

Chapter 8

Interacting systems

In chapter 6 we have concentrated on systems containing independent particles. We would now like to focus on systems containing interacting particles. The most accurate description is quantum mechanical, but in practice this is often found to be too difficult. Fortunately, a semi-classical treatment turns out to be sufficiently accurate at all temperatures except the lowest. Semi-classical means that we describe the internal states of the atoms or molecules quantum mechanically, but the translations, rotations, and vibrations of the particles (effectively the nuclei) classically.

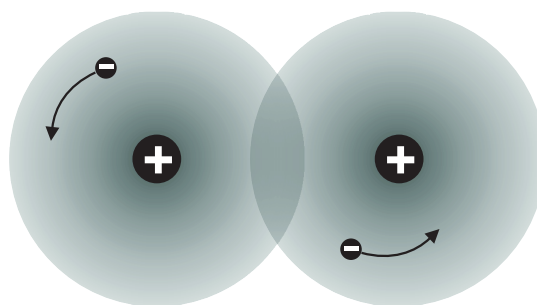
8.1 Intermolecular interactions

To focus on the essentials we will treat the simplest case, namely that of neutral spherical atoms.¹ Suppose we have two atoms, fixed at positions \mathbf{r}_1 and \mathbf{r}_2 , as in Fig. 8.1. We can write the total ground state energy of the two atoms as

$$\epsilon_0(\mathbf{r}_1, \mathbf{r}_2) = \epsilon_0(\mathbf{r}_1) + \epsilon_0(\mathbf{r}_2) + \varphi(\mathbf{r}_1, \mathbf{r}_2). \quad (8.1)$$

¹Noble gases such as argon and krypton are excellent examples of neutral spherical atoms. Additionally, we may treat nearly spherical *molecules*, such as methane, in a similar way. For “atom” one should then read “spherical molecule”.

Figure 8.1: Pictorial representation of the interaction between two (spherical) molecules. The nuclei (+) are much heavier than the electrons (-). In the Born-Oppenheimer approximation, the nuclei move in effective (electronically averaged) potentials. Nuclear translation, rotations, and vibrations can therefore be treated by using classical mechanics.



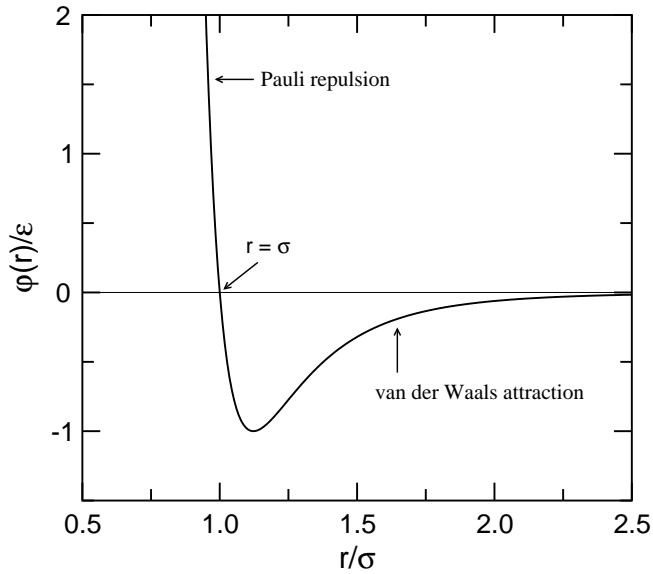


Figure 8.2: The total interatomic interaction between two neutral spherical atoms is well described by the Lennard-Jones formula, Eq. (8.3). At large distances the van der Waals attraction is dominant. At short distances the atoms repel each other because of the Pauli exclusion principle. The diameter of the atom may be defined as the distance σ where these two forces exactly cancel out.

Here $\epsilon_0(\mathbf{r}_1)$ is the ground state energy of atom 1 in the absence of atom 2, and similarly for $\epsilon_0(\mathbf{r}_2)$. So the term $\varphi(\mathbf{r}_1, \mathbf{r}_2)$ is the correction to the sum of two unperturbed ground state energies of the atoms. This term is also called the interatomic interaction or interatomic potential. Because of the rotational symmetry of the atoms, the interatomic potential only depends on the distance $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ between the two atoms, i.e.

$$\varphi(\mathbf{r}_1, \mathbf{r}_2) = \varphi(r_{12}). \quad (8.2)$$

It is also clear that because of its definition $\varphi(\infty) = 0$. At finite distances, the electrons in one atom will feel the electrons in the other atom. A classical picture would be the following: the charge distribution in an atom is not constant, but fluctuates in time around its average. Consequently, the atom has a fluctuating dipole moment which is zero on average. The instantaneous dipoles in the atoms, however, influence each other in a way which makes each dipole orient a little in the field of the other. This leads to the so-called van der Waals attraction between two neutral atoms. The van der Waals attraction becomes stronger as the atoms get closer to one another. At a certain point, however, the atoms will repel each other because of the Pauli exclusion principle. The total interatomic interaction as a function of distance is very well described by the Lennard-Jones formula (see Fig. 8.2)

$$\varphi(r) = 4\epsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\}. \quad (8.3)$$

The parameter ϵ is the depth of the interaction well, and σ is the diameter of the atom. The values of ϵ and σ are characteristic for each atomic species. For example

for argon $\epsilon/k_B = 117.7$ K and $\sigma = 0.3504$ nm, for krypton $\epsilon/k_B = 164.0$ K and $\sigma = 0.3827$ nm, and for methane $\epsilon/k_B = 148.9$ K and $\sigma = 0.3783$ nm. We note that the magnitudes of ϵ are much lower than the magnitude of the ground state energy ϵ_0^e of the electronically averaged potential between two covalently bound atoms in a two-atomic molecule, as in section 6.3 and Fig. 6.1. Of course, in the case of two-atomic molecules there are also van der Waals attractions between the (non-bonded) atoms on different molecules. These interactions have been ignored in chapter 6, but may be included in a way similar to the following treatment.

We are now going to calculate the total energy of a system of N particles (atoms or molecules) in the semi-classical approximation. This means that we need to add terms representing the kinetic energy explicitly. Regarding the potential energy, for simplicity we are going to assume that it may be approximated as a sum of pair interactions (in practice this is often a reasonable assumption):

$$\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \varphi(r_{ij}). \quad (8.4)$$

The double sum is constructed such that each pair interaction is counted only once. The total energy can then be expressed as

$$E = \sum_{i=1}^N \frac{1}{2m} (p_{xi}^2 + p_{yi}^2 + p_{zi}^2) + N\epsilon_0 + \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N). \quad (8.5)$$

Here $p_{xi} = mv_{xi}$ is the x -component of the momentum of particle i .

8.2 The semi-classical partition function

To make use of the statistical mechanical machinery developed in the previous chapters, we need to be able to specify the state of the system in a countable number of ways. The state may be specified by providing N numbers n_{xi} , N numbers n_{yi} , N numbers n_{zi} , and similarly for m_{xi} to m_{zi} , such that the positions and momenta of the particles are given by

$$\begin{aligned} n_{xi}\Delta x < r_{xi} &\leq (n_{xi} + 1)\Delta x \\ n_{yi}\Delta x < r_{yi} &\leq (n_{yi} + 1)\Delta x \\ n_{zi}\Delta x < r_{zi} &\leq (n_{zi} + 1)\Delta x \\ m_{xi}\Delta p < p_{xi} &\leq (m_{xi} + 1)\Delta p \\ m_{yi}\Delta p < p_{yi} &\leq (m_{yi} + 1)\Delta p \\ m_{zi}\Delta p < p_{zi} &\leq (m_{zi} + 1)\Delta p \end{aligned}$$

Δx and Δp may be interpreted as the precision with which we are able to specify the position and momentum of a particle. If we combine all these integer numbers into one index n , we can calculate the probability to encounter the system in state n , analogous to our treatment chapter 7. In the canonical ensemble we have

$$P_n = \frac{1}{Q'} \exp \{-\beta E_n\} \quad (8.6)$$

$$Q' = \sum_n \exp \{-\beta E_n\}, \quad (8.7)$$

where we have labeled the partition function as Q' , to distinguish it from the quantum mechanical partition function Q . If we now further write out Q' , ignoring the constant internal energy $N\epsilon_0$, we find

$$\begin{aligned} Q' &= \sum_{n_{x1}} \dots \sum_{n_{zN}} \sum_{m_{x1}} \dots \sum_{m_{zN}} \exp \left\{ -\beta \sum_i \frac{1}{2m} (p_{xi}^2 + p_{yi}^2 + p_{zi}^2) - \beta \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) \right\} \\ &= \frac{1}{(\Delta x \Delta p)^{3N}} \int dp_{x1} \dots \int dp_{zN} \int dr_{x1} \dots \int dr_{zN} \\ &\quad \times \exp \left\{ -\beta \sum_i \frac{1}{2m} (p_{xi}^2 + p_{yi}^2 + p_{zi}^2) - \beta \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) \right\} \\ &= \frac{(2\pi m k_B T)^{3N/2}}{(\Delta x \Delta p)^{3N}} \int dr_{x1} \dots \int dr_{zN} \exp \{-\beta \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N)\} \\ &= \frac{(2\pi m k_B T)^{3N/2}}{(\Delta x \Delta p)^{3N}} Z, \end{aligned} \quad (8.8)$$

where

$$\boxed{Z \equiv \int dr_{x1} \dots \int dr_{zN} \exp \{-\beta \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N)\}.} \quad (8.9)$$

The integrals in Z must be taken over the entire system's volume. Z is called the configuration integral or configuration sum-of-states.

We continue reasoning as in section 7.1.2. The average energy $\langle E \rangle$ must be equal to the thermodynamic energy U , therefore

$$\left(\frac{\partial A/T}{\partial 1/T} \right)_{N,V} = U = \langle E \rangle = -k_B \left(\frac{\partial \ln Q'}{\partial 1/T} \right)_{N,V}. \quad (8.10)$$

Integrating we find

$$\frac{A}{T} = -k_B \ln Q' - S_0 \quad (8.11)$$

$$A = -k_B T \ln (e^{S_0/k_B} Q'). \quad (8.12)$$

S_0 is nothing but an integration constant fixing the zero point of entropy. Let us now try to find an S_0 such that

$$Q^{\text{clas}} = e^{S_0/k_B} Q' = Q^{\text{quant}}, \quad (8.13)$$

i.e. such that the semi-classical partition function agrees with the quantum mechanical result. We can easily do this for the case of an ideal gas. The quantum mechanical partition function of an ideal gas is given by Eqs. (5.30) and (5.31):

$$Q^{\text{quant}} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} \frac{1}{N!} V^N. \quad (8.14)$$

Semi-classically, because $\Phi = 0$ for an ideal gas, we have for the configuration integral

$$Z = \int dr_{x1} \dots \int dr_{zN} 1 = V^N, \quad (8.15)$$

and therefore

$$Q^{\text{clas}} = e^{S_0/k_B} \frac{(2\pi m k_B T)^{3N/2}}{(\Delta x \Delta p)^{3N}} V^N. \quad (8.16)$$

Equating we find

$$e^{S_0/k_B} = \left(\frac{\Delta x \Delta p}{h} \right)^{3N} \frac{1}{N!}. \quad (8.17)$$

In summary, the (semi-)classical statistical physics of a system in the canonical ensemble may be described by the following three equations:

$$A = -k_B T \ln Q \quad (8.18)$$

$$Q = e^{S_0/k_B} Q' = \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} \frac{1}{N!} Z \quad (8.19)$$

$$Z = \int d^{3N} r e^{-\beta \Phi(r^{3N})}, \quad (8.20)$$

where we have used the abbreviated form $d^{3N} r = dr_{x1} \dots dr_{zN}$.

An alternative derivation for the appearance of the factor $1/h^{3N}$ is given in the Appendix of this chapter.

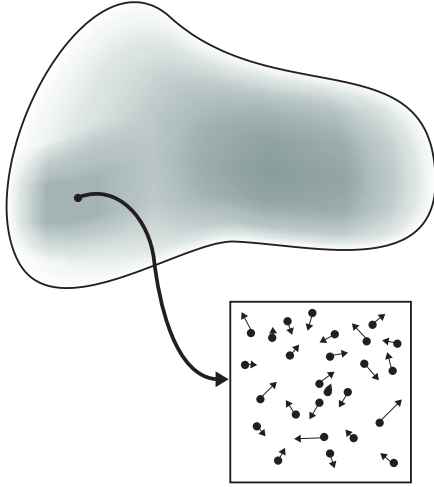


Figure 8.3: Schematic representation of phase space. A point in phase space corresponds to a certain set of coordinates and momenta of all particles in the system. The phase space distribution function F gives the probability of encountering the system in (near) this state. F is represented in this picture by shades of gray.

8.3 The classical phase space distribution function

In the previous section we have divided up phase space in little “cubes” of size $(\Delta x \Delta p)^{3N}$ in order to have a numerable number of states. In classical dynamics we usually characterise the state of a system by a point in phase space. That is, a state is specified by giving the coordinates and momenta of all the particles:

$$(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N) = (r^{3N}, p^{3N}).$$

The probability to encounter the system in a neighbourhood of size $(d^{3N}r, d^{3N}p)$ near this point is $F(r^{3N}, p^{3N})d^{3N}r d^{3N}p$, where $F(r^{3N}, p^{3N})$ is the *phase space distribution function*, see Fig. 8.3. We can find an expression for the phase space distribution function by rewriting Eq. (8.6) as follows:

$$P_n = \left(\frac{\exp\{-\beta E_n\}}{Q' \Delta x^{3N} \Delta p^{3N}} \right) \Delta x^{3N} \Delta p^{3N}. \quad (8.21)$$

We can imagine making the cubes smaller and smaller. In the limit $\Delta x \rightarrow 0$ and $\Delta p \rightarrow 0$ we are allowed to make the replacement $\Delta x^{3N} \mapsto d^{3N}r$ and $\Delta p^{3N} \mapsto d^{3N}p$ and use *continuous* values for the coordinates and momenta. The term between brackets in Eq. (8.21) then becomes the phase space distribution function, where the energy E_n must be replaced by the energy (or Hamiltonian) \mathcal{H} at the phase point (r^{3N}, p^{3N}) :

$$F(r^{3N}, p^{3N}) = \frac{\exp\{-\beta \mathcal{H}(r^{3N}, p^{3N})\}}{\int d^{3N}r \int d^{3N}p \exp\{-\beta \mathcal{H}(r^{3N}, p^{3N})\}}. \quad (8.22)$$

Note that F is properly normalised, i.e.

$$\int d^{3N}r \int d^{3N}p F(r^{3N}, p^{3N}) = 1, \quad (8.23)$$

as is required for a probability distribution function.

From Eq. (8.5) we observe that the (semi-)classical Hamiltonian consists of two parts, a kinetic part $K(p^{3N})$ which only depends on the momenta and a potential part $\Phi(r^{3N})$ which only depends on the coordinates. Therefore the phase space distribution function factors as (prove this!)

$$F(r^{3N}, p^{3N}) = F^r(r^{3N})F^p(p^{3N}), \quad (8.24)$$

where

$$F^r(r^{3N}) = \frac{\exp\{-\beta\Phi(r^{3N})\}}{\int d^{3N}r \exp\{-\beta\Phi(r^{3N})\}} = \frac{1}{Z} \exp\{-\beta\Phi(r^{3N})\} \quad (8.25)$$

is the probability distribution for observing the system at configuration space point r^{3N} , and

$$F^p(p^{3N}) = \frac{\exp\{-\beta K(p^{3N})\}}{\int d^{3N}p \exp\{-\beta K(p^{3N})\}} \quad (8.26)$$

is the probability distribution for observing the system at momentum space point p^{3N} .

We can factor the momentum distribution some more, since the kinetic energy is a sum of N single particle energies $\sum_i p_i^2/2m$:

$$F^p(p^{3N}) = \prod_{i=1}^N f^p(\mathbf{p}_i), \quad (8.27)$$

where

$$f^p(\mathbf{p}_i) = \frac{\exp\{-\beta p_i^2/2m\}}{\int d^3p \exp\{-\beta p^2/2m\}}. \quad (8.28)$$

More explicitly, performing the integral, we find the single particle momentum distribution

$$f^p(p_x, p_y, p_z) = \left(\frac{1}{2\pi mk_B T}\right)^{3/2} \exp\left\{-\frac{1}{2mk_B T} (p_x^2 + p_y^2 + p_z^2)\right\}. \quad (8.29)$$

This is called the Maxwell-Boltzmann momentum distribution. It applies to all semi-classical systems at temperature T , i.e. not only to ideal gases, but also to

non-ideal gases, liquids, and solids. As a consequence the average absolute velocity of a particle is the same in a liquid and a gas, provided the temperature is the same. Of course, the frequency of collisions in a liquid is much higher than that in a gas. That is why a molecule will travel much further per second in a gas than in a condensed phase even though the single molecule velocity distributions are identical in the two phases.

Note that the average momentum $\langle p_x \rangle$ predicted by Eq. (8.29) is zero. Its second moment $\langle p_x^2 \rangle$, however, is not zero. In fact, it is easy to show that the average kinetic energy per particle (in three dimensional space) is given by (Problem 8-1)

$$\langle K \rangle / N = \frac{1}{2m} \langle p_x^2 + p_y^2 + p_z^2 \rangle = \frac{3}{2} k_B T. \quad (8.30)$$

We will use this in section 8.4 to measure the temperature in a molecular dynamics simulation. Note that for an ideal gas the kinetic energy is the only energy term present (because $\Phi = 0$). Thus we confirm the result $U = \langle K \rangle = \frac{3}{2} N k_B T$ for an ideal gas.

Eq. (8.30) is an example of the more general *equipartition theorem*, which states that for a classical system each quadratic term in the Hamiltonian will, on average, “receive” an energy of $\frac{1}{2} k_B T$. So besides terms such as $p_{xi}^2/2m$, also terms such as $m\omega^2 x^2/2$ will have an average energy of $\frac{1}{2} k_B T$.

8.4 Molecular dynamics simulations

8.4.1 “Experimental” statistical physics

Numerical simulations are the “experimental” tool of statistical physicists. Such a tool is absolutely necessary because the interactions between particles are usually too complex to allow a theoretical analysis of the macroscopic system properties. The analytically solvable models we have encountered up to now, such as the ideal gas and the harmonic crystal, are rare exceptions.

In this chapter we will introduce the molecular dynamics (MD) simulation technique. MD enables us to calculate structural and thermodynamic properties, as well as dynamical properties, of realistic molecular systems, provided they exclude chemical reactions and other phenomena of a quantum mechanical nature. There is another important technique, called Monte Carlo (MC) simulation, which enables us to efficiently sample the phase space in a specified ensemble. This also yields structural and thermodynamic properties, but no dynamical properties. We will not treat the Monte Carlo technique here.

8.4.2 Force fields

Usually one simulates a box containing a number of N particles (atoms). The total potential energy Φ is usually divided up into terms depending on the coordinates of individual particles, pair, triplets, etc.

$$\Phi = \sum_i \varphi_1(\mathbf{r}_i) + \sum_i \sum_{j>i} \varphi_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_i \sum_{j>i} \sum_{k>j} \varphi_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots \quad (8.31)$$

The first term in Eq. (8.31) represents the effect of an external field on the system. The remaining terms represent particle interactions. Non-bonded interactions between atoms are usually described by a Lennard-Jones potential, as we encountered in section 8.1, supplemented with Coulombic terms if the atoms are charged. Bonded interactions within molecules typically consist of a harmonic potential between two bonded atoms, a bending potential for three consecutively bonded atoms, and a dihedral potential for four consecutively bonded atoms.

In its simplest implementation, the molecular dynamics method generates a path on a constant energy surface in phase space, $\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = U$, by solving Newton's equations of motion for all the particles. According to Newton, the force on each particle leads to an acceleration given by

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla_i \Phi(\mathbf{r}^N). \quad (8.32)$$

Since Newton's equations are second order equations, the paths of all particles are completely determined once the initial positions and initial velocities are given.

8.4.3 Numerical integration

How should we solve Eq. (8.32) on a computer? In order to concentrate on essential points, we simplify our notation for the time being and restrict ourselves to just one degree of freedom. Then we may write

$$\frac{dx}{dt} = v, \quad (8.33)$$

$$\frac{dv}{dt} = \frac{F}{m}, \quad (8.34)$$

where $F = -d\Phi/dx$ is the force acting on this particular coordinate. The simplest solution to this problem is

$$x(t + \Delta t) = x(t) + v(t) \Delta t, \quad (8.35)$$

$$v(t + \Delta t) = v(t) + \frac{F(t)}{m} \Delta t, \quad (8.36)$$

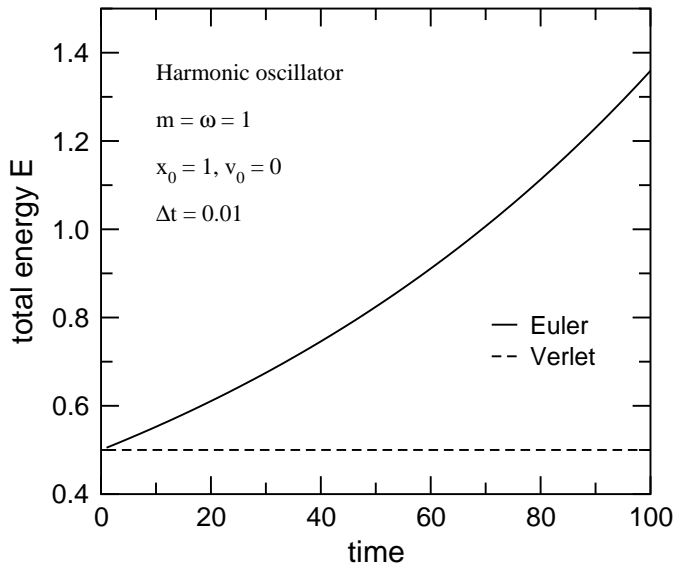


Figure 8.4: Total energy of a harmonic oscillator $E = \Phi + K$ with $K = \frac{1}{2}mv^2$ and $\Phi = \frac{1}{2}m\omega^2x^2$. In this example we have chosen $m = 1$ and $\omega = 1$. Results are given for integration with the Euler algorithm (solid line) and Verlet leap-frog algorithm (dashed line), both with a time step of $\Delta t = 0.01$. Note that the period (time for one oscillation) is 2π .

which must be repeated as often as needed to reach the time of interest. This algorithm is called the first order Euler algorithm. Applying it to the simple case of a harmonic oscillator reveals that this algorithm does not conserve energy; actually the error of the energy grows exponentially with time, see Fig. 8.4.

An astonishingly simple solution to the above problem is to write:

$$x(t + \Delta t) = x(t) + \dot{x}(t) \Delta t + \frac{1}{2} \ddot{x}(t) (\Delta t)^2 + \frac{1}{6} \dddot{x}(t) (\Delta t)^3 + \dots, \quad (8.37)$$

$$x(t - \Delta t) = x(t) - \dot{x}(t) \Delta t + \frac{1}{2} \ddot{x}(t) (\Delta t)^2 - \frac{1}{6} \dddot{x}(t) (\Delta t)^3 + \dots \quad (8.38)$$

After adding these two equations we obtain

$$x(t + \Delta t) = 2x(t) - x(t - \Delta t) + \ddot{x}(t) (\Delta t)^2 + \mathcal{O}(\Delta t^4). \quad (8.39)$$

This propagator is correct to order $(\Delta t)^4$. Instead of the position and velocity both at time t , we need the positions at time t and at time $t - \Delta t$ in order to advance the system by Δt . The price we pay for the better algorithm is that it doesn't look very nice, so let's make it look nicer. To this end we introduce new names

$$x(t) - x(t - \Delta t) = v\left(t - \frac{1}{2}\Delta t\right) \Delta t, \quad (8.40)$$

$$x(t + \Delta t) - x(t) = v\left(t + \frac{1}{2}\Delta t\right) \Delta t. \quad (8.41)$$

For the time being these equations only serve to define the new symbols $v\left(t - \frac{1}{2}\Delta t\right)$

and $v\left(t + \frac{1}{2}\Delta t\right)$. The propagator now reads

$$v\left(t + \frac{1}{2}\Delta t\right) = v\left(t - \frac{1}{2}\Delta t\right) + \frac{F(t)}{m}\Delta t. \quad (8.42)$$

$$x(t + \Delta t) = x(t) + v\left(t + \frac{1}{2}\Delta t\right)\Delta t, \quad (8.43)$$

The second line is nothing but repeating Eq. (8.41), while the first line is Eq. (8.39) rewritten in our new notation. Consequently the algorithm still is correct up to fourth order in Δt . It is called the Verlet leap-frog algorithm.

Obviously we now would like to know about velocities. From an analysis similar to the one just given we deduce that the velocity $\dot{x}(t)$ at time t is given by the obvious equation

$$\dot{x}(t) = \frac{1}{2} \left\{ v\left(t + \frac{1}{2}\Delta t\right) + v\left(t - \frac{1}{2}\Delta t\right) \right\}, \quad (8.44)$$

correct to second order in Δt . It is important to stress again that this does not influence the propagator, which is correct to fourth order. For small enough time-steps Δt , the Verlet algorithm performs an excellent job at conserving total energy, see Fig. 8.4.

Extension of this method to a system with $3N$ Cartesian coordinates is trivial.

8.4.4 Bulk systems and periodic boundary conditions

Often we are interested in the bulk properties of a certain material. Bulk systems are macroscopically large and consist of 10^{20} particles or more, while simulation boxes are limited to about 10^6 particles, but usually consist of 100 000 or less particles. In such small boxes most particles will be close to the system boundary and therefore not behave as a bulk particle at all. This problem is alleviated by the use of periodic boundary conditions, see Fig. 8.5.

First the simulation box is surrounded in all directions by copies of itself. Notice that we only have to keep track of the positions of the particles in the central box and that we then automatically know the positions of the particles in the other boxes. Next we do two things. (1) We remove the confining boundaries. Thus, each particle which leaves the central box automatically enters this box through the wall opposite the one through which it left the box. (2) We let each particle interact with all other particles within a certain cut-off radius, possibly including particles in one of the surrounding boxes. The cut-off radius is limited by the fact that we do not want a particle to interact with one of its own images. An even stronger restriction is that we do not want a particle to interact with a second particle and at the same time with some copy of this second particle. In this case the cut-off radius is at most $L/2$ with L the length of an edge of a cubic box.

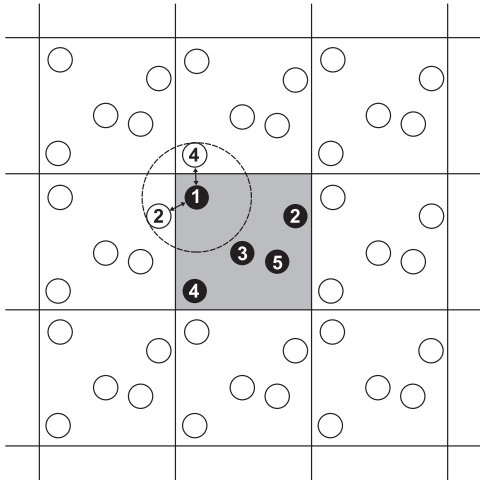


Figure 8.5: Periodic boundaries in a two-dimensional system. The central box (gray area) is surrounded by identical copies. When a particle leaves the central box, it enters through the opposite wall. Particles in the central box interact with all other particles within some cut-off radius, possibly including “image” particles in one of the surrounding boxes. In this example, particle 1 has a cut-off radius indicated by the circle. It interacts (arrows) with particles 2 and 4 in surrounding boxes.

8.4.5 Simulating Different Ensembles

As already stressed, the Verlet leap-frog algorithm conserves energy and thereby samples the microcanonical (N, V, U) ensemble. Then, what is the temperature? We know that strictly speaking $1/T = (\partial S/\partial U)_{N,V}$. Although there is a way to proceed along these lines, it is rather complicated and we will not do so. We know that if the system is large enough, all ensembles are equivalent. Now, our systems usually are not very large, but the application of the periodic boundary conditions certainly makes them infinitely large in a special sense. Actually we perform a limited sampling, only checkerboard configurations are sampled, of an infinitely large system. So let us assume that our system, consisting of N particles in volume V and having energy U , may be considered to be a system consisting of N particles in volume V at temperature T , which we just don't know. By applying the canonical ensemble probability distribution, we may then calculate the average kinetic energy $\langle K \rangle$, obtaining

$$\langle K \rangle = (3N - 3) \frac{1}{2} k_B T. \quad (8.45)$$

Here $(3N - 3)$ is the number of degrees of freedom, 3 for each particle minus 3 because the center of mass of the box is fixed. In our (N, V, U) simulation the kinetic energy K is a fluctuating quantity. For large enough systems its average equals $(3N - 3) \frac{1}{2} k_B T$.

Now suppose we want to run a canonical (N, V, T) ensemble. We may use the kinetic temperature

$$\hat{T} \equiv \frac{2K}{(3N - 3)k_B} \quad (8.46)$$

as an estimate of T . We know that its average must be T and we even know its fluctuations. A rather ad hoc procedure would be to draw velocities from the

Maxwell-Boltzmann distribution for the initial velocities and subsequently to rescale all velocities at every time step by a factor

$$\chi = \sqrt{1 + \frac{\Delta t}{\tau} \left(\frac{T}{\widehat{T}} - 1 \right)}. \quad (8.47)$$

This will change the kinetic temperature \widehat{T} every time-step according to

$$\widehat{T} \longrightarrow \widehat{T} \left[1 + \frac{\Delta t}{\tau} \left(\frac{T}{\widehat{T}} - 1 \right) \right]. \quad (8.48)$$

If the characteristic time τ is chosen to be equal to Δt this algorithm forces \widehat{T} to be equal to T at all times and we lose the natural fluctuations of the kinetic energy. Therefore τ is chosen by trial and error to be such that the fluctuations of the kinetic energy are about right. The procedure just described is usually referred to as applying the Berendsen thermostat. An alternative is the so-called Nosé-Hoover thermostat, which steers the temperature towards the required value in a much gentler way and correctly generates states in the canonical ensemble.

Other ensembles may be simulated as well. For example, to control the pressure P , the system box is allowed to change its volume during the simulation.

8.4.6 Limitations

The computational demands of molecular dynamics, the interaction forces between every atom and its 25 to 50 nearest neighbours must be recalculated every time step, puts restrictions on the accessible length and time scales. A typical simulation box used for simulation of a liquid has edges of the order of 10 nm and contains some 100 000 atoms, though occasionally even larger boxes are being used. The evaluation of a single time step then takes about a second of computer time, which is predominantly spent on the calculation of the non-bonded interactions between the atoms. With time steps in the order of a femtosecond (10^{-15} s), a week of computer time corresponds to about a nanosecond (10^{-9} s) in real time. Of course, these numbers will vary considerably depending on the details of the system, the force field (where in particular long-range Coulombic interactions are demanding), the efficiency of the algorithm, and the available hardware.

The above discussion clearly illustrates that the capabilities of atomistic molecular dynamics simulations are limited, yet even within these boundaries interesting physical phenomena can be studied. In fact, by taking full advantage of the principles of statistical mechanics, it is possible to extract thermodynamic, structural, and dynamic properties from relatively small simulation boxes.

Appendix

In this Appendix we will give an alternative derivation of the classical partition function Q , starting from a quantum mechanical description. For simplicity we consider just one particle in one dimension. The partition function is a sum of Boltzmann factors over all possible (energy) states:

$$\begin{aligned} Q &= \sum_n e^{-\beta E_n} \\ &= \sum_n \langle \psi_n | e^{-\beta \mathcal{H}} | \psi_n \rangle, \end{aligned} \quad (8.49)$$

where ψ_n is an eigenstate of the Hamilton operator \mathcal{H} of energy (eigenvalue) E_n , i.e. $\mathcal{H}\psi_n = E_n\psi_n$. Note that the exponential of an operator A , operating on a function f is defined in terms of the equivalent Taylor series:

$$e^A f = \sum_{k=0}^{\infty} \frac{1}{k!} A^k f = f + Af + \frac{1}{2}A(Af) + \frac{1}{6}A(A(Af)) + \dots \quad (8.50)$$

We now proceed as follows. The sum in the second line of Eq. (8.49) defines the *trace* of the operator $e^{-\beta \mathcal{H}}$ over the complete basis set of eigenfunctions ψ_n . Because the trace is invariant under exchange of complete basis sets, we may as well choose any other complete basis ϕ_n , resulting in the same partition function:

$$Q = \sum_n \langle \phi_n | e^{-\beta \mathcal{H}} | \phi_n \rangle. \quad (8.51)$$

We now choose the particular (complete) basis

$$\phi_n(x) = \frac{1}{\sqrt{L}} e^{i2\pi nx/L}, \quad (8.52)$$

where L is the space accessible to the particle.

Note that the Hamilton operator consists of a kinetic and potential energy operator, $\mathcal{H} = \mathcal{K} + \Phi$, where usually the kinetic operator depends on the momentum $p = \frac{\hbar}{i} \frac{d}{dx}$ and the potential operator depends on the position x . It is well known from quantum mechanics that the momentum and position of a particle do not commute, specifically $[p, x] = \hbar/i$. Therefore the kinetic and potential energy operators also do not commute, $[K, \Phi] \neq 0$, and we cannot simply factorize the operator $e^{-\beta \mathcal{H}}$:

$$e^{-\beta(K+\Phi)} \neq e^{-\beta K} e^{-\beta \Phi}. \quad (8.53)$$

However, in the classical limit we can regard \hbar as very small, and we do have

$$e^{-\beta(K+\Phi)} \approx e^{-\beta K} e^{-\beta \Phi} \approx e^{-\beta \Phi} e^{-\beta K} \quad (\text{classical limit}). \quad (8.54)$$

So in the classical limit we can write the partition function as:

$$\begin{aligned}
Q &= \sum_n \int_0^L dx \frac{1}{\sqrt{L}} e^{-i2\pi nx/L} e^{\beta \frac{\hbar^2}{2m} \frac{d^2}{dx^2}} e^{-\beta\Phi(x)} \frac{1}{\sqrt{L}} e^{i2\pi nx/L} \\
&= \sum_n \int_0^L dx \frac{1}{L} e^{-\beta \frac{1}{2m} (\hbar 2\pi n/L)^2} e^{-\beta\Phi(x)} \\
&= \int_{-\infty}^{\infty} dp \frac{L}{\hbar 2\pi} \int_0^L dx \frac{1}{L} e^{-\beta \frac{p^2}{2m} - \beta\Phi(x)} \\
&= \frac{1}{h} \int dp \int dx e^{-\beta\mathcal{H}}.
\end{aligned} \tag{8.55}$$

This is the result we were after. Generalisation to $3N$ coordinates and $3N$ momenta leads to the expression

$$Q = \frac{1}{h^{3N} N!} \int d^{3N} p \int d^{3N} x e^{-\beta\mathcal{H}}, \tag{8.56}$$

where the factor $N!$ appears because of indistinguishability of identical particles. It is easy to check that Eq. (8.56) is equivalent to Eq. (8.19).

Problems

8-1. Average kinetic energy per particle. Prove Eq. (8.30). Then calculate the r.m.s. velocity $\sqrt{\langle v^2 \rangle}$ of a nitrogen molecule in the air at room temperature.

8-2. Barometric height formula. The density $\rho_\alpha = N_\alpha/V$ of a certain molecule α in a column of air above the earth surface decreases with increasing height. If we denote the height above earth with z , we find

$$\rho_\alpha(z) = \rho_\alpha(0) \exp\left(-\frac{m_\alpha g z}{k_B T}\right),$$

where g is the gravitational constant and m_α the mass of the molecule. Prove this. (You may assume that the temperature is constant everywhere and that the air behaves as an ideal gas.)

8-3. Gravitational energy of an ideal gas particle above the earth surface. Consider again a column of air above the earth surface. Using the outcome of the previous problem, the single-particle probability density of encountering a particle of mass m at position \mathbf{r} with a momentum \mathbf{p} is given by

$$F(\mathbf{r}, \mathbf{p}) = C \exp\left(-\frac{mgz}{k_B T}\right) \exp\left(-\frac{p^2}{2mk_B T}\right).$$

where C is a normalisation constant. Calculate the average gravitational energy $mg \langle z \rangle$ of the particle.

Chapter 9

Non-ideal gasses and liquids

In real liquids and gases there are correlations in the positions of the molecules. The aim of almost all modern theories of liquids is to calculate the radial distribution function by means of statistical thermodynamical reasoning. Alternatively, the radial distribution function can be measured directly in computer simulations. We will discuss its use in calculating the energy and pressure of a fluid. We will also briefly discuss its use in perturbation theory for the free energy. We show how the configuration integral and pressure can be calculated by a diagrammatic expansion method. Finally, we introduce the use of lattice models to facilitate the calculation of the free energy and pressure of fluids and mixtures.

9.1 The radial distribution function

9.1.1 Definition

Imaging we have placed ourselves on a certain molecule in a liquid or gas. Now let us count the number of molecules in a spherical shell of thickness dr at a distance r , i.e. we count the number of molecules within a distance between r and $r + dr$. If r is very large the measured number of molecules will be equal to the volume of the spherical shell times the density, so equal to $4\pi r^2 dr N/V$. At distances smaller than the diameter of the molecules we will find no molecules at all. We now define the radial distribution function $g(r)$ by equating the number of molecules in the spherical shell of thickness dr at a distance r to

$$4\pi r^2 \frac{N}{V} g(r) dr. \tag{9.1}$$

According to our remarks above, $g(\infty) = 1$ and $g(0) = 0$. A typical $g(r)$ is given in Fig. (9.1). We see that $g(r) = 0$ when r is smaller than the molecular diameter σ . The first peak is caused by the attractive part of the potential; at distances where

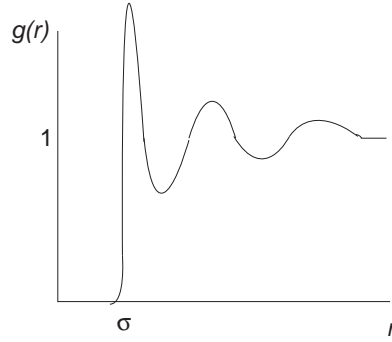


Figure 9.1: A typical radial distribution function in a liquid of spherical molecules with diameter σ .

the potential has its minimum there are more particles than average. Consequently at distances less than σ further away there are less particles than average.

9.1.2 Relation between $g(r)$ and energy, compressibility and pressure

Once we know the radial distribution function, we can derive all non-entropic thermodynamic properties. The simplest is the energy

$$U = U^{\text{int}} + \frac{3}{2}Nk_B T + \frac{1}{2}N\frac{N}{V} \int_0^\infty dr 4\pi r^2 g(r) \varphi(r). \quad (9.2)$$

The first term originates from the internal energies of the molecules, the second from the translations, and the third from the interactions. The average total potential energy equals $\frac{1}{2}N$ times the average interaction of one particular molecule with all others; the factor $\frac{1}{2}$ serves to avoid double counting. The contribution of all particles in a spherical shell of thickness dr at a distance r to the average interaction of one particular particle with all others is $4\pi r^2 dr (N/V) g(r) \varphi(r)$. Integration finally yields Eq. (9.2).

We can also calculate the compressibility κ_T . This is done as follows (where again $\rho = N/V$ is the particle number density and d^3r is shorthand for $4\pi r^2 dr$):

$$\begin{aligned} \langle N \rangle \rho k_B T \kappa_T &= \langle N^2 \rangle - \langle N \rangle^2 \\ &= \left\langle \rho \int_V d^3r_1 \rho \int_V d^3r_2 g(r_{12}) \right\rangle + \langle N \rangle - \left\langle \rho \int_V d^3r_1 \rho \int_V d^3r_2 \right\rangle \\ &= \left\langle \rho \int_V d^3r_1 \rho \int_V d^3r_2 (g(r_{12}) - 1) \right\rangle + \langle N \rangle \\ &= \left\langle \rho \int_V d^3r_1 \rho \int_{\mathbb{R}^3} d^3r_2 (g(r_{12}) - 1) \right\rangle + \langle N \rangle \\ &= \left\langle \rho \int_V d^3r_1 \right\rangle \left\langle \rho \int_{\mathbb{R}^3} d^3r (g(r) - 1) \right\rangle + \langle N \rangle \end{aligned} \quad (9.3)$$

Dividing by $\langle N \rangle$ we find

$$\rho k_B T \kappa_T = \left\langle \rho \int_{\mathbb{R}^3} d^3r (g(r) - 1) \right\rangle + 1. \quad (9.4)$$

This shows that the compressibility of a fluid is intimately connected to the radial distribution function of its constituent molecules.

We will now consider the pressure of a non-ideal fluid. If the density of the fluid is not too high the radial distribution function is given by

$$g(r) \approx \exp \{-\beta\varphi(r)\}, \quad (9.5)$$

where $\varphi(r)$ is the pair interaction potential. We can link the pressure of such a semi-dilute system to the pair interaction $\varphi(r)$, and hence to its $g(r)$, in the following way.

For not too high densities we may terminate the virial equation Eq. (2.62) after the second term, i.e., the pressure of a semi-dilute fluid is to a good approximation given by

$$Pv = RT \left(1 + B_2(T) \frac{1}{v} \right). \quad (9.6)$$

This implies a connection between the compressibility and the second virial coefficient $B_2(T)$. Differentiating the above equation to v yields:

$$\begin{aligned} \left(\frac{\partial P}{\partial v} \right)_{N,T} v + P &= -RT B_2(T) \frac{1}{v^2} \\ -\frac{1}{\kappa_T} + \frac{RT}{v} \left(1 + B_2(T) \frac{1}{v} \right) &= -RT B_2(T) \frac{1}{v^2} \\ \frac{1}{\kappa_T} &= \frac{RT}{v} \left(1 + 2B_2(T) \frac{1}{v} \right) \\ \rho k_B T \kappa_T &= 1 - 2B_2(T) \frac{1}{v}, \end{aligned} \quad (9.7)$$

where we have used that $\rho = N/V = N_{Av}/v$. Comparing the two expressions for the compressibility, Eqs. (9.4) and (9.7), we can write the second virial coefficient as a three-dimensional integral over the pair interaction $\varphi(r)$:

$$\boxed{B_2(T) = -\frac{1}{2} N_{Av} \int_{\mathbb{R}^3} d^3r (e^{-\beta\varphi(r)} - 1)}. \quad (9.8)$$

The above equation is very important because it allows us to calculate the pressure of a fluid knowing only the pair interaction $\varphi(r)$ between its constituent molecules. In the next section we will apply this to a hard sphere fluid.

9.2 The hard sphere fluid

The second virial coefficient B_2 of a hard sphere fluid (with spheres of diameter σ) can easily be calculated

$$B_2 = -\frac{1}{2}N_{Av} \int d^3r (e^{-\beta\varphi(r)} - 1) = 2\pi N_{Av} \int_0^\sigma dr r^2 = \frac{2}{3}\pi N_{Av} \sigma^3. \quad (9.9)$$

This expression is valid for not-too-high densities. Using a computer one has calculated that the pressure for more general densities is given by:

$$\frac{P}{\rho k_B T} = 1 + 4\eta + 10\eta^2 + 18.365\eta^3 + 28.24\eta^4 + 39.5\eta^5 + 56.6\eta^6 + \dots \quad (9.10)$$

$$\eta = \frac{4}{3}\pi \left(\frac{1}{2}\sigma\right)^3 \frac{N}{V}, \quad (9.11)$$

where η is the volume fraction of spheres. We can write approximately

$$\frac{P}{\rho k_B T} = 1 + 4\eta + 10\eta^2 + 18\eta^3 + 28\eta^4 + 40\eta^5 + 54\eta^6 + \dots \quad (9.12)$$

Extrapolating and summing we find

$$\frac{P}{\rho k_B T} = 1 + \sum_{n=1}^{\infty} (n^2 + 3n)\eta^n = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \quad (9.13)$$

This is called Carnahan and Starling's equation for the pressure of a hard sphere fluid. Monte Carlo simulations of hard sphere fluids have shown that Eq. (9.13) is nearly exact at all possible volume fractions.

The entropy of a non-ideal gas is mostly determined by the repulsive part of the potential energy, because this part of the potential determines the number of states that contributes to the configuration integral. The entropy of a hard sphere fluid may therefore serve as a first approximation to the entropy of any fluid with spherical particles. The free energy of the hard sphere fluid, and concordingly all thermodynamic properties, can be calculated from $P = -(\partial A/\partial V)_T$. Using Eq. (9.13) we find

$$A^{HS} = -Nk_B T \ln \left(\frac{q^{\text{int}} e V}{\Lambda^3 N} \right) + Nk_B T \frac{\eta(4 - 3\eta)}{(1 - \eta)^2}, \quad (9.14)$$

where q^{int} is the one-particle partition function of the internal degrees of freedom of the molecule. This formula plays an important role in perturbation theory which we will briefly discuss in the next section.

9.3 Perturbation theory

In this section we will briefly sketch a very important technique, called perturbation theory. In perturbation theory we write the pair interaction as

$$\varphi(r) = \varphi^0(r) + \varphi'(r). \quad (9.15)$$

A good choice is one in which $\varphi^0(r)$ is the repulsion and $\varphi'(r)$ the attraction. The free energy calculated with only $\varphi^0(r)$ we will call A^0 . To a good approximation the following expression is valid:

$$A = A^0 + \frac{1}{2}N\frac{N}{V} \int_0^\infty dr 4\pi r^2 g^0(r) \varphi'(r). \quad (9.16)$$

If we choose, as above, for $\varphi^0(r)$ the repulsive part of the potential, then A^0 will be given by A^{HS} in Eq. (9.14). $g^0(r)$ is the radial distribution function of the ‘reference system’ with interaction $\varphi^0(r)$. If we take for $\varphi^0(r)$ a hard core repulsion, then $g^0(r)$ is the radial distribution function of a hard sphere fluid; this function is well known from Monte Carlo simulations. Formula (9.16) leads to excellent predictions.

Using perturbation theory we may derive Van der Waals’ equation of state. To this end we add the following additional approximation:

$$\begin{aligned} g^{HS}(r) &= 0 \text{ for } r < \sigma \\ &= 1 \text{ for } r \geq \sigma \\ A^{HS} &= -Nk_B T \ln \left(\frac{q^{\text{int}} e V}{\Lambda^3 N} \right) - Nk_B T \ln(1 - 4\eta) \end{aligned} \quad (9.17)$$

The free energy of the system then becomes

$$A = -Nk_B T \ln \left(\frac{q^{\text{int}} e}{\Lambda^3 N} \right) - Nk_B T \ln(V - nb) - a \frac{n^2}{V}, \quad (9.18)$$

with

$$\begin{aligned} a &= -\frac{1}{2}N_{av}^2 4\pi \int_\sigma^\infty dr r^2 \varphi(r), \\ b &= \frac{2}{3}\pi\sigma^3 N_{av}. \end{aligned} \quad (9.19)$$

Because $\varphi(r) < 0$ for $r > \sigma$ the constant a is positive.

9.4 Relation between fugacity and the configuration integral

The intermolecular interactions in a non-ideal system contribute to all thermodynamic properties. In this section we will focus on the fugacity and fugacity coefficient. According to section 3.9.2 we may write the chemical potential as follows:

$$\begin{aligned}\mu(P, T) &= \mu^*(T) + RT \ln P + RT \ln \phi(P, T) \\ &= \mu^*(T) + RT \ln f(P, T).\end{aligned}\quad (9.20)$$

Here ϕ is the fugacity coefficient and $f = \phi P$ the fugacity. For an ideal gas we have $\phi = 1$ and $f = P$. So $RT \ln \phi$ is the correction to ideal behaviour. We therefore expect a simple relation between ϕ and that part of the partition function Q that depends on the intermolecular interactions, i.e. between ϕ and Z .

When we are dealing with molecules instead of point particles, we also need to take into account the internal states of the molecules. The semi-classical partition function and free energy are then given by more general versions of Eqs. (8.18) and (8.19):

$$Q = \frac{(q^{int})^N}{\Lambda^{3N} N!} Z, \quad (9.21)$$

$$A = -Nk_B T \ln \left(\frac{q^{int} e}{\Lambda^3 N} \right) - k_B T \ln Z_N, \quad (9.22)$$

where q^{int} is the one-particle partition function of the internal degrees of freedom of the molecule, and Λ denotes the so-called thermal De Broglie wave length $\sqrt{\hbar^2/(2\pi m k_B T)}$. We have given Z a subscript N to indicate that Z is a function of N . For an ideal gas we have $Z_N = V^N$. Using $\mu = (\partial A / \partial N)_{V, T}$ we then easily calculate the chemical potential. Substituting in this expression $V = Nk_B T / P$ and comparing the result with Eq. (9.20), we find for an ideal gas:

$$\mu^*(T) = -RT \ln \left(\frac{q^{int}}{\Lambda^3} k_B T \right). \quad (9.23)$$

For a non-ideal system we find, with Eq. (8.19):

$$\begin{aligned}\mu &= -RT \ln \left(\frac{q^{int}}{\Lambda^3 N} \right) - RT \ln \left(\frac{\partial Z_N}{\partial N} \right)_{V, T} \\ &= -RT \ln \left(\frac{q^{int}}{\Lambda^3 N} \right) - RT \ln \frac{Z_N}{Z_{N-1}}.\end{aligned}\quad (9.24)$$

Here we have written the derivative of $\ln Z_N$ to N as $\ln Z_N - \ln Z_{N-1}$. From Eqs. (9.20), (9.23) and (9.24) follows:

$$\ln \phi = -\ln \left(\frac{PV}{Nk_B T} \right) - \ln \left(\frac{1}{V} \frac{Z_N}{Z_{N-1}} \right). \quad (9.25)$$

This is the looked-after relation between ϕ and Z . When applied to an ideal gas, this equation yields $\phi = 1$, as could have been expected. For non-ideal gasses both terms contribute.

From the treatment above follows that, as long as the partition function can be written as in Eq. (9.21), the chemical potential consists of a contribution μ^* which only depends on the temperature and a contribution that only depends on P and T . μ^* is totally determined by the internal states of individual molecules. The (P, T) -dependent part

$$\ln f = -\ln \left(\frac{1}{Nk_B T} \frac{Z_N}{Z_{N-1}} \right) \quad (9.26)$$

is totally determined by the configuration integral. This conclusion is valid for systems in any state of aggregation, as long as Q may be written as in Eq. (9.21).

9.5 Diagrammatic expansions

9.5.1 The configuration integral

Let us try to calculate the configuration integral. Assume we have a system with pair interactions:

$$\Phi(r^{3N}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \varphi(r_{ij}) \quad (9.27)$$

Then

$$\begin{aligned} Z_N &= \int d^3r_1 \dots \int d^3r_N \exp \{-\beta\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N)\} \\ &= \int d^3r_1 \dots \int d^3r_N \prod_{i=1}^{N-1} \prod_{j=i+1}^N \exp \{-\beta\varphi(r_{ij})\} \end{aligned} \quad (9.28)$$

For an ideal gas we have $\exp \{-\beta\varphi(r_{ij})\} = 1$. Let us now introduce the function $f(r)$ by

$$\exp \{-\beta\varphi(r_{ij})\} = 1 + f(r) \quad (9.29)$$

A qualitative picture of $f(r)$ is given in Fig. (9.2). For a semidilute fluid it is essentially the radial distribution function shifted down by one. It is important to note that $f(r)$ tends to zero as r goes to infinity. The configuration integral is then given by

$$Z_N = \int d^3r_1 \dots \int d^3r_N \prod_{i=1}^{N-1} \prod_{j=i+1}^N (1 + f(r_{ij})) \quad (9.30)$$

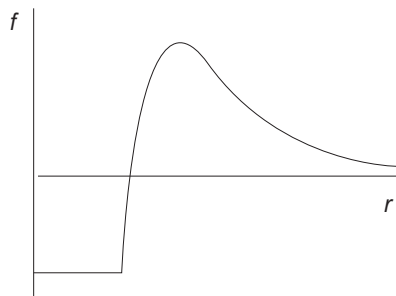


Figure 9.2: Qualitative picture of the function $f(r) = \exp\{-\beta\varphi(r_{ij})\} - 1$.

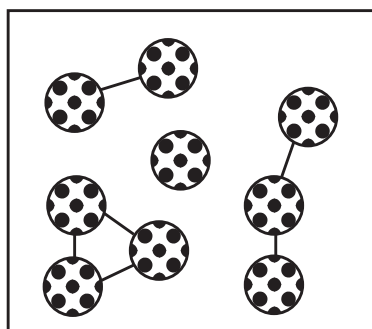


Figure 9.3: One of the terms in Eq. (9.30). A line between two molecules means that the associated term contains a factor $f(r_{ij})$. With every chequered molecule we associate integration of its position over the volume.

We need to expand the continued product and integrate and sum all terms. Expanding the continued product yields all terms that can be made by either associating or not associating with each molecular pair (i, j) a factor $f(r_{ij})$ in the integrand. There are $\frac{1}{2}N(N-1)$ pairs, and hence $2^{\frac{1}{2}N(N-1)}$ terms in Eq. (9.30). One of these is depicted in Fig. (9.3). A line between two molecules i and j means that the integrand of the associated term contains a factor $f(r_{ij})$. With every chequered molecule we associate integration of its position vector over the entire available volume.

Voyaging further in this direction is not very appealing.

9.5.2 The density

We shall now show that it is relatively easy to derive a formula for the density.

The density $\rho(\mathbf{r}_1)$ at position \mathbf{r}_1 equals N times the probability to find particle number one at \mathbf{r}_1 . In a homogenous system the density is independent of position, hence

$$\begin{aligned} \rho &= \frac{N}{Z_N} \int d^3r_2 \dots \int d^3r_N \exp\{-\beta\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N)\} \\ &= \frac{N}{Z_N} \int d^3r_2 \dots \int d^3r_N \prod_{i=1}^{N-1} \prod_{j=i+1}^N (1 + f(r_{ij})) \end{aligned} \quad (9.31)$$

Note that particle number one is positioned at \mathbf{r}_1 , and that the coordinates of all other particles are integrated.

Figure 9.4: Example of a term where particle 1 is not connected to any other particle.

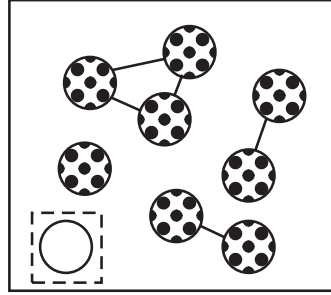
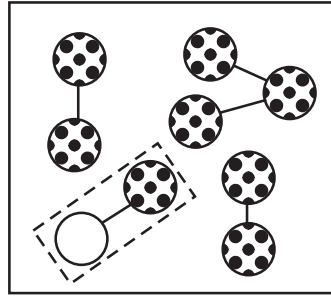


Figure 9.5: Example of a term where particle 1 is connected to another particle j , while both are unconnected to any other particle.



Now expand the product in Eq. (9.31), and collect

- a all terms where particle number one is not connected to any other particle. One of these terms is depicted in Fig. (9.4). This way we collect all possible terms that we can generate with particles 2 to N . The contribution of all these terms is therefore equal to Z_{N-1} .
- b all terms where particle number one is connected to particle i , while both are unconnected to any other particle; subsequently sum over i . One of these terms is depicted in Fig. (9.5). All terms contain a factor

$$a_2 = \int d^3r_2 f(r_{12}) \quad (9.32)$$

All other particles can be combined in all possible ways; this leads to a factor Z_{N-2} . Summing over i yields a factor $(N-1)$.

- c all terms where particles 1, i and j are mutually connected, while none of the three are connected to any other particle; subsequently sum over i and j . Some of these terms are depicted in Fig. (9.6). Summing over i and j yields a factor $\frac{1}{2}(N-1)(N-2)$; then there is a factor Z_{N-3} . And finally the factor

$$a_3 = \int d^3r_2 \int d^3r_3 \{2f(r_{12})f(r_{23}) + f(r_{12})f(r_{13}) + f(r_{12})f(r_{13})f(r_{23})\} \quad (9.33)$$

- d etcetera.

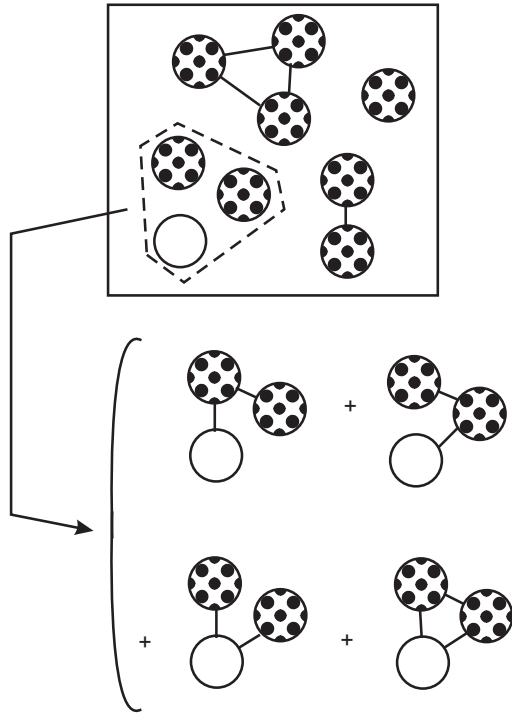


Figure 9.6: Example of terms where particles 1, i and j are mutually connected, while none of the three are connected to any other particle.

The result now is

$$\begin{aligned}
 \rho &= N \frac{Z_{N-1}}{Z_N} + a_2 N \frac{Z_{N-1}}{Z_N} (N-1) \frac{Z_{N-2}}{Z_{N-1}} + \frac{1}{2} a_3 N \frac{Z_{N-1}}{Z_N} (N-1) \frac{Z_{N-2}}{Z_{N-1}} (N-2) \frac{Z_{N-3}}{Z_{N-2}} \\
 &= z + a_2 z^2 + \frac{1}{2} a_3 z^3 + \dots \\
 &= \sum_{n=1}^{\infty} \frac{1}{(n-1)!} a_n z^n
 \end{aligned} \tag{9.34}$$

We now have the density as a power series in the activity $z = \frac{f}{k_B T}$.

9.5.3 Connection to the virial equation

From the Gibbs-Duhem relation follows

$$\left(\frac{\partial P}{\partial \mu} \right)_T = \rho \tag{9.35}$$

$$\left(\frac{\partial P}{\partial z} \right)_T = \left(\frac{\partial \mu}{\partial z} \right)_T \left(\frac{\partial P}{\partial \mu} \right)_T = \frac{k_B T}{z} \rho \tag{9.36}$$

Substituting in Eq. (9.34) yields:

$$\frac{P}{k_B T} = \sum_{n=1}^{\infty} \frac{1}{n!} a_n z^n \tag{9.37}$$

Instead of P as a power series in z we would rather have P as a power series in ρ . To this end we invert Eq. (9.34) and use the result in Eq. (9.37):

$$\begin{aligned} z &= \rho + b_2\rho^2 + b_3\rho^3 + \dots \\ b_2 &= -a_2 \\ b_3 &= 2a_2^2 - \frac{1}{2}a_3 \end{aligned} \tag{9.38}$$

$$\begin{aligned} \frac{P}{k_B T} &= \rho + B_2\rho^2 + B_3\rho^3 + \dots \\ B_2 &= -\frac{1}{2}a_2 \\ B_3 &= -\frac{1}{3}(a_3 - 3a_2^2) \end{aligned} \tag{9.39}$$

Note that the expression for the second virial coefficient B_2 is in agreement with our result derived earlier in Eq. (9.8).

9.6 Lattice gas

We have found that all interesting information regarding interacting systems is contained in the configuration integral Z . Unfortunately this integral can be calculated analytically for just a few simple cases. One solution is to perform simulations, as discussed in section 8.4. Another solution is to use physical insight, and make meaningful approximations which allow us to calculate Z . A famous example is the lattice gas, which may be used to derive the van der Waals equation of state.

Suppose we have a gas of N particles. The partition function is

$$Q = \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} \frac{1}{N!} Z. \tag{9.40}$$

To determine the configuration integral Z we divide space into M little cubes of volume approximately equal to that of one particle. We will now write all integrals as sums over all cubes multiplied by Δ , the volume of one cube. The configuration integral then equals a sum over a finite number of different configurations. A configuration is generated by placing each particle in any of the cubes, as in Figure 9.7. So:

$$Z = \sum_{\text{conf}} e^{-\beta\Phi(\text{conf})} \Delta^N. \tag{9.41}$$

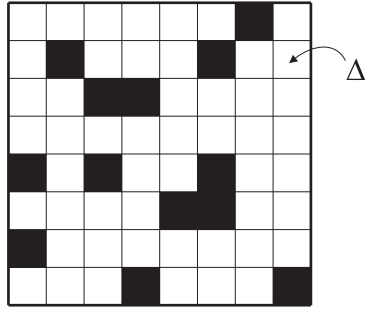


Figure 9.7: Two-dimensional representation of a lattice gas. Space is divided into cubes of size Δ , approximately equal to the size of one molecule. A configuration is generated by placing N particles (black squares) on the lattice.

Here $\Phi(\text{conf})$ is the potential energy of that particular configuration, i.e. a sum over all pair interactions $\varphi(r_{ij})$. We now approximate

$$\varphi(r_{ij}) = \begin{cases} \infty & \text{if } i \text{ and } j \text{ are in the same cube} \\ -\epsilon & \text{if } i \text{ and } j \text{ are in neighbouring cubes} \\ 0 & \text{otherwise.} \end{cases} \quad (9.42)$$

Despite the simplicity of the above model, we are still not able to calculate Z . We therefore make the *mean field assumption*

$$\Phi(\text{conf}) = \begin{cases} \infty & \text{if at least one cube is doubly occupied} \\ \Phi & \text{otherwise.} \end{cases} \quad (9.43)$$

So we assume that the energy of each possible configuration is approximately the same. The configuration integral then is

$$Z = \Omega e^{-\beta\Phi} \Delta^N, \quad (9.44)$$

where Ω is the number of possible configurations such that no cube is occupied more than once. So we need to estimate Ω and Φ . In this case

$$\Omega = \frac{M!}{(M-N)!} \quad (9.45)$$

$$\Phi = \frac{1}{2} N z \frac{N}{M} (-\epsilon), \quad (9.46)$$

where $M = V/\Delta$ and z is the coordination number of the lattice (number of neighbours per cube). The first of these two equations is trivial. To calculate Φ we note that each occupied cube has z neighbours, of which on average a fraction N/M is occupied. The interaction energy with each of these neighbours is $(-\epsilon)$. We have N particles, hence the additional factor N . We have double counted each interaction, hence the factor $\frac{1}{2}$. It is then an easy task (see Problem 9-9) to prove that

$$\begin{aligned} A &= -\frac{3}{2} N k_B T \ln \left(\frac{2\pi m k_B T}{h^2} \right) - k_B T \ln \left(\frac{M!}{(M-N)! N!} \right) \\ &\quad - \frac{1}{2} N z \frac{N}{M} \epsilon - N k_B T \ln \Delta. \end{aligned} \quad (9.47)$$

For the pressure we then find

$$P = -\frac{k_B T}{\Delta} \ln \left(1 - \frac{N}{M} \right) - \frac{1}{2} z \epsilon \Delta \frac{N^2}{V^2}. \quad (9.48)$$

Making use of the approximation

$$\ln(1+x) \approx \frac{x}{1+\frac{1}{2}x}, \quad (9.49)$$

we finally find

$$\begin{aligned} P &= \frac{k_B T}{\Delta} \frac{N/M}{1 - \frac{1}{2}N/M} - \frac{1}{2} z \epsilon \Delta \frac{N^2}{V^2} \\ &= \frac{nRT}{V - nb} - a \frac{n^2}{V^2} \end{aligned} \quad (9.50)$$

$$b = \frac{1}{2} N_{Av} \Delta \quad (9.51)$$

$$a = \frac{1}{2} z \epsilon \Delta N_{Av}^2. \quad (9.52)$$

The lattice gas is therefore approximately equal to a van der Waals gas.

9.7 The regular mixture

We now consider a binary liquid mixture of N_A molecules A and N_B molecules B . The partition function now is

$$Q = \left(\frac{2\pi m_A k_B T}{h^2} \right)^{3N_A/2} \left(\frac{2\pi m_B k_B T}{h^2} \right)^{3N_B/2} \frac{1}{N_A! N_B!} Z_{N_A, N_B}. \quad (9.53)$$

Note that we need to account for indistinguishability of A and B particles separately, hence the factor $1/(N_A! N_B!)$. To calculate the configuration integral Z_{N_A, N_B} , again we will use a lattice approach. We let the molecules A and B be of the same volume Δ , and divide space in $N = N_A + N_B = V/\Delta$ cubes, see Figure 9.8. Note that, contrary to the lattice gas of the previous section, we now assume that *all* lattice sites are occupied, which represents the relative incompressibility of a liquid. The configuration integral now is

$$Z_{N_A, N_B} = \sum_{\text{conf}} e^{-\beta \Phi_{N_A, N_B}(\text{conf})} \Delta^{N_A + N_B}. \quad (9.54)$$

Here $\Phi_{N_A, N_B}(\text{conf})$ is the potential energy of the given configuration. This is a sum of all pair interactions, each approximated as

$$\varphi(r_{ij}) = \begin{cases} \infty & \text{if } i \text{ and } j \text{ are in the same cube} \\ -\epsilon_{ij} & \text{if } i \text{ and } j \text{ are in neighbouring cubes} \\ 0 & \text{otherwise.} \end{cases} \quad (9.55)$$

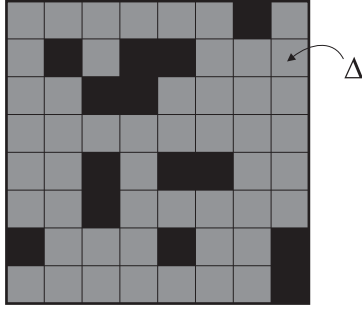


Figure 9.8: Two-dimensional representation of a lattice binary liquid mixture. Space is divided into cubes of size Δ , approximately equal to the size of each molecule. A configuration is generated by placing N_A particles A (black squares) and N_B particles B (grey squares) on the lattice.

Note that neighbouring pairs can have an interaction energy $-\epsilon_{AA}$, $-\epsilon_{BB}$, or $-\epsilon_{AB}$, depending on the molecular species at hand. This defines our model.

We now again make the mean field assumption Eq. (9.43). The configuration integral then becomes

$$Z_{N_A, N_B} = \Omega_{N_A, N_B} e^{-\beta \Phi_{N_A, N_B}} \Delta^{N_A + N_B}, \quad (9.56)$$

with

$$\Omega_{N_A, N_B} = (N_A + N_B)! \quad (9.57)$$

$$\begin{aligned} \Phi_{N_A, N_B} &= \frac{1}{2} N_A [z x_A (-\epsilon_{AA}) + z x_B (-\epsilon_{AB})] \\ &\quad + \frac{1}{2} N_B [z x_A (-\epsilon_{AB}) + z x_B (-\epsilon_{BB})]. \end{aligned} \quad (9.58)$$

The calculation of Ω_{N_A, N_B} is trivial. To calculate Φ_{N_A, N_B} we note that each molecule A has z neighbouring cubes of which on average $z N_A / N = z x_A$ are occupied by an A molecule, with each of which the interaction energy is $(-\epsilon_{AA})$; with the other $z N_B / N = z x_B$ neighbours the interaction energy is $(-\epsilon_{AB})$ each. The same arguments apply to the B molecules. In the end, we have double counted each interaction, hence the factors $\frac{1}{2}$. For the free energy we find (Problem 9-10)

$$\begin{aligned} A_{N_A, N_B} &= -\frac{3}{2} N_A k_B T \ln \left(\frac{2\pi m_A k_B T}{h^2} \right) - N_A k_B T \ln \Delta \\ &\quad -\frac{3}{2} N_B k_B T \ln \left(\frac{2\pi m_B k_B T}{h^2} \right) - N_B k_B T \ln \Delta \\ &\quad - k_B T \ln \left(\frac{(N_A + N_B)!}{N_A! N_B!} \right) + \Phi_{N_A, N_B}. \end{aligned} \quad (9.59)$$

In principle all thermodynamic properties can be calculated now.

To connect to usual practice in thermodynamics, we will rewrite Eq. (9.59) a little more. First we note that for $N_B = 0$ we have

$$A_{N_A} = -\frac{3}{2} N_A k_B T \ln \left(\frac{2\pi m_A k_B T}{h^2} \right) - N_A k_B T \ln \Delta + \Phi_{N_A}. \quad (9.60)$$

An analogous expression can be written down for $N_A = 0$. We therefore write

$$A_{N_A, N_B} = A_{N_A} + A_{N_B} + \Delta A_{\text{mix}} \quad (9.61)$$

$$\Delta A_{\text{mix}} = N_A k_B T \ln x_A + N_B k_B T \ln x_B + \{\Phi_{N_A, N_B} - \Phi_{N_A} - \Phi_{N_B}\}. \quad (9.62)$$

ΔA_{mix} is called the free energy of mixing. We can further simplify the energetic contribution:

$$\begin{aligned} & \Phi_{N_A, N_B} - \Phi_{N_A} - \Phi_{N_B} \\ &= \frac{1}{2} N_A [z x_A (-\epsilon_{AA}) + z x_B (-\epsilon_{AB})] + \frac{1}{2} N_B [z x_A (-\epsilon_{AB}) + z x_B (-\epsilon_{BB})] \\ & \quad - \frac{1}{2} N_A z (-\epsilon_{AA}) - \frac{1}{2} N_B z (-\epsilon_{BB}) \\ &= (N_A + N_B) \frac{1}{2} z [x_A x_A (-\epsilon_{AA}) - x_A (-\epsilon_{AA}) \\ & \quad + x_B x_B (-\epsilon_{BB}) - x_B (-\epsilon_{BB}) + x_A x_B (-\epsilon_{AB} - \epsilon_{AB})] \\ &= (N_A + N_B) x_A x_B \frac{1}{2} z [\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}] \\ &\equiv (N_A + N_B) x_A x_B a. \end{aligned} \quad (9.63)$$

So the free energy of mixing is given by

$$\Delta A_{\text{mix}} = N_A k_B T \ln x_A + N_B k_B T \ln x_B + (N_A + N_B) x_A x_B a. \quad (9.64)$$

The chemical potential per mole of component A then becomes

$$\begin{aligned} \mu_A &= N_{Av} \left(\frac{\partial A}{\partial N_A} \right)_{T, N_B} \\ &= \mu_A^{\text{pure}} + RT \ln x_A + (1 - x_A)^2 N_{Av} a, \end{aligned} \quad (9.65)$$

where μ_A^{pure} is the molar chemical potential for a liquid of pure A . Note that when the interactions between A and B are symmetrical, meaning $\epsilon_{AA} = \epsilon_{AB} = \epsilon_{BB}$, we have $a = 0$. In that case we speak of an ideal liquid. This expression for the chemical potential of an ideal liquid was used in section 4.2.3.

In Problem 9-11 we will consider the case where molecule B is larger than molecule A .

Problems

9-1. Van der Waals fluid. Experimentally, the second virial coefficient of CH_4 is found to be equal to

$$\frac{B_2}{v_c} = 0.430 - 0.886 \frac{T_c}{T} - 0.694 \left(\frac{T_c}{T} \right)^2 \quad (9.66)$$

where $T_c = 190.6$ K and $v_c = 99.2$ $\text{cm}^3 \text{mol}^{-1}$. Describe the intermolecular interaction with a square-well potential, i.e. with potential energy ∞ for $r < \sigma$, $-\epsilon$ for $\sigma \leq r \leq \lambda\sigma$, and 0 for $r > \lambda\sigma$. Use the parameters $\epsilon/k_B = 142.5$ K, $\sigma = 0.3355$ nm and $\lambda = 1.60$. Calculate the experimental and theoretical values of B_2 for a few temperatures between 100 K and 300 K.

9-2. Star polymers. A star polymer consists of f polymer “arms”, each bound with one end to a central point. This causes the density of polymers near the central point to be much higher than further away. If we dissolve many star polymers in a solvent, the polymer chains will cause an effective repulsion between the different star polymer centres. The closer the centres are, the larger the repulsion.

It is possible to derive the effective interaction between the central points. The outcome of such a calculation (we will not present the details here), in the limit of a large number of arms f , is that the effective potential energy between two central points at distance r is given by:

$$\phi(r) = -\frac{5}{18} k_B T f^{3/2} \ln \left(\frac{r}{\sigma} \right) \quad (r \leq \sigma)$$

and $\phi(r) = 0$ for $r > \sigma$. Here σ is the average diameter of the star polymer particle.

We will use the virial equation here to calculate the osmotic pressure Π . At not too high densities of star polymers, we may approximate

$$\begin{aligned} \Pi &= \frac{N k_B T}{V} \left(1 + B_2 \frac{n}{V} \right) \\ B_2 &= \frac{1}{2} N_{Av} \int d^3r \left(1 - \exp \left\{ -\frac{\phi(r)}{k_B T} \right\} \right) \end{aligned}$$

where $n = N/N_{Av}$ is the number of moles of star polymer particles.

- Plot the effective interaction versus distance r .
- Calculate the second virial coefficient B_2 of star-polymers. What is the limit for $f \rightarrow \infty$? With what other system does this limit correspond?
- Give an expression for the osmotic pressure Π of the star polymers as a function of the number of arms f , the particle density N/V , and temperature T .

9-3. Carnahan and Starling's equation. Prove the last step in Eq. (9.13).

9-4. Carnahan and Starling's equation (2). Show that Eq. (9.13) follows from Eq. (9.14).

9-5. Free energy of a Van der Waals fluid. Derive Eq. (9.18) from Eq. (9.17).

9-6. Parameters of the Van der Waals fluid. The parameters of the Van der Waals equation of state can be calculated from knowledge of the critical temperature and pressure:

$$a = \frac{27 R^2 T_c^2}{64 P_c} \quad b = \frac{RT_c}{8P_c}$$

Using this, show that for a Lennard-Jones potential follows

$$\frac{\epsilon}{k} = \frac{81}{64} T_c \quad \frac{\epsilon}{\sigma^3} = \frac{27}{4} \pi P_c$$

With this result, calculate ϵ/k and σ for the molecules Ar, CH₄, N₂ and CO₂. Given:

Ar: $T_c = 150.9$ K, $P_c = 48.98$ bar;

N₂: $T_c = 126.1$ K, $P_c = 33.94$ bar;

CH₄: $T_c = 190.6$ K, $P_c = 46.04$ bar;

CO₂: $T_c = 304.2$ K, $P_c = 73.82$ bar.

Compare your answers with the following experimental values, which have been fit to second virial coefficients:

Ar: $\epsilon/k_B = 177.7$ K, $\sigma = 0.3504$ nm;

N₂: $\epsilon/k_B = 95.2$ K, $\sigma = 0.3745$ nm;

CH₄: $\epsilon/k_B = 148.9$ K, $\sigma = 0.3783$ nm;

CO₂: $\epsilon/k_B = 198.2$ K, $\sigma = 0.4328$ nm.

From computer simulations it is found that for real Lennard-Jones fluids:

$$\frac{\epsilon}{k_B} = 0.722T_c \quad \frac{\epsilon}{\sigma^3} = 7.42P_c$$

Calculate ϵ/k_B and σ for Ar, CH₄, N₂ and CO₂ using this expression too.

9-7. Fugacity and virial equation. Calculate the fugacity coefficient of a gas obeying the virial equation.

9-8. P as power series in ρ instead of z . Check Eqs. (9.38) and (9.39).

9-9. Pressure of a lattice gas. Prove Eqs. (9.47) and (9.48).

9-10. Free energy of a binary mixture. Prove Eq. (9.59).

9-11. Binary mixture of large and small molecules. Consider a binary liquid mixture of N_A molecules A and N_B molecules B . The volumes per molecule are v_A and v_B respectively, where we assume $v_B = pv_A$ and $p > 1$ is an integer number. Both molecules are inflexible. The partition function of the system is:

$$Q = \left(\frac{2\pi m_A k_B T}{h^2} \right)^{3N_A/2} \left(\frac{2\pi m_B k_B T}{h^2} \right)^{3N_B/2} \frac{1}{N_A! N_B!} Z_{N_A, N_B}$$

$$Z_{N_A, N_B} = \int d^{3N_A} r \int d^{3N_B} x \exp \{ -\beta \Phi(r^{3N_A}, x^{3N_B}) \}.$$

Here $\Phi(r^{3N_A}, x^{3N_B})$ is the potential energy of the system if the A molecules are at positions \mathbf{r}_1 to \mathbf{r}_{N_A} and the B molecules are at positions \mathbf{x}_1 to \mathbf{x}_{N_B} . We assume that the interactions between the molecules are merely hard repulsions, and that there are no attractions. The number of configurations the system can have without two or more molecules overlapping is called Ω_{N_A, N_B} . We assume that the volume of the system equals

$$V = N_A v_A + N_B v_B,$$

i.e. there is no unoccupied space (incompressible liquid).

- Give the formula for Ω_{N_A, N_B} . Do this along the following route: First divide the volume in cubes of size v_B and place the N_B molecules of kind B . Then subdivide the remaining cubes in smaller cubes of size v_A and place the molecules of kind A .
- Again calculate Ω_{N_A, N_B} , but now in the following way: Again first place the molecules of kind B , but now in a space that has been divided in cubes of size v_A . Next place the molecules of kind A in the remaining cubes.
- Show that the configuration integral in case (a) may be written as

$$Z_{N_A, N_B} = \Omega_{N_A, N_B}^{(a)} v_A^{N_A} v_B^{N_B},$$

and in case (b) as

$$Z_{N_A, N_B} = \Omega_{N_A, N_B}^{(b)} v_A^{N_A} v_A^{N_B},$$

and show that both formulas give the same result.

- Calculate ΔA_{mix} in

$$A_{N_A, N_B} = A_{N_A} + A_{N_B} + \Delta A_{\text{mix}}$$

- Calculate μ_A and μ_B , the molar chemical potentials of component A and component B .

Appendix A

Useful mathematical relations and physical constants

A.1 Gaussian integrals

We will often need to evaluate integrals of the form

$$I_n(\alpha) = \int_0^\infty dx x^n e^{-\alpha x^2}. \quad (\text{A.1})$$

Solutions to these integrals can easily be generated by “differentiating under the integral sign”:

$$I_{n+2}(\alpha) = \int_0^\infty dx x^{n+2} e^{-\alpha x^2} = -\frac{\partial}{\partial \alpha} I_n(\alpha). \quad (\text{A.2})$$

Knowledge of the solution for $n = 0$ allows us to generate solutions for all even n , whereas the solution for $n = 1$ allows us to generate solutions for all odd n .

Although the solution for $n = 1$ can easily be found, $I_1(\alpha) = 1/(2\alpha)$, the solution for $n = 0$ requires some more thought. It can be calculated by considering the following integral in the two-dimensional plane:

$$\int_0^\infty dx \int_0^\infty dy e^{-\alpha(x^2+y^2)}. \quad (\text{A.3})$$

Because we can factorize the exponential this is clearly equal to $[I_0(\alpha)]^2$. Changing from (x, y) to polar coordinates (r, ϕ) , taking into account the Jacobian, we find

$$I_0^2(\alpha) = \int_0^\infty dr \int_0^{\pi/2} d\phi r e^{-\alpha r^2} = \frac{\pi}{4\alpha}. \quad (\text{A.4})$$

Hence $I_0(\alpha) = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$.

The integrals I_n appear so often that we write down the values of some of them explicitly. We have

$$I_0 = \frac{1}{2} \left(\frac{\pi}{\alpha} \right)^{1/2}, \quad I_2 = \frac{1}{4} \left(\frac{\pi}{\alpha^3} \right)^{1/2}, \quad I_4 = \frac{3}{8} \left(\frac{\pi}{\alpha^5} \right)^{1/2}, \dots \quad (\text{A.5})$$

and

$$I_1 = \frac{1}{2\alpha}, \quad I_3 = \frac{1}{2\alpha^2}, \quad I_5 = \frac{1}{\alpha^3}, \dots \quad (\text{A.6})$$

A.2 Relations between partial derivatives

Suppose there is a relation between the variables x , y , and z :

$$F(x, y, z) = 0, \quad (\text{A.7})$$

meaning that only two of them are independent. We could rearrange this equation to give x as a function of y and z as

$$x = x(y, z). \quad (\text{A.8})$$

If we make infinitesimal changes dy and dz in y and z , there will be an infinitesimal change in x according to

$$dx = \left(\frac{\partial x}{\partial y} \right)_z dy + \left(\frac{\partial x}{\partial z} \right)_y dz. \quad (\text{A.9})$$

Similarly, writing $y = y(x, z)$,

$$dy = \left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial y}{\partial z} \right)_x dz. \quad (\text{A.10})$$

Substituting Eq. (A.10) in Eq. (A.9), we find

$$dx = \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z dx + \left[\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x + \left(\frac{\partial x}{\partial z} \right)_y \right] dz. \quad (\text{A.11})$$

We now take x and z as the independent variables. First we choose $dz = 0$ and a non-zero value for dx . Dividing both sides of Eq. (A.11) by dx we find

$$1 = \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z, \quad (\text{A.12})$$

or

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial y}{\partial x}\right)_z^{-1}.} \quad (\text{A.13})$$

Second, we choose $dx = 0$ and a non-zero value for dz . Dividing Eq. (A.11) by dz we find

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = - \left(\frac{\partial x}{\partial z}\right)_y, \quad (\text{A.14})$$

or

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1.} \quad (\text{A.15})$$

This is sometimes called the -1 rule, or cyclical relation.

Do not confuse the -1 rule with the well-known chain rule of differentiation. A derivation of the chain rule goes as follows. Suppose again that x , y and z are not independent, being related by $F(x, y, z) = 0$. Let us consider some other function G of x , y and z . Because x , y and z are interrelated, G may be expressed in terms of only two of the variables, say

$$G = G(x, y). \quad (\text{A.16})$$

This can be rearranged to give

$$x = x(G, y), \quad (\text{A.17})$$

so

$$dx = \left(\frac{\partial x}{\partial G}\right)_y dG + \left(\frac{\partial x}{\partial y}\right)_G dy. \quad (\text{A.18})$$

Dividing both sides by dz , holding G constant, we find the chain rule:

$$\boxed{\left(\frac{\partial x}{\partial z}\right)_G = \left(\frac{\partial x}{\partial y}\right)_G \left(\frac{\partial y}{\partial z}\right)_G.} \quad (\text{A.19})$$

Note the common G outside each partial differential.

Other relations may be constructed when needed. For example, suppose again that x , y and z are not independent. We again may write $x = x(y, z)$ and form a differential for x :

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz. \quad (\text{A.20})$$

Let us consider some other function H , also of y and z . The derivative of x with respect to z at constant H (not to be confused with the partial derivative of x with respect to z at constant y) can be found by dividing both sides by dz , holding H constant:

$$\left(\frac{\partial x}{\partial z}\right)_H = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_H + \left(\frac{\partial x}{\partial z}\right)_y. \quad (\text{A.21})$$

A.3 Geometric series

The geometric series $S_n(x)$ is defined as

$$S_n(x) = \sum_{k=0}^n x^k = 1 + x + x^2 + \dots + x^n. \quad (\text{A.22})$$

Multiplying both sides by x we find

$$xS_n(x) = x + x^2 + x^3 + \dots + x^{n+1}. \quad (\text{A.23})$$

Subtracting these two equations yields

$$(1-x)S_n(x) = 1 - x^{n+1}. \quad (\text{A.24})$$

So we find

$$\boxed{\sum_{k=0}^n x^k = \frac{1 - x^{n+1}}{1 - x}.} \quad (\text{A.25})$$

For $-1 < x < 1$ the series converges as $n \rightarrow \infty$, in which case

$$\sum_{k=0}^{\infty} x^k = \frac{1}{1-x} \quad (|x| < 1). \quad (\text{A.26})$$

A.4 Taylor series

A Taylor series is a series expansion of a function around a certain point. In one dimension, the Taylor series of a function f around the point $x = a$ is given by

$$f(x) = f(a) + f'(a)(x-a) + \frac{1}{2}f''(a)(x-a)^2 + \frac{1}{6}f'''(a)(x-a)^3 + \dots + \frac{1}{n!}f^{(n)}(a)(x-a)^n + \dots, \quad (\text{A.27})$$

where $f^{(n)}(a)$ denotes the n -th derivative of f at $x = a$.

Here follow a few examples:

$$\exp(x) = 1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \dots + \frac{1}{n!}x^n + \dots \quad (\text{A.28})$$

$$\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \dots + \frac{(-1)^{n-1}}{n}x^n + \dots \quad (\text{A.29})$$

$$\cos(x) = 1 - \frac{1}{2}x^2 + \frac{1}{24}x^4 + \dots + \frac{\cos(n\pi/2)}{n!}x^n + \dots \quad (\text{A.30})$$

$$\sin(x) = x - \frac{1}{6}x^3 + \frac{1}{120}x^5 + \dots + \frac{\sin(n\pi/2)}{n!}x^n + \dots \quad (\text{A.31})$$

A.5 Logarithms and exponentials

When manipulating logarithms and exponentials remember the following rules:

$$\exp(a+b) = \exp(a)\exp(b) \quad (\text{A.32})$$

$$\exp(a \ln b) = b^a \quad (\text{A.33})$$

$$\exp(ab) = (\exp(a))^b = (\exp(b))^a \quad (\text{A.34})$$

$$\ln(ab) = \ln(a) + \ln(b) \quad (\text{A.35})$$

$$\ln(b^a) = a \ln(b) \quad (\text{A.36})$$

Derivatives are given by

$$\frac{d}{dx} b \exp(ax) = ab \exp(ax) \quad (\text{A.37})$$

$$\frac{d}{dx} a^x = \ln(a) a^x \quad (\text{A.38})$$

$$\frac{d}{dx} b \ln(cx^a) = b \frac{a}{x} \quad (\text{A.39})$$

and integrals by

$$\int \exp(ax) dx = \frac{1}{a} \exp(ax) \quad (\text{A.40})$$

$$\int \ln(ax) dx = x \ln(ax) - x \quad (\text{A.41})$$

A.6 Physical constants

Planck's constant, $h = 6.62607 \times 10^{-34}$ J s

atomic mass unit, $u = 1.66054 \times 10^{-27}$ kg

Boltzmann's constant, $k_B = 1.38065 \times 10^{-23}$ J/K

Avogadro's number, $N_{Av} = 6.02214 \times 10^{23}$ mol⁻¹

Universal gas constant, $R = 8.3145$ J/K mol⁻¹

Speed of light, $c = 2.99792 \times 10^8$ m/s