term in Δt^2 and reads

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 \tag{10.11}$$

$$v(t+\Delta t) = v(t) + \frac{f(t)}{m}\Delta t \tag{10.12}$$

However, it suffers from a tremendous energy drift and the Euler algorithm should be avoided at any time. Another popular algorithm is the so-called Leap Frog algorithm. It evaluates the velocities at half-integer time steps and uses these velocities to compute new positions. The velocities at half-integer time steps are defined as follows

$$v(t-\Delta t/2) = \frac{r(t) - r(t-\Delta t)}{\Delta t} \tag{10.13}$$

$$v(t+\Delta t/2) = \frac{r(t+\Delta t) - r(t)}{\Delta t} \tag{10.14}$$

The latter equation yields an expression for the new positions, based on the old positions and velocities

$$r(t+\Delta t) = r(t) + v(t+\Delta t/2)\Delta t \tag{10.15}$$

Combining Eqs. 10.13 and 10.14 and the Verlet algorithm (10.7), we arrive at the following update for the velocities

$$v(t+\Delta t/2) = v(t-\Delta t/2) + \Delta t\frac{f(t)}{m} \tag{10.16}$$

It is important to note that the kinetic and potential energy are not defined at the same time, and hence we cannot compute the total energy directly in the Leap Frog scheme. In the velocity Verlet algorithm, the positions and velocities are computed at equal times. The update of the coordinates in this algorithm is based on a Taylor expansion for the coordinates

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 \tag{10.17}$$

while the update of the velocities is

$$v(t+\Delta t) = v(t) + \frac{f(t+\Delta t) + f(t)}{2m}\Delta t \tag{10.18}$$

In this algorithm, we can only compute the new velocities after we have computed the new coordinates and from these the new forces. This scheme is, however, equivalent to the original Verlet algorithm.

Question 80 (Verlet and velocity Verlet algorithm)
Show that the Verlet and velocity Verlet algorithm are equivalent. Hint: Rewrite Eq. 10.17 for $r(t+2\Delta t)$ *and give an expression for* $r(t+\Delta t)$ *using Eq. 10.17. Add the two expressions and substitute Eq. 10.18.*

Question 81 (Verlet algorithm is time-reversible)
Show that the Verlet- and Leap-Frog algorithms are time-reversible and the Euler algorithm is not.

10.6 Computer Experiments

In a Molecular Dynamics simulation, thermodynamic properties, e.g., temperature, pressure, radial distribution functions, etc., can be measured during the simulation. This is done in a similar way as in Monte Carlo, see for example section 6.4. The temperature T can be measured by computing the average kinetic energy $\langle E_{\mathrm{kin}} \rangle$. For a three-dimensional Lennard-Jones system, the temperature T is calculated by

$$k_B T = \frac{2 \times \langle E_{\mathrm{kin}} \rangle}{3} \tag{10.19}$$

The pressure P can be measured using the usual virial equation (Eq. 6.13). In addition to the static equilibrium properties, one can also measure dynamic equilibrium properties in a Molecular Dynamics simulation. In the next section, we discuss some of the transport properties that can be calculated.

Question 82 (Molecular Dynamics of a Lennard-Jones System)
Enclosed is a Molecular Dynamics (MD) program for a Lennard-Jones fluid in the NVE *ensemble. Unfortunately, the program does not conserve the total energy because it contains three errors.*

1. *Find the three errors in the code. Hint: there are two errors in* `integrate.f` *and one in* `force.f`*. See the file* `system.inc` *for documentation about some of the variables used in this code.*

2. *How is one able to control the temperature in this program? After all, the total energy of the system should be constant (not the temperature).*

3. *To test the energy drift* ΔE *of the numerical integration algorithm for a given time step* Δt *after* $n_{\max}$ *integration steps, one usually computes [40]*

$$\Delta E\left(n_{\max}\Delta t\right) = \frac{1}{n_{\max}} \sum_{n=1}^{n_{\max}} \left| \frac{E\left(0\right) - E\left(n\Delta t\right)}{E\left(0\right)} \right| \tag{10.20}$$

In this equation, $E(x)$ *is the total energy (kinetic+potential energy) of the system at time* x*. Make a plot of* ΔE *as a function of the time step. Do you expect that this plot will be different at a higher density or at a higher temperature?*

4. *In the current version of the code, the equation of motion are integrated by the velocity Verlet algorithm. Make a plot of the energy drift* ΔE *for the following integration algorithms:*
    - *Euler (never use this one except here !!!)*
    - *Verlet*
    - *velocity Verlet*

10.7 Diffusion

Diffusion is the process whereby an initially nonuniform concentration profile (e.g. an ink drop in water) evolves in time. Diffusion is caused by the thermal motion of the particles in the fluid. The macroscopic law that describes diffusion is known as Fick's law, which states that the flux **j** of the diffusing species is proportional to the negative gradient in the concentration of that species:

$$\mathbf{j} = -D\nabla c \tag{10.21}$$

where the constant of proportionality D is the diffusion coefficient. In this chapter, we limit ourselves to self-diffusion. This means that we study diffusion of a labeled species among other identical species. We now compute the concentration profile of the tagged species, under the assumption that at time $t = 0$, the tagged species was concentrated at the origin. To compute the time evolution of the concentration profile, we combine Fick's law with conservation of the total amount of labeled material:

$$\frac{\partial c(r,t)}{\partial t} + \nabla \cdot \mathbf{j}(r,t) = 0 \tag{10.22}$$

Combining Eq. 10.22 with Fick's law (Eq. 10.21), we arrive at

$$\frac{\partial c(r,t)}{\partial t} - D\nabla^2 c(r,t) = 0 \tag{10.23}$$

which can be solved with the initial condition

$$c(r,0) = \delta(r) \tag{10.24}$$

to yield for a three-dimensional system

$$c(r,t) = \frac{1}{(4\pi D t)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right) \tag{10.25}$$

We can rewrite this equation using the time dependence of the second moment of $c(r,t)$ instead of $c(r,t)$ itself, which reads

$$\langle r^2(t)\rangle \equiv \int d\mathbf{r} c(r,t) r^2 \tag{10.26}$$

where we used the normalization

$$\int d\mathbf{r} c(r,t) = 1 \tag{10.27}$$

We obtain

$$\frac{\partial}{\partial t}\int d\mathbf{r} r^2 c(r,t) = D\int d\mathbf{r} r^2 \nabla^2 c(r,t) \tag{10.28}$$

The left-hand side of this equation is equal to

$$\frac{\partial}{\partial t}\int d\mathbf{r} r^2 c(r,t) = \frac{\partial\langle r^2(t)\rangle}{\partial t} \tag{10.29}$$

and the right-hand side equals

$$D\int d\mathbf{r} r^2 \nabla^2 c(r,t) = 6D \tag{10.30}$$

where we used partial integration. In conclusion, we find

$$\frac{\partial\langle r^2(t)\rangle}{\partial t} = 6D \tag{10.31}$$

This relation was first derived by Einstein around 1905. It relates the diffusion coefficient D to the width of the concentration profile. We stress that D is a macroscopic transport coefficient, whereas $\langle r^2(t)\rangle$ is a microscopic property as it is the mean-squared distance over which the tagged particles have moved in a time t. In a computer simulation, D can be measured by measuring for every particle i the distance traveled in time t, $\Delta\mathbf{r}_i(t)$. To be more specific, we plot the mean-squared displacement

$$\langle \Delta r(t)^2\rangle = \frac{\sum_{i=1}^{N}\Delta\mathbf{r}_i(t)^2}{N} \tag{10.32}$$

as a function of t. For long times, $\langle \Delta r(t)^2\rangle$ varies linearly with t and the slope is given by 6D (see Fig. 10.1). The displacement can be re-expressed simply as the time integral of the velocity of the tagged particle:

$$\Delta\mathbf{r}(t) = \int_0^t dt'\mathbf{v}(t') \tag{10.33}$$

There is a relation between the diffusion coefficient and the particle velocities. If we consider only one Cartesian component of the mean-squared displacement, the diffusion reads

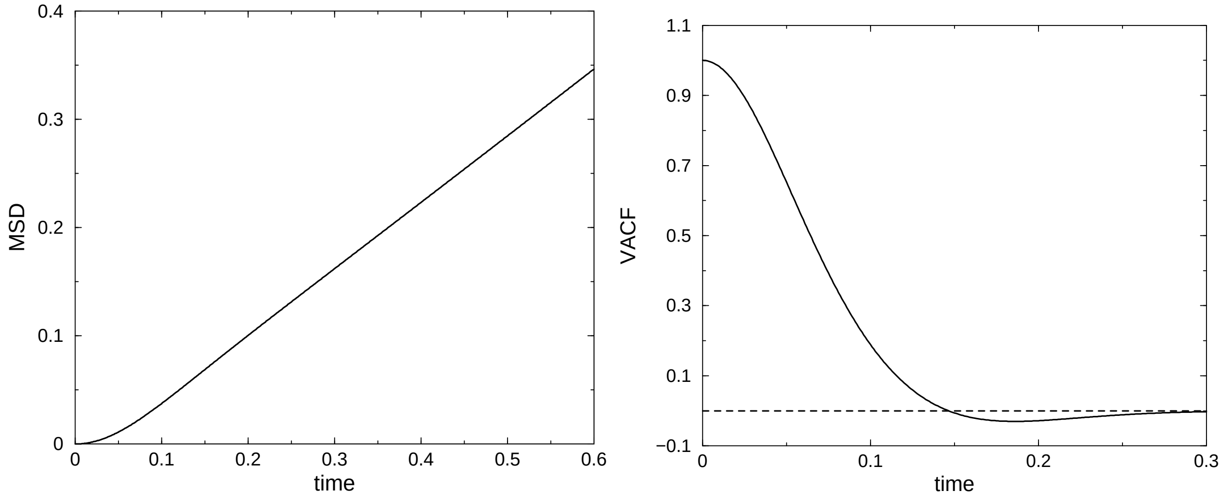
$$2D = \lim_{t\to\infty}\frac{\partial\langle x^2(t)\rangle}{\partial t} \tag{10.34}$$

We can now rewrite $x(t)$ as the time integral of the x-component of the velocity of the tagged particle

$$\begin{aligned}\langle x^2(t)\rangle &= \left\langle\left(\int_0^t dt' v_x(t')\right)^2\right\rangle \\ &= \int_0^t\int_0^t dt'dt''\langle v_x(t')v_x(t'')\rangle \\ &= 2\int_0^t\int_0^{t'} dt'dt''\langle v_x(t')v_x(t'')\rangle \end{aligned} \tag{10.35}$$

where $\langle v_x(t')v_x(t'')\rangle$ equals the velocity autocorrelation function (VACF). It describes the correlations between velocities at different times along an equilibrium trajectory. Combining Eq. 10.34 with Eq. 10.35, we obtain

$$\begin{aligned} D &= \lim_{t\to\infty}\int_0^t dt''\langle v_x(t-t'')v_x(0)\rangle \\ &= \int_0^t d\tau\langle v(\tau)v(0)\rangle \end{aligned} \tag{10.36}$$



(a) Mean-squared displacement

(b) Velocity autocorrelation function

Figure 10.1: (a) Mean-squared displacement (Eq. 10.32) and (b) the normalized velocity autocorrelation function ($\langle v(0)v(t)\rangle / \langle v(0)^2\rangle$) for a Lennard-Jones system ($T^\star = 1.5$, $\rho^\star = 0.88$) as a function of time.

where we changed the integration variable to $\tau = t - t''$, and we used that the VACF is invariant under a change of the time origin and time inversion

$$\langle v_x(t')v_x(t)\rangle = \langle v_x(t'-t)v_x(0)\rangle \tag{10.37}$$

We now related the diffusion coefficient D to the integral of the velocity autocorrelation function. Note that both methods for calculating the diffusivity D (Eqs. 10.31 and 10.36) result in exactly the same value. More information on computing diffusivities can be found in Ref. [41].

Question 83 (Velocity autocorrelation function)
Why is the VACF in Fig. 10.1 negative for some t*?*

Question 84 (Self Diffusion)
An important quantity of a liquid or gas is the so called self diffusivity D*. There are two methods to calculate* D*:*

1. *by integrating the velocity autocorrelation function:*

$$D = \frac{1}{3}\int_0^\infty \left\langle \mathbf{v}(t) \cdot \mathbf{v}\left(t + t'\right)\right\rangle dt' \tag{10.38}$$

2. *by calculating the mean-squared displacement:*

$$D = \lim_{t' \to \infty} \frac{\left\langle \left| \mathbf{x}\left(t + t'\right) - \mathbf{x}(t) \right|^2 \right\rangle}{6t'} \tag{10.39}$$

Use the given computer program to answer the following questions (make sure that the errors of question 82 are corrected):

1. *What is the unit of* D *in SI units? How can one transform* D *into dimensionless units?*

2. *Why should we be very careful with calculating of the mean-squared displacement when particles are transformed to the central box?*

3. *For Lennard-Jones liquids, Naghizadeh and Rice report the following equation for the self diffusivity ($T^* < 1.0$ and $P^* < 3.0$) [42]*

$$^{10}\log\left(D^*\right) = 0.05 + 0.07P^* - \frac{1.04 + 0.1P^*}{T^*} \tag{10.40}$$

Try to confirm this equation with simulations.

10.8 Molecular Dynamics at Constant Temperature

Molecular Dynamics studies the natural time evolution of a classical system of N particles in volume V, while the total energy E is a constant of motion. Therefore, the time averages obtained in a conventional MD simulation are micro-canonical ensemble averages. However, it is often more convenient to perform simulations in other ensembles. There are basically two possible ways. One way is to combine MD simulations with Monte Carlo moves. The second approach is completely dynamical in origin and is based on reformulating the Lagrangian equations of motion (see for example Ref. [8]). Here, we focus on constant temperature simulations. Below we describe the simplest approach: The Andersen thermostat to simulate a constant temperature ensemble [43].

We first specify what we mean by constant temperature. From a statistical physics point of view, we can impose a temperature on a system by bringing it into thermal contact with a heat bath. Under these conditions, the probability of finding the system in a given energy state is given by the Boltzmann distribution and, for a classical system, the Maxwell-Boltzmann velocity distribution follows:

$$P(p) = \left(\frac{1}{2\pi m k_B T}\right)^{3/2} \exp[-\beta p^2/(2m)] \tag{10.41}$$

We then obtain a simple relation between the imposed temperature T and the kinetic energy per particle

$$k_B T = m\langle v_\alpha^2 \rangle \tag{10.42}$$

where v_α is the α-th component of the velocity. However, the condition of constant temperature is not equivalent to the condition that the kinetic energy per particle is constant. To show this, we can determine the relative variance of the kinetic energy per particle in a canonical ensemble. To this end we calculate the second and fourth moments of the Maxwell-Boltzmann distribution.

$$\begin{aligned} \langle p^2 \rangle &= \int d\mathbf{p} p^2 P(p) = 3mk_B T \\ \langle p^4 \rangle &= \int d\mathbf{p} p^4 P(p) = 15(mk_B T)^2 \end{aligned} \tag{10.43}$$

The relative variance of the kinetic energy of a single particle is

$$\frac{\langle p^4 \rangle - \langle p^2 \rangle^2}{\langle p^2 \rangle^2} = \frac{2}{3} \tag{10.44}$$

Thus, in a canonical ensemble, the instantaneous kinetic temperature fluctuates. If we keep the average kinetic energy per particle fixed, as in isokinetic MD simulations, then we do not simulate the true constant-temperature ensemble. In practice the differences between the isokinetic schemes and the canonical schemes are often negligible.

Question 85 (Temperature fluctuations)
Show that the relative variance of the temperature for a system of N *particles in the canonical ensemble equals*

$$\frac{\sigma_T^2}{\langle T^2 \rangle} = \frac{2}{3N} \tag{10.45}$$

What is the meaning of this result in the thermodynamic limit?

In the canonical MD scheme of Andersen the system is coupled to a heat bath that imposes the desired temperature. The coupling to a heat bath is represented by stochastic forces that act occasionally on randomly selected particles. These stochastic collisions with the heat bath can be considered as Monte Carlo moves that transport the system from one constant-energy shell to another. Between stochastic collisions, the system evolves at constant energy according to the normal Newton's equations of motion. The stochastic collisions ensure that all accessible constant-energy shells are visited according to their Boltzmann weight. A constant-temperature simulation using the Andersen thermostat consists of the following steps:

1. Start with an initial set of positions and momenta $\{\mathbf{r}^N(0), \mathbf{p}^N(0)\}$ and integrate the equations of motion for a time Δt.
2. A number of particles is selected to undergo a collision with the heat bath. The probability that a particle is selected in a time step of length Δt is $\nu \Delta t$, where ν is the frequency of stochastic collisions which determines the coupling strength to the heat bath.
3. If particle i has been selected to undergo a collision, its new velocity will be drawn from a Maxwell-Boltzmann distribution corresponding to the desired temperature T. All other particles are unaffected.

Question 86 (Andersen Thermostat)
In this question, we illustrate the strong and weak points of the Andersen thermostat. We first show that the thermostat produces good results for time-independent canonical ensemble averages. Use the given computer program and make sure that the errors of question 82 are corrected.

1. *Calculate the velocity distribution of a Lennard-Jones fluid from a Molecular Dynamics simulation using the Andersen thermostat for temperature* $T^\star = 2.0$, *density* $\rho^\star = 0.8442$ *and number of particles* $N = 256$. *Employ two different collision rates* $\nu^\star = 0.01$ *and* $\nu^\star = 0.001$. *Compare the distribution with the Maxwell-Boltzmann distribution (Eq. 10.41).*
2. *Determine the equation of state* $P(\rho)$ *(Eq. 6.39) and the radial distribution function* $g(r)$ *of the Lennard-Jones fluid for* $T^\star = 2.0$ *and* $N = 256$. *Compare the results with Monte Carlo simulations.*
3. *Above we have shown that the Andersen thermostat yield good results for time-independent properties. However, as the method is based on a stochastic scheme, one may explore whether it can also be used to determine dynamic properties, such as the mean-squared displacement. Determine the mean-squared displacement as a function of time for various values of the collision frequency* $\nu^\star$ *of the Lennard-Jones fluid at* $T^\star = 2.0$ *and* $N = 256$. *Does the mean-squared displacement depend on the value of the collision rate?*

```
program mdAndersen                       MD at constant temperature

call init(temp)                          initialization
call force(f,en)                         determine the forces
t=0
do while (t.lt.tmax)                     MD loop
   call integrate(1,f,en,temp)           first part of the equations of motion
   call force(f,en)
   call integrate(2,f,en,temp)           second part of the equations of motion
   t=t+dt
   call sample                           sample averages
enddo
end


subroutine integrate(switch,f,en,temp)   integrate equations of motion
if(switch.eq.1) then                     first step velocity Verlet
   do i=1,npart
      x(i)=x(i)+dt*v(i)+dt*dt*f(i)/2     update positions
      v(i)=v(i)+dt*f(i)/2                update velocity
   enddo
elseif (switch.eq.2) then                second step velocity Verlet
   tempa=0
   do i=1,npart
      v(i)=v(i)+dt*f(i)/2                second update velocity
      tempa=tempa+v(i)**2
   enddo
   tempa=tempa/(s*npart)                 instantaneous temperature
   sigma=sqrt(temp)                      Andersen heat bath
   do i=1,npart
      if(ranf().lt.nu*dt) then           test for collision with bath
          v(i)=gauss(sigma)              give particle Gaussian velocity
      endif
   enddo
endif
return
end
```

Table 10.5: Pseudo computer code for a Molecular Dynamics simulation using the velocity Verlet algorithm with the Andersen thermostat.

Part III

Appendix

Appendix A

Assignments

A.1 Capillary Condensation between Two Flat Walls

If we immerse a slit-like pore in a big reservoir, the liquid phase can be stable between the walls while the bulk reservoir is still in the vapor phase. This phenomenon is called capillary condensation. The vapor/liquid transition is shifted by the confinement in comparison with the bulk transition.

1. Modify the programs in `LJ-DifferentEnsembles` in such a way that it performs simulations between two planar walls in the xy direction. The walls are located at $z = 0$ and $z = H$. Hence, the separation between the walls equals H. Apply periodic boundary conditions in the x and y directions and employ the following interactions for the particles with the wall:
$$\phi(z) = \begin{cases} -\epsilon \left[\left(\frac{\sigma}{z}\right)^5 + \left(\frac{\sigma}{H-z}\right)^5 \right] & \sigma \leq z \leq H - \sigma \\ \infty & \text{otherwise} \end{cases} \tag{A.1}$$
in which σ and ϵ are the Lennard-Jones parameters for particle-particle interactions.

2. Perform a series of simulations at $H/\sigma = 2, 3, 5$ and $H/\sigma = 10$ in the grand-canonical ensemble at fixed temperature $T^\star = 0.5$ and varying chemical potentials. Plot the adsorption isotherms (average density $\langle\rho\rangle$ as a function of μ). Explain the trend of the adsorption isotherms. Does the vapor/liquid transition shift to lower or higher chemical potential upon decreasing the wall separation? Explain.

3. Perform Gibbs ensemble simulations for the bulk system and for a confined system with $H/\sigma = 2$ and 5 for different temperatures. Estimate the critical temperature using the scaling laws Eqs. 8.9 and 8.10. Does the critical temperature depend on the wall separation? Explain.

A.2 Adsorption Inside a Pore

The behavior of liquids inside confined geometries (i.e. small pores) is in principle different from the behavior of a bulk liquid. In this exercise, we will investigate the adsorption of Lennard-Jones particles inside a small cylindrical pore of radius L. Particles have the following interaction with the pore wall

$$\phi(r) = \begin{cases} \epsilon \left(\frac{\sigma}{L-r}\right)^{10} & r < L \\ \infty & r \geq L \end{cases} \tag{A.2}$$

in which ϵ and σ are the Lennard-Jones parameters for particle-particle interactions. The pore is centered at $r = 0$.

1. Modify the program `LJ-DifferentEnsembles` to simulate this system in the grand-canonical ensemble.
2. Modify the program in such a way that the radial density (e.g. the local density at distance r from the center of the pore) is calculated.
3. At a fixed pore radius L and fixed temperature $T^{\star} = 0.5$, perform series simulations at different chemical potentials, starting either from a low chemical potential or a high chemical potential. How can the hysteresis in the adsorption isotherm (average density $\langle \rho \rangle$ as a function of μ) be explained? Hint: perform the simulation also at $T^{\star} = 5$. What is the influence of the pore length on this transition?
4. Use the thermodynamic integration scheme of Ref. [44] to compute the coexistence densities between the low and high density phase. Investigate the effect of confinement (different L) on this transition as a function of $T^{\star}$. How does the critical temperature of this transition scale with the pore radius?
5. Construct a model to investigate the possible influence of corrugation of the pores wall on the phase coexistence.

A.3 Gibbs Ensemble Simulation of Methane and Ethane

In chapter 8 we have introduced the Gibbs ensemble method to locate vapor/liquid coexistence. In this exercise, the vapor/liquid phase diagram of the Lennard-Jones potential was computed. The purpose of this assignment is to calculate the vapor/liquid phase diagram of methane (CH_4) and ethane (CH_3-CH_3) and to compare the simulation results with available experimental data. A popular approach to simulate hydrocarbons is the so-called united atom model, in which a carbon atom together with its attached hydrogen atoms are considered as a *single* interaction site [45]. The united atom approach often works well to describe liquid alkanes, but it fails for solids. We assume that the interactions between these "united atoms" can be described by a Lennard-Jones potential. This means that the phase diagram of methane can be computed using the given Gibbs ensemble simulation code (`LJ-DifferentEnsembles`).

1. According to Ref. [46], the Lennard-Jones parameters of methane are $\epsilon/k_B = 158.8\text{K}$ and $\sigma = 3.72\text{Å}$ when the Lennard-Jones potential is truncated and shifted at $r_{\text{cut}} = 12\text{Å}$ (Eq. 6.4). What is the value of r_{cut} in reduced units? Modify the cut-off radius in the given simulation code and compute the vapor/liquid part of the phase diagram of methane. Compare the computed critical temperature, critical pressure, and coexistence densities with the available experimental data [47].
2. In the united atom model, ethane is described as a dumbbell in which the two CH_3 united atoms have a fixed bond length of 1.53 Å. The Lennard-Jones parameters of the CH_3 groups are $\epsilon/k_B = 108.0\text{K}$ and $\sigma = 3.76\text{Å}$ (again for $r_{\text{cut}} = 12\text{Å}$) [46]. Modify the given Gibbs ensemble simulation code to simulate ethane. As ethane is a rigid, linear molecule, it is necessary to include trial moves in which attempts are made to rotate an ethane molecule around its center of mass. In addition, when an ethane molecule is inserted in one of the boxes, not only the position should be chosen at random but also the orientation of the molecule.

3. Compute the vapor/liquid part of the phase diagram of ethane and compare your results with the available experimental data of Ref. [47].

4. Investigate how sensitive the computed phase diagrams for methane and ethane depend on the Lennard-Jones parameters, i.e. changing ϵ and σ by 10% while keeping $r_{\text{cut}} = 12\text{Å}$.

A.4 Free Energy Difference between *fcc* and *hcp*

The face-centered cubic (*fcc*) and the hexagonal-close-packed (*hcp*) phase are two different crystal structures. Both close-packed structures consist of hexagonal close-packed two- dimensional layers of particles that are stacked up in the vertical direction. We can now construct the crystal by stacking layers. For each new layer there are two distinct possibilities to stack it on the previous layer in such a way that all the particles fit in the triangular holes between the particles in the previous layer. We now denote the two positions of the new layer by B and C and the position of the previous layer by A. Using this notation, the layers in the *fcc* phase are stacked in a ABCABC sequence, while the *hcp* phase corresponds to an ABAB sequence. The free energy difference for *fcc* and *hcp* is known to be very small at the melting density (with packing fraction $\eta = \pi\sigma^3 N/6V = 0.545$) and at close packing $\eta = \pi\sqrt{2}/6$ for hard spheres with a diameter of σ. See also Ref. [48].

1. Show that the packing fraction η at close packing is $\pi\sqrt{2}/6$.

2. Modify the program in `EinsteinCrystal` such that the simulation can also be started with a *hcp* crystal.

3. Determine the free energy difference between *fcc* and *hcp* for Lennard-Jones particles at fixed temperature $T^\star = 0.5$ and $T^\star = 2$ for $\rho^\star = 1.2$.

To compute the free energy for hard spheres, we have to modify our integration path. The problem is that there is no linear coupling scheme that switches off the hard-core interactions and switches on the Einstein spring constants simultaneously. We now switch on the spring constants while leaving on the hard-core interactions:

$$E(\lambda) = E_{HS} + \lambda \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{r}_{i,0})^2 \tag{A.3}$$

where N is the number of particles and $\mathbf{r}_{i,0}$ are the ideal lattice positions. The free energy difference between the system with coupling parameter $\lambda_{\max}$ and the hard-sphere solid is given by (see also Eq. 9.16)

$$F_{HS} = F(\lambda_{\max}) - \int_0^{\lambda_{\max}} d\lambda \left\langle \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{r}_{i,0})^2 \right\rangle_\lambda \tag{A.4}$$

For sufficiently high $\lambda_{\max}$ the hard spheres do not "feel" each other and the free energy reduces to that of a non-interacting Einstein crystal.

4. The mean-squared displacement of a non-interacting Einstein crystal is given by

   $$\left\langle r^2 \right\rangle = \frac{1}{N} \frac{\partial F(\lambda)}{\partial \lambda} \tag{A.5}$$

   For an Einstein crystal at a fixed center of mass, this leads to

   $$\left\langle r^2 \right\rangle = \frac{3}{2\beta\lambda} \times \frac{N-1}{N} \tag{A.6}$$

Measure the mean-squared displacement as a function of λ in a simulation. For which λ does the mean-squared displacement correspond with that of a non-interacting Einstein crystal? Use this value of λ in the sequel.

5. Determine the free energy difference between the *fcc* and *hcp* crystal for hard spheres at the melting density. Estimate the error in the free energy difference using 5 different runs.

A.5 Grand-Canonical MC; Umbrella Sampling in N

Vapor-liquid phase coexistence is usually determined using the Gibbs ensemble method. Another method to determine phase coexistence is using grand-canonical ensemble simulations and by determining the probability distribution function for the density $p(\rho)$ (i.e., the probability to find a certain density ρ). The grand potential of the system $\Omega(\mu, V, T)$ is a function of this probability distribution function:

$$\Omega(\mu, V, T) = -k_B T \ln p(\rho) + \text{constant} \tag{A.7}$$

Below the critical point, $p(\rho)$ shows one peak at a density that corresponds to the gas phase at low fugacity, but the peak moves to higher density for higher fugacities.

1. Modify the program in `LJ-DifferentEnsembles` in order to sample the probability distribution function for the density. Run a simulation at $T^\star = 0.95$ at different values of the fugacities. Plot $p(\rho)$ for varying fugacities.

Close to the vapor/liquid transition $p(\rho)$ is double-peaked, and the two peaks correspond to the gas and liquid phase. Phase coexistence occurs when the area under the two peaks is equal [49]. In order to determine $p(\rho)$ sufficiently accurate, one has to employ umbrella sampling (section 9.5). The most convenient biasing function is

$$W(N) = \alpha(N - N_0)^2 \tag{A.8}$$

in which N is the number of particles in the system and α and N_0 are constants. Using this biasing function, we force our system to contain particle numbers in a window around N_0. The width of this window is determined by α.

2. Implement this biasing function in the program and calculate the unbiased distribution $p(\rho)$. Using different values for N_0, we are able to obtain the whole distribution $p(\rho)$ and hence $\Omega(\mu, V, T)$ up to a constant. The unknown constant can be obtained by shifting $-k_B T \ln p(\rho)$ for different N_0 such that they fall on top of each other. Use this method to determine the phase coexistence as a function of temperature.

A.6 Common Tangent Construction

In question 78 we used the functions $\mu(P)$ for the liquid- and solid phase to calculate the pressure and densities at equilibrium. Another way to locate phase coexistence is the so-called common tangent construction, for which we have to plot the free energy density $f = F/V$ as a function of the (particle number) density $\rho = N/V$.

1. Make such a plot for the system of question 78 and show that

$$\mu = \left(\frac{\partial f}{\partial \rho}\right)_{T,V} \tag{A.9}$$

and

$$P = -f + \rho \left(\frac{\partial f}{\partial \rho} \right)_{T,V} \tag{A.10}$$

2. Suppose that phase I and II are in equilibrium. Show that from $\Delta P = P_I - P_{II} = 0$, $\Delta\mu = \mu_I - \mu_{II} = 0$ and Eqs. A.9 and A.10 follows that

$$\mu = \frac{f_1 - f_2}{\rho_1 - \rho_2} \tag{A.11}$$

3. Prove that the common tangent construction (i.e. the coexistence densities) is not affected when the function $X(\rho) = a\rho + b$ (in which a and b are arbitrary constants) is subtracted from $f(\rho)$.

4. Perform the common tangent construction for the system of question 78 and compare the result with thermodynamic integration. Hint: first fit the function $X(\rho) = a\rho + b$ to $f(\rho)$ and substract this function from $f(\rho)$.

Appendix B

Essential Thermodynamics

B.1 Thermodynamic States

Thermodynamics gives a macroscopic description of systems. A system in equilibrium is said to be in a *thermodynamic state*, which is characterized by *state variables*, e.g. volume V, temperature T, pressure P and amount of material. Often the amount of material is expressed in terms of the number of moles n. Throughout this work we shall use the number of particles $N = N_{av}n$, in which N_{av} is Avogadro's number ($N_{av} = 6.02214 \times 10^{23}$ particles per mol). *Equations of state* are relations between state variables that express physical properties of the system. The ideal gas is an idealized dilute gas that satisfies the equation of state

$$PV = nRT = Nk_BT \tag{B.1}$$

where $R = 8.3145\,\mathrm{J mol^{-1} K^{-1}}$ is the gas constant and $k_B = R/N_{av} = 1.38066 \times 10^{-23}\,\mathrm{J/K}$ is Boltzmann's constant. For a full thermodynamic description of a system a second equation of state is necessary. Often an *energy equation* is chosen, which expresses the energy or a free energy in terms of the state variables. For an ideal gas of point particles the energy equation is

$$U(V, T) = U(T) = \frac{3}{2}Nk_BT \tag{B.2}$$

in which $U(V, T)$ is the energy of the system as a function volume and temperature. Note that the energy equation is not completely independent of the equation of state, e.g. using the general relations Eq. B.10 and Eq. B.39 it follows from Eq. B.1 that for an ideal gas $(\partial U/\partial V)_{T,N} = 0$, which is consistent with Eq. B.2. On the other hand, Eq. B.2 cannot be derived from Eq. B.1 alone. The interdependence arises because both equations can be derived from the dependence of the free energy F on N, V and T. Indeed, from Eq. B.16 we see that the pressure P for *any* system is given by $P = -(\partial F/\partial V)_{T,N}$. This is essentially the equation of state, resulting in Eq. B.1 for an ideal gas. The entropy in the form $S = -(\partial F/\partial T)_{V,N}$ can be used in Eq. B.15 to obtain the energy from $U = F + TS$.

State variables are called *extensive* if they are proportional to the extent of the system, i.e. if their values double when the volume, energy and number of particles are simultaneously doubled and *intensive* if they are not affected by such a doubling. The *molar* value of an extensive variable is an intensive variable obtained by dividing the extensive variable by N the number of mols in the system [*]. It is denoted by an overline. For example, the molar volume $\overline{V} \equiv V/N$. As the intensive properties of a one-component material do not change when particles are added

---

[*] In thermodynamics one often divides by $n = N/N_{av}$. This alternative definition of molar variables leads to values that are N_{av} times larger.

or removed in such a way that pressure and temperature remain constant, we may define molar quantities as partial derivatives as well, e.g. for the molar volume

$$\overline{V} = \frac{V}{N} = \left(\frac{\partial V}{\partial N}\right)_{P,T} \tag{B.3}$$

This definition is easily generalized to define *partial molar variables* in multi-component systems, e.g. the partial molar volume with respect to species i is defined as

$$\overline{V}_i = \left(\frac{\partial V}{\partial N_i}\right)_{P,T,N_{j \neq i}} \tag{B.4}$$

Here the notation indicates that for all components j the number of particles N_j should be kept constant, except for the component i with respect to which the partial molar volume is calculated.

B.2 Processes

The thermodynamic state of a system can change during processes. The process is described by *path variables*, e.g. q, the heat added or w, the work done on the system. Contrary to state variables, path variables are no system properties, they do not have a specific value for a system. The *the heat of a system* or *the work of a system* does not exist, not even if the system is in thermodynamical equilibrium. In thermodynamics one distinguishes two classes of processes: *reversible* and *irreversible* processes. During a reversible process the system is in (or infinitesimally close to) a thermodynamic state at all moments, implying that all thermodynamic state variables are well-defined throughout the course of the process. During irreversible processes a system may be far out of equilibrium and one or more state variables may be undefined (e.g. there may be pressure waves or temperature gradients present in the system and the concept of *the* pressure P or *the* temperature T of the system does not make sense). In practice, reversible processes are idealized versions of real processes that proceed very slowly, while real spontaneous processes are irreversible.

B.3 First Law of Thermodynamics

The internal energy U of a system is an extensive state function that can only change by heat q that is added to the system or work w that is done on the system:

$$\Delta U = q + w \tag{B.5}$$

Important forms of work are volume work (compression or expansion under external pressure P), where $dw = -PdV$ and addition or removal of particles from a reservoir with chemical potential μ, where $dw = \mu dN$.

B.4 Second Law of Thermodynamics

There exists an extensive state function S, called entropy. When heat is reversibly added to the system, the entropy changes according to:

$$dS = \frac{dq_{\text{rev}}}{T} \tag{B.6}$$

in which T is the absolute temperature (in Kelvin). Note that during the process the temperature T may change, but at any moment T is well-defined because the process is reversible. An isolated system has constant energy U, constant volume V and constant number of particles N. During irreversible processes in an isolated system the entropy of the system increases

$$(\Delta S)_{U,V,N,\mathrm{irr}} > 0 \tag{B.7}$$

Note that since this process is *irreversible* Eq. B.6 needs not to hold and we can *not* conclude that $q_{\mathrm{irr}} > 0$ from Eq. B.7. Using the entropy and the definition of heat capacity C_V at constant V or C_P at constant P we may write

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N} \tag{B.8}$$

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_{P,N} = T\left(\frac{\partial S}{\partial T}\right)_{P,N} \tag{B.9}$$

B.5 The Basic Machinery

The first and second law can be combined to give

$$dU = TdS - PdV + \mu dN \tag{B.10}$$

From this formula it is seen that U is the *characteristic state function* for systems in which S, V and N are constant or can be easily controlled. Irreversible processes at constant S, V and N lead to a decrease of internal energy

$$(\Delta U)_{S,V,N,\mathrm{irr}} < 0 \tag{B.11}$$

For systems with other control variables other characteristic state function are available.

- *Enthalpy* (H) for S, P and N

$$H = U + PV \tag{B.12}$$

$$dH = TdS + VdP + \mu dN \tag{B.13}$$

$$(\Delta H)_{S,P,N,\mathrm{irr}} < 0 \tag{B.14}$$

- *Free energy or Helmholtz free energy* (F or A) for N, V and T

$$F = U - TS \tag{B.15}$$

$$dF = -SdT - PdV + \mu dN \tag{B.16}$$

$$(\Delta F)_{N,V,T,\mathrm{irr}} < 0 \tag{B.17}$$

- *Gibbs free energy* (G) for N, P and T

$$G = U - TS + PV = F + PV = H - TS \tag{B.18}$$

$$dG = -SdT + VdP + \mu dN \tag{B.19}$$

$$(\Delta G)_{P,N,T,\mathrm{irr}} < 0 \tag{B.20}$$

From Eq. B.19 it follows that G increases proportional to N if the system is (mentally) built up by adding molecules, meanwhile adjusting the volume and adding heat in such a way that P and T remain constant. This proofs that $G = \mu N$ which expresses that the chemical potential is the molar Gibbs free energy $\mu = \overline{G}$. From $G = \mu N$ it follows directly that $dG = \mu dN + Nd\mu$. Upon combining with Eq. B.19 we find the *Gibbs-Duhem* relation

$$VdP - SdT - Nd\mu = 0 \tag{B.21}$$

This relation shows that the three intensive variables P, T and μ can not be varied independently.

B.6 Definitions and Relations

For any state function $f(x, y, z)$, we can write

$$df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz \tag{B.22}$$

Therefore, the first derivatives of characteristic functions can be used as *thermodynamic definition* for certain state variables, i.e. from

$$dF = -SdT - PdV + \mu dN \tag{B.23}$$

follows immediately that

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V,N} \tag{B.24}$$

$$-P = \left(\frac{\partial F}{\partial V}\right)_{T,N} \tag{B.25}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} \tag{B.26}$$

Differentiation of Eqs. B.10, B.13, B.16 and B.19 with respect to N leads to several equivalent definitions of chemical potential

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial H}{\partial N}\right)_{S,P} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{T,P} = \overline{G} \tag{B.27}$$

It depends on the control variables of the system which definition is preferred. These definitions should be used carefully. E.g. note that the molar free energy $\overline{F}$ is not equal to μ, even though the expressions look similar:

$$\overline{F} = \frac{F}{N} = \left(\frac{\partial F}{\partial N}\right)_{P,T} = \mu - P\left(\frac{\partial V}{\partial N}\right)_{P,T} \tag{B.28}$$

For an ideal gas, this reduces to $\overline{F}_{IG} = \mu - k_B T$. If temperature is a control variable, then one gets two definitions for the entropy:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \tag{B.29}$$

If entropy is a control variable, then one could define temperature by

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \left(\frac{\partial H}{\partial S}\right)_{P,N} \tag{B.30}$$

The thermodynamic definitions of pressure

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,V} = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \tag{B.31}$$

give experimental access to the volume dependence of U and F. Similarly, the thermodynamic definitions of volume

$$V = \left(\frac{\partial H}{\partial P}\right)_{S,N} = \left(\frac{\partial G}{\partial P}\right)_{T,N} \tag{B.32}$$

give the pressure dependence of H and G. The temperature dependence of U and H is found from heat capacity measurements as is seen in Eq. B.8 and Eq. B.9. The temperature dependence of F and G is found from *Gibbs-Helmholtz relations*, which are derived by combining Eq. B.15 with Eq. B.8, and Eq. B.18 with Eq. B.9 respectively:

$$\left(\frac{\partial F/T}{\partial T}\right)_{V,N} = -\frac{U}{T^2} \tag{B.33}$$

$$\left(\frac{\partial G/T}{\partial T}\right)_{P,N} = -\frac{H}{T^2} \tag{B.34}$$

Integrating experimental data properly thus forms the basis of tabulating the energy, enthalpy and the (Gibbs) free energy as a function of T and P.

B.7 Maxwell Relations

Maxwell relations are relations between derivatives of state variables. These derivatives are a twice differentiated state function. The relations are obtained by interchanging the order of differentiation. Take e.g. the Gibbs free energy. From Eq. B.19 it follows that

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \tag{B.35}$$

and

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N} \tag{B.36}$$

The identity

$$\left(\frac{\partial^2 G}{\partial P \partial T}\right)_N = \left(\frac{\partial^2 G}{\partial T \partial P}\right)_N \tag{B.37}$$

leads to

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N} \tag{B.38}$$

Similarly, using Eq. B.16 leads to

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N} \tag{B.39}$$

These relations could not easily be guessed from physical arguments alone. They show that, although S can not be measured experimentally, its derivatives with respect to P, V and T (see Eqs. B.8 and B.9) can be experimentally determined. Again, we find that integrating experimental data forms the basis of tabulation of entropy as a function of T and P.

B.8 Phase Equilibrium

If a system at given P, T and N contains two or more phases of the same type of particles, then the two phases will exchange volume, heat and particles until the minimum Gibbs free energy is reached. At the moment that equilibrium has been reached one of the two phases may have disappeared. If both phases are still present, then they are both at pressure P, temperature T and

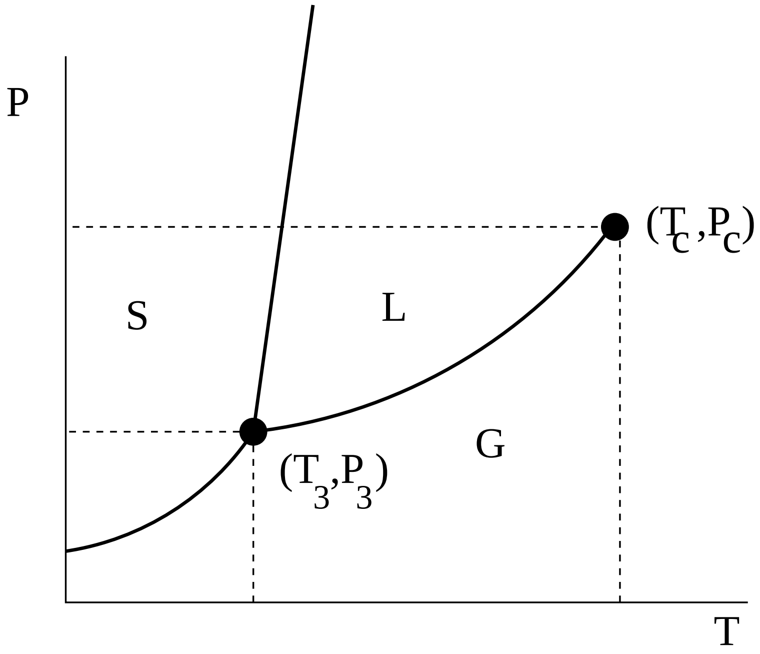


Figure B.1: Typical (T, P)-phase diagram indicating the regions where the solid (S), liquid (L) and gas (G) are stable. The bold lines indicate phase coexistence. The vapor-liquid coexistence ends at the critical point (T_c, P_c). At the triple point (T_3, P_3) there is a coexistence between three phases (gas, liquid and solid). The solid/liquid coexistence does not have a critical point. See also Fig. 6.6 for the corresponding (ρ, T)-diagram.

they have equal chemical potential μ. This follows directly from the Gibbs free energy which is at a minimum

$$dG = 0 = -SdT + VdP + \mu_I dn_I + \mu_{II} dn_{II} = \mu_I dn_I + \mu_{II} dn_{II} \tag{B.40}$$

in which μ_i is the chemical potential of phase i and dn_i is the change in molecules for phase i. As $dn_I = -dn_{II} \neq 0$ it follows directly that $\Delta\mu = \mu_I - \mu_{II} = 0$.

A (T, P)-phase diagram displays the phase transition lines and points, where two or more phases are in equilibrium with each other, i.e. where the chemical potential at the given P and T are the same for these phases (see Fig. B.1). The points with two phases in equilibrium are located on phase equilibrium lines, e.g. the melting and boiling lines. Where two of these lines intersect three phase equilibrium is possible, and such a point is called triple point. If a line ends in a point without intersection with other lines, this is called a critical point.

Along phase equilibrium lines in Fig. B.1 not only extensive variables, like S and V, are different for both phases, but also the molar value for all components j, like the molar entropy $\overline{S} = S/N$ and the molar volume $\overline{V} = V/N$. Approaching a critical point the differences of such molar quantities become smaller, at a critical point they become equal. Applying the Gibbs-Duhem relation to two phases in equilibrium, the slope of phase equilibrium lines in Fig. B.1 can be expressed in terms of the differences $\Delta\overline{S}$ and $\Delta\overline{V}$. Using the first law of thermodynamics, we can write the differential of G as Eq. B.19

$$dG = -SdT + VdP + \mu dN \tag{B.41}$$

On the other hand, the Gibbs free energy is an extensive quantity, and can hence be written as $G(N, P, T) = \mu N$ and we arrive at

$$dG = \mu dN + N d\mu \tag{B.42}$$

Subtracting the two equations for dG we find the Gibbs-Duhem equation

$$N d\mu = -S dT + V dP \tag{B.43}$$

If we now consider two phases, say phase I and phase II, in coexistence, we can write

$$\begin{aligned} N_I d\mu_I &= -S_I dT_I + V_I dP_I \\ N_{II} d\mu_{II} &= -S_{II} dT_{II} + V_{II} dP_{II} \end{aligned} \tag{B.44}$$

Using the conditions for phase equilibria: $\mu_I = \mu_{II} = \mu$, $T_I = T_{II} = T$, and $P_I = P_{II} = P$, we arrive at

$$0 = -(S_I - S_{II}) dT + (V_I - V_{II}) dP \tag{B.45}$$

and the slope of the coexistence curve at μ is predicted by

$$\left(\frac{dP}{dT}\right)_{\text{coex}} = \frac{\Delta S}{\Delta V} = \frac{\Delta \overline{S}}{\Delta \overline{V}} = \frac{\Delta \overline{H}}{T \Delta \overline{V}} = \frac{\Delta H}{T \Delta V} \tag{B.46}$$

where the enthalpy is defined as $H = U + PV$ (so $\Delta H = H_I - H_{II}$), while $\Delta G = G_I = G_{II} = \Delta U - T\Delta S + P\Delta V = 0$ at coexistence. For calculating the equilibrium vapor pressure of a solid or a liquid, it is often justified to assume that the vapor is an ideal gas, i.e. $\overline{V}_{\text{vap}} = k_B T/P$ and that the liquid molar volume is negligibly small, $\Delta \overline{V} \approx \overline{V}_{\text{vap}}$. Then

$$\left(\frac{d \ln P}{dT}\right)_{\text{coex}} \approx \frac{\Delta_{\text{vap}} \overline{H}}{k_B T^2} \tag{B.47}$$

which is known as the Clausius-Clapeyron equation.

Appendix C

Essential Mathematics

Elementary Statistical Thermodynamics does not make use of any sophisticated mathematics. Here we briefly review the mathematics that is most frequently used. Below, we give neither a proper derivation nor a proof of any of the results that we quote. However, in some cases we do provide a non-rigorous ”justification”. We assume that the reader is familiar with the most common functions and algebraic manipulations.

C.1 Properties of $\ln x$ and $\exp x$

The essential properties of logarithms and exponentials are - of course - well known $\cdots$ but still often forgotten. Often, we use $\exp(x)$ for e^x.

$$\begin{aligned}
\ln(a \times b) &= \ln a + \ln b && \text{(C.1)}\\
\ln(a/b) &= \ln a - \ln b && \text{(C.2)}\\
\ln(a^b) &= b \times \ln a && \text{(C.3)}\\
{}^g\log(a) &= \ln(a)/\ln(g) && \text{(C.4)}\\
\exp(a+b) &= (\exp a) \times (\exp b) && \text{(C.5)}\\
\exp(\ln(a)) &= a && \text{(C.6)}\\
(\exp(a))^x &= \exp(ax) && \text{(C.7)}
\end{aligned}$$

C.2 Chain Rule

When differentiating a function $F(u)$, where $u(x)$ is a function of the independent variable x, we can use the so-called chain rule

$$\frac{\partial F(u(x))}{\partial x} = \frac{\partial F(u)}{\partial u} \times \frac{\partial u(x)}{\partial x} \tag{C.8}$$

More generally, if $F(u)$ is a function of u and u is a function of $v \cdots$ and y is a function of z, then

$$\frac{\partial F}{\partial z} = \frac{\partial F(u)}{\partial u} \times \frac{\partial u(v)}{\partial v} \times \frac{\partial v(w)}{\partial w} \times \cdots \times \frac{\partial y(z)}{\partial z}$$

C.3 Derivative of $\exp(ax)$ and $\ln(x)$

The derivative of $\exp(ax)$:

$$\frac{\partial \exp(ax)}{\partial x} = a \exp(ax) \tag{C.9}$$

This result can easily be derived from the definition of $\exp(ax)$:

$$\exp(ax) = \sum_{n=0}^{\infty} \frac{(ax)^n}{n!} = \lim_{n\to\infty} (1 + \frac{ax}{n})^n \tag{C.10}$$

Conversely, the primitive function of $\exp(ax)$ is $a^{-1}\exp(ax)$. The derivative of $\ln x$ with respect to x is

$$\frac{\partial \ln x}{\partial x} = \frac{1}{x} \tag{C.11}$$

This is easily derived from Eq. C.9. If $y = \ln x$, then $x = \exp(y)$, hence

$$\frac{\partial \ln x}{\partial x} = \frac{\partial y}{\partial \exp y} = \frac{1}{\exp y} = \frac{1}{x} \tag{C.12}$$

Conversely, the primitive function of $1/x$ is $\ln x$.

C.4 Taylor Expansion

If $f(x)$ and all its derivatives are smooth functions of x, then we can write:

$$f(x+a) = f(x) + \left(\frac{\partial f}{\partial x}\right)_x a + \frac{1}{2!}\left(\frac{\partial^2 f}{\partial x^2}\right)_x a^2 + \cdots + \frac{1}{n!}\left(\frac{\partial^n f}{\partial x^n}\right)_x a^n + \cdots \tag{C.13}$$

The first two terms in the Taylor expansion are often used to approximate $f(x + a)$ if a is sufficiently small

$$f(x+a) \approx f(x) + \left(\frac{\partial f}{\partial x}\right)_x a$$

Specific examples are:

$$\begin{aligned} \exp(x) &\approx 1 + x \\ \ln(1+x) &\approx x \\ \sqrt{1+x} &\approx 1 + \frac{1}{2}x \\ (1+x)^n &\approx 1 + nx \\ \sin(x) &\approx x \end{aligned}$$

where, in all cases, it has been assumed that $|x| \ll 1$. For functions of more than one variable, this can be generalized to

$$f(x_1 + \Delta x_1, x_2 + \Delta x_2, \cdots, x_n + \Delta x_n) \approx f(x_1, x_2, \cdots, x_n) + \sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i}\right) \Delta x_i \tag{C.14}$$

C.5 Geometric Series

Consider the sum

$$S = \sum_{i=0}^{n} ax^i \tag{C.15}$$

Clearly,

$$xS = \sum_{i=0}^{n} ax^{i+1} = S - a + ax^{n+1} \tag{C.16}$$

Hence

$$S(1-x) = a(1-x^{n+1}) \tag{C.17}$$

or

$$S = \frac{a(1-x^{n+1})}{1-x} \tag{C.18}$$

If $|x| < 1$, we can take the limit $n \to \infty$

$$S_{n\to\infty} = \frac{a}{1-x} \tag{C.19}$$

so

$$\sum_{i=0}^{\infty} x^i = \frac{1}{1-x} \tag{C.20}$$

for $|x| < 1$. Differentiating both sides of Eq. C.20 with respect to x and multiplying with x we get another useful expression

$$\sum_{i=0}^{\infty} i \times x^i = \frac{x}{(1-x)^2} \tag{C.21}$$

for $|x| < 1$.

C.6 Factorials and Permutations

The symbol N! denotes the "factorial" of N. For positive, integer N, it is defined as

$$N! = N \times (N-1) \times (N-2) \times \cdots \times 2 \times 1 \tag{C.22}$$

In addition, $0! \equiv 1$. The number of permutations of a set of N labeled objects is equal to N! . This can be demonstrated by induction. The number of ways in which a single object can be ordered is clearly equal to 1, which is equal to 1!. Hence, the relation holds for $N = 1$. The next step is to show that if the relation holds for N objects, it also holds for $N + 1$ objects. This is easily demonstrated as follows. Assuming that there are N! permutations for N objects, then for every permutation there are $N+1$ positions in the sequence where we could insert object $N+1$. Hence the total number of permutations for $(N + 1)$ objects is $(N + 1) \times N! = (N + 1)!$. This completes the proof.

Now consider the following question: we have N labeled objects and we wish to count the number of distinct ways that these objects can be divided into two sets, such that one set contains M elements and the other $N - M$ elements. For instance, 3 objects can be distributed in 3 ways over a subset of size one and a subset of size 2:

$$(1, 2\ 3),\ (2, 3\ 1) \text{ and } (3, 1\ 2) \tag{C.23}$$

Note that we do not count different permutations within one subset as distinct. To compute this number in general, we consider all possible permutations of N objects. There are N! such permutations. For every permutation, we attribute the first M elements to one set, and the remaining $N-M$ elements to the other. In this way, we get that the total number of permutations with M elements in one set and $N - M$ in the other is equal to N!. However, in this counting procedure, we have considered different permutations of the objects in either set as distinct. To get the total number of ways to distribute N objects over the two subsets, we should divide by the number of permutations in the set of M objects and in the set of $N-M$ objects. The result is that the number of ways to divide N objects over two subsets of size M and $N-M$ respectively, is given by the so-called binomial coefficient

$$\binom{N}{M} \equiv \frac{N!}{M!(N-M)!} \tag{C.24}$$

The binomial summation formula is

$$\sum_{M=0}^{N} \binom{N}{M} p^M q^{N-M} = (p+q)^N \tag{C.25}$$

The related expression

$$\sum_{M=0}^{N} M \binom{N}{M} p^M q^{N-M} = Np(p+q)^{N-1} \tag{C.26}$$

is obtained by differentiating both sides of Eq. C.25 with respect to p and multiplying by p.

C.7 Binomial and Multinomial Distributions

As explained above, the number of ways to distribute N objects over two classes, in such a way that M objects end up in class I and $N-M$ objects in class II is given by

$$\frac{N!}{M!(N-M)!} \equiv \binom{N}{M} \tag{C.27}$$

For example: the number of ways to throw N coins, such that M are head and $N-M$ are tail, is $\binom{N}{M}$. If we assume that the probability of head and tail are both equal to $1/2$, then the probability that I throw M heads and $N-M$ tails is

$$P(M, N-M) = \binom{N}{M} \left(\frac{1}{2}\right)^N \tag{C.28}$$

In the more general case that the probabilities for the two events are not equal - say the probability to throw head is p, then the probability to throw head M times and tail $N-M$ times is

$$P(M, N-M) = \binom{N}{M} p^M (1-p)^{N-M} \tag{C.29}$$

Of course, the sum of the probabilities of all different outcomes should add up to one

$$\sum_{M=0}^{N} \binom{N}{M} p^M (1-p)^{N-M} = (p+(1-p))^N = (1)^N = 1 \tag{C.30}$$

To give a specific example, consider two containers, one with volume V_1 and the other with volume V_2. We assume that the probability that a molecule will be in volume 1 is equal to $V_1/(V_1+V_2)$. The probability to find a molecule in volume 2 is then $1 - V_1/(V_1+V_2) = V_2/(V_1+V_2)$. The probability to find M molecules in V_1 and $N-M$ molecules in V_2 is then

$$P(M, N-M) = \binom{N}{M} \frac{V_1^M V_2^{N-M}}{(V_1+V_2)^N} . \tag{C.31}$$

The probability to find *all* molecules in volume 1 is

$$P(N,0) = \frac{V_1^N}{(V_1+V_2)^N} \tag{C.32}$$

In case we distribute N objects over a larger number of classes - say m - the number of realizations is given by

$$\frac{N!}{\prod_{i=1}^{m} M_i!} \tag{C.33}$$

where M_i is the number of objects in class i and

$$\sum_{i=1}^{m} M_i = N \tag{C.34}$$

C.8 Some Integrals

Certain integrals occur time and again in statistical mechanics. First of all, there are the integrals of the type:

$$\int_0^\infty dx\, x^n \exp(-ax) \tag{C.35}$$

All these integrals can be derived through integration by parts from the integral

$$\int_0^\infty dx\ \exp(-ax) = 1/a \tag{C.36}$$

For instance

$$\begin{aligned}\int_0^\infty dx\, x \exp(-ax) &= \left[-\frac{x}{a}\exp(-ax)\right]_0^\infty + \int_0^\infty dx\ \frac{\exp(-ax)}{a} \\ &= \frac{1}{a^2}\end{aligned} \tag{C.37}$$

The general result is

$$\int_0^\infty dx\, x^n \exp(-ax) = \frac{n!}{a^{n+1}} \tag{C.38}$$

This result can also be obtained by noting that

$$x^n \exp(-ax) = (-1)^n \left(\frac{\partial^n \exp(-ax)}{\partial a^n}\right) \tag{C.39}$$

and that therefore

$$\int_0^\infty dx\, x^n \exp(-ax) = (-1)^n \left(\frac{\partial^n (1/a)}{\partial a^n}\right) = \frac{n!}{a^{n+1}} \tag{C.40}$$

A second type of integral of particular importance is the Gaussian integral

$$I = \int_{-\infty}^{\infty} dx\ \exp(-cx^2) \tag{C.41}$$

A trick to compute this integral, is to consider its square

$$I^2 = \left(\int_{-\infty}^{\infty} dx\ \exp(-cx^2)\right)^2 = \int_{-\infty}^{\infty} dx\ \exp(-cx^2) \int_{-\infty}^{\infty} dy\ \exp(-cy^2) \tag{C.42}$$

We can write the latter product of integrals as

$$\int_{-\infty}^{\infty} dx\ \exp(-cx^2) \int_{-\infty}^{\infty} dy\ \exp(-cy^2) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dy\ dx\ \exp(-cx^2)\exp(-cy^2) \tag{C.43}$$

The latter integral is a two-dimensional integral. It can be simplified by using the polar coordinates r and ϕ, such that $x = r\cos\phi$ and $y = r\sin\phi$. Clearly, $x^2 + y^2 = r^2$. The integration range for ϕ is $\{0, 2\pi\}$ and r ranges from 0 to ∞. Finally, we replace the area element $dx\ dy$ by $rd\phi\ dr$. We can then write

$$\begin{aligned} I^2 &= \int_0^{2\pi} d\phi \int_0^{\infty} dr\ r\exp(-cr^2) \\ &= 2\pi\int_0^{\infty} \frac{1}{2}dr^2\ \exp(-cr^2) \\ &= \pi\int_0^{\infty} dr^2\ \exp(-cr^2) \\ &= \frac{\pi}{c} \end{aligned} \tag{C.44}$$

where, in the third line, we have used $dr^2 = 2r\ dr$. To arrive at the last equality, we used Eq. C.36. Hence

$$\int_{-\infty}^{\infty} dx\ \exp(-cx^2) = \sqrt{\frac{\pi}{c}} \tag{C.45}$$

This means of course that

$$\int_0^{\infty} dx\ \exp(-cx^2) = \frac{1}{2}\sqrt{\frac{\pi}{c}} \tag{C.46}$$

Another useful expression is

$$\int_0^{\infty} dx\ x^{2n}\exp[-ax^2] = \frac{1\times 3\times 5\times\cdots(2n-1)}{a^n 2^{n+1}}\sqrt{\frac{\pi}{a}} \tag{C.47}$$

C.9 Stirling's Approximation

In statistical thermodynamics the factor $N!$ often appears for very large values of N. Then one can consider N as a continuous variable and $N!$ as a continuous function of N that can be differentiated with respect to N. Stirling's approximation for $\ln N!$ is very often used. In its simplest form it is obtained from

$$\ln N! = \sum_{k=1}^{N}\ln k \approx \int_1^N dx \ln x = [x\ln x - x]_1^N = N\ln N - N + 1 \approx N\ln N - N \tag{C.48}$$

which is equivalent to

$$N! = \left(\frac{N}{e}\right)^N \tag{C.49}$$

Note that differentiation of Eq. C.48 gives

$$\frac{d\ln N!}{dN} \approx \ln N = \ln N! - \ln(N-1)! \tag{C.50}$$

In some cases Eq. C.48 is not accurate enough. From Eqs. C.38 and C.45 above, we can derive a better approximation for $N!$.

$$N! = \int_0^\infty dx\, x^N \exp(-x) = \int_0^\infty dx\ \exp(-x + N \ln x) \tag{C.51}$$

where we have used Eq .C.38 with $a = 1$. The integrand is sharply peaked at $x = N$. The value of the exponent at $x = N$ is $-N + N \ln N$. The first derivative is zero (we are at a maximum). The second derivative is $-1/N$. Hence, we can approximate the integral by

$$\begin{aligned} N! &\approx \int_0^\infty dx\ \exp(-N + N \ln N - \frac{(x-N)^2}{2N}) \\ &= \int_{-N}^\infty du\ \exp(-N + N \ln N - \frac{u^2}{2N}) \end{aligned} \tag{C.52}$$

where we have defined $u \equiv x - N$. As the function is sharply peaked, we can replace the lower limit of the integration by $-\infty$. We then have

$$\begin{aligned} N! &\approx \exp(-N + N \ln N) \int_{-\infty}^\infty du\ \exp(-\frac{u^2}{2N}) \\ &= \exp(-N + N \ln N)\sqrt{2\pi N} \\ &= N^N \exp(-N)\sqrt{2\pi N} \end{aligned} \tag{C.53}$$

where we have used Eq. C.45. This is Stirling's approximation for $N!$. In fact, Stirling's approximation is the first term of a series

$$N! = N^N \exp(-N)\sqrt{2\pi N} \left(1 + \frac{1}{12N} + \frac{1}{288N^2} - \frac{139}{51840N^3} + \cdots\right) \tag{C.54}$$

C.10 Lagrange Multipliers

Lagrange Multipliers can be used to find the minimum or maximum of a function $f(x_1, x_2, \cdots x_n)$ subject to the constraint $g(x_1, x_2, \cdots x_n) = 0$. Changes in f can be written as

$$df = \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2 + \cdots + \frac{\partial f}{\partial x_n} dx_n \tag{C.55}$$

If all x_i would be independent, then all dx_i would be independent too and therefore this equation could be solved by setting each partial derivative

$$\frac{\partial f}{\partial x_i} \tag{C.56}$$

to zero. However, as $g(x_1, x_2, \cdots x_n)$ is kept constant, the x_i are no longer independent and the simple solution (all $\partial f/\partial x_i = 0$) is no longer valid. As $g(x_1, x_2, \cdots x_n)$ is kept constant, also

$$0 = dg = \frac{\partial g}{\partial x_1} dx_1 + \frac{\partial g}{\partial x_2} dx_2 + \cdots + \frac{\partial g}{\partial x_n} dx_n \tag{C.57}$$

Multiplying this equation by an unknown parameter λ and adding the two equations leads to

$$\left(\frac{\partial f}{\partial x_1} + \lambda \frac{\partial g}{\partial x_1}\right) dx_1 + \left(\frac{\partial f}{\partial x_2} + \lambda \frac{\partial g}{\partial x_2}\right) dx_2 + \cdots + \left(\frac{\partial f}{\partial x_n} + \lambda \frac{\partial g}{\partial x_n}\right) dx_n = 0 \tag{C.58}$$

The value of λ is chosen in such a way that

$$\frac{\partial f}{\partial x_n} + \lambda \frac{\partial g}{\partial x_n} = 0 \tag{C.59}$$

which means that

$$\left(\frac{\partial f}{\partial x_1} + \lambda \frac{\partial g}{\partial x_1} \right) dx_1 + \left(\frac{\partial f}{\partial x_2} + \lambda \frac{\partial g}{\partial x_2} \right) dx_2 + \cdots + \left(\frac{\partial f}{\partial x_{n-1}} + \lambda \frac{\partial g}{\partial x_{n-1}} \right) dx_{n-1} = 0 \tag{C.60}$$

Now the $n-1$ variables dx_i are independent, which implies that

$$\frac{\partial f}{\partial x_k} + \lambda \frac{\partial g}{\partial x_k} = 0 \tag{C.61}$$

for any $k = 1, 2, \cdots n$. The parameter λ is called the Lagrange multiplier. In practice one often first solves Eq. C.61 first for all k, while treating λ as an unknown parameter, and then determines the value of λ such that the constraint $g(x_1, x_2, \cdots x_n) = 0$ holds for the solution that was found in that first step.

C.11 Dirac's delta function

Dirac's delta function $\delta(x)$ has the property

$$\int_{-\infty}^{\infty} dx f(x) \delta(x-a) = f(a) \tag{C.62}$$

and

$$\delta(x-a) = 0 \tag{C.63}$$

for $x \neq a$. The delta function of another function $g(x)$ is given by

$$\delta(g(x)) = \sum_i \frac{\delta(x-x_i)}{|g'(x_i)|} \tag{C.64}$$

in which the x_i are the solutions of $g(x_i) = 0$.

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