

Chapter 8

Classical Gases and Liquids

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8.1 Introduction

Because there are only a few problems in statistical mechanics that can be solved exactly, we need to find approximate solutions. We introduce several perturbation methods that are applicable when there is a small expansion parameter. Our discussion of interacting classical particle systems will involve some of the same considerations and difficulties that are encountered in quantum field theory (no knowledge of the latter is assumed). For example, we will introduce diagrams that are analogous to Feynman diagrams and find divergences analogous to those found in quantum electrodynamics. We also discuss the spatial correlations between particles due to their interactions and the use of hard spheres as a reference system for understanding the properties of dense fluids.

8.2 Density Expansion

Consider a gas of N identical particles each of mass m at density $\rho = N/V$ and temperature T . We will assume that the total potential energy U is a sum of two-body interactions $u_{ij} = u(|\mathbf{r}_i - \mathbf{r}_j|)$, and write U as

$$U = \sum_{i < j}^N u_{ij}. \quad (8.1)$$

The exact form of $u(r)$ for electrically neutral molecules and atoms must be constructed by a first principles quantum mechanical calculation. Such a calculation is very difficult, and for many purposes it is sufficient to choose a simple phenomenological form for $u(r)$. The most important features of $u(r)$ are a strong repulsion for small r and a weak attraction at large r . A common

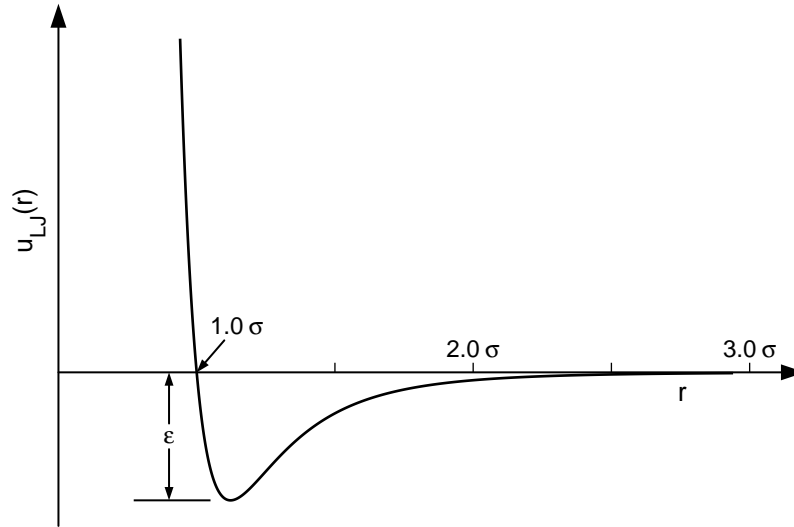


Figure 8.1: Plot of the Lennard-Jones potential $u_{\text{LJ}}(r)$, where r is the distance between the particles. The potential is characterized by a length σ and an energy ϵ .

phenomenological form of $u(r)$ is the *Lennard-Jones* or 6-12 potential shown in Figure 8.1:

$$u_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (8.2)$$

The values of σ and ϵ for argon are $\sigma = 3.4 \times 10^{-10}$ m and $\epsilon = 1.65 \times 10^{-21}$ J.

The attractive $1/r^6$ contribution to the Lennard-Jones potential is due to the induced dipole-dipole interaction of two neutral atoms.¹ The resultant attractive interaction is called the *van der Waals* potential. The rapidly increasing repulsive interaction as the separation between atoms is decreased for small r is a consequence of the Pauli exclusion principle. The $1/r^{12}$ form of the repulsive potential in (8.2) is chosen only for convenience.

The existence of many calculations and simulation results for the Lennard-Jones potential encourages us to consider it even though there are more accurate forms of the interparticle potential for modeling the interactions in real fluids, proteins, and other complex molecules.

An even simpler form of the interaction between particles is the *hard core* interaction

$$u_{\text{HC}}(r) = \begin{cases} \infty & (r < \sigma) \\ 0 & (r > \sigma) \end{cases} \quad (8.3)$$

A system of particles in three dimensions with the interaction (8.3) is called a system of *hard spheres* with σ the diameter of the spheres; the analogous systems in two and one dimensions are called *hard disks* and *hard rods*. Although this interaction has no attractive part, we will see that it is very useful in understanding the properties of liquids.

¹A simple classical model of this induced dipole-dipole effect is described in John J. Brehm and William J. Mullin, *Introduction to the Structure of Matter*, John Wiley & Sons (1989), pp. 517–521.

Both the hard core interaction and Lennard-Jones potential are short-range. The hard core interaction is zero for $r > \sigma$ and the Lennard-Jones potential can often be neglected for $r \gtrsim 2.3\sigma$.²

Problem 8.1. The Lennard-Jones potential

- (a) Show that the minimum of the Lennard-Jones potential is at $r_{\min} = 2^{1/6}\sigma$ and that $u_{\text{LJ}}(r_{\min}) = -\epsilon$.
- (b) Given a potential $u(r)$, the force in the radial direction is given by $f(r) = -du(r)/dr$. At what value of r is $f_{\text{LJ}}(r) = -du_{\text{LJ}}(r)/dr$ a minimum?
- (c) What is the value of $u_{\text{LJ}}(r)$ at $r = 2.3\sigma$? □

We will consider only classical systems in this chapter and hence assume that the condition $\lambda \ll n^{-1/3}$ is satisfied. The partition function for N identical particles in the semiclassical limit is given by (see Section 6.2)

$$Z_N = \frac{1}{N! h^{3N}} \int e^{-\beta(K+U)} d\mathbf{p}_1 d\mathbf{p}_2 \dots d\mathbf{p}_N d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N, \quad (8.4)$$

where the kinetic energy $K = \sum_i p_i^2/2m$ and the potential energy U is given in (8.1).

Because the potential energy does not depend on the momenta of the particles and the kinetic energy does not depend on the positions of the particles, we can write Z_N in the form

$$Z_N = \frac{1}{N! h^{3N}} \int e^{-\beta K} d\mathbf{p}_1 d\mathbf{p}_2 \dots d\mathbf{p}_N \int e^{-\beta U} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (8.5a)$$

$$= \frac{V^N}{N! h^{3N}} \int e^{-\beta K} d\mathbf{p}_1 d\mathbf{p}_2 \dots d\mathbf{p}_N \frac{1}{V^N} \int e^{-\beta U} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (8.5b)$$

$$= Z_{\text{ideal}} \frac{1}{V^N} \int e^{-\beta U} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N, \quad (8.5c)$$

where

$$Z_{\text{ideal}} = \frac{1}{N! h^{3N}} V^N \int e^{-\beta K} d\mathbf{p}_1 d\mathbf{p}_2 \dots d\mathbf{p}_N. \quad (8.6)$$

The factor of V^N in (8.6) is due to the integration over \mathbf{r} with $U = 0$. It is straightforward to do the momentum integrals in (8.6); the result for Z_{ideal} is given in (6.25). The corresponding free energy of an ideal classical gas is $F_{\text{ideal}} = -kT \ln Z_{\text{ideal}}$ (see (6.26), page 299).

We adopt the notation $\langle \dots \rangle_0$ to denote an average over the positions of the particles in an ideal gas. That is, each particle in an ideal classical gas has a probability $d\mathbf{r}/V$ of being in the volume $d\mathbf{r}$. We use this notation to rewrite (8.5c) as

$$Z_N = Z_{\text{ideal}} \langle e^{-\beta U} \rangle_0. \quad (8.7)$$

²Because the Lennard-Jones potential at $r = 2.3\sigma$ is not exactly zero, truncating it at $r = 2.3\sigma$ introduces a discontinuity in the potential. This discontinuity can be avoided by adding a constant to the potential so that $u_{\text{LJ}} = 0$ at $r = 2.3\sigma$.

The contribution F_c to the free energy from the correlations between the particles due to their interactions has the form

$$F_c = F - F_{\text{ideal}} = -kT \ln \frac{Z}{Z_{\text{ideal}}} = -kT \ln \langle e^{-\beta U} \rangle_0. \quad (8.8)$$

We see that the evaluation of the free energy due to the interactions between particles can be reduced to the evaluation of the ensemble average in (8.8).

In general, we cannot calculate F_c exactly for arbitrary densities. We know that the ideal gas equation of state, $PV/NkT = 1$, is a good approximation for a dilute gas for which the intermolecular interactions can be ignored. For this reason we first seek an approximation for F_c for low densities where the interactions between the particles are not too important. If the interactions are short-range, it is plausible that we can obtain an expansion of the pressure and hence F_c in powers of the density. This expansion is known as the density or *virial expansion*³ and is written as

$$\frac{PV}{NkT} = 1 + \rho B_2(T) + \rho^2 B_3(T) + \rho^3 B_4(T) + \dots \quad (8.9)$$

The quantities B_n are known as *virial coefficients* and involve the interaction of n particles. The first four virial coefficients are given by the expressions ($B_1 = 1$)

$$B_2(T) = -\frac{1}{2V} \int f_{12} \, d\mathbf{r}_1 d\mathbf{r}_2, \quad (8.10a)$$

$$B_3(T) = -\frac{1}{3V} \int f_{12} f_{13} f_{23} \, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3, \quad (8.10b)$$

$$B_4(T) = -\frac{1}{8V} \int (3f_{12} f_{23} f_{34} f_{41} + 6f_{12} f_{23} f_{34} f_{41} f_{13} + f_{12} f_{23} f_{34} f_{41} f_{13} f_{24}) \, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4, \quad (8.10c)$$

where $f_{ij} = f(|\mathbf{r}_i - \mathbf{r}_j|)$, and

$$\boxed{f(r) = e^{-\beta u(r)} - 1}. \quad (8.11)$$

The function $f(r)$ defined in (8.11) is known as the *Mayer f function*.⁴ We will give a simple derivation of the second virial coefficient in Section 8.3. The derivation of the third and higher order virial coefficients is much more involved and is given in Section 8.4.3.

Problem 8.2. Density expansion of the free energy

The density expansion of the free energy F_c is usually written as

$$-\beta \frac{F_c}{N} = \sum_{p=1}^{\infty} \frac{b_p \rho^p}{p+1}, \quad (8.12)$$

³The word *virial* is related to the Latin word for force. Rudolf Clausius named a certain function of the force between particles as “the virial of force.” This name was subsequently applied to the virial expansion because the terms in this expansion are related to the forces between particles.

⁴The f function is named after Joseph Mayer (1920–1983), a chemical physicist who is known for his work in statistical mechanics and the application of statistical mechanics to liquids and dense gases. He was the husband of Maria Goeppert Mayer (1906–1972), who shared the Nobel Prize for physics in 1963. Maria Goeppert Mayer was not able to obtain a tenured faculty position until 1960 because of sexism and nepotism rules. The two of them wrote an influential text on statistical mechanics, J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, John Wiley & Sons (1940).

where the b_p are known as *cluster integrals*. Use the thermodynamic relation $P = \partial F / \partial V_{T,V}$ between the pressure and the free energy to show that B_n and b_{n-1} are related by

$$B_n = -\frac{n-1}{n} b_{n-1}. \quad (8.13)$$

□

The density expansion in (8.9) and (8.12) is among the few expansions known in physics that has a nonzero radius of convergence for a wide class of interparticle potentials. Most expansions, such as the low temperature expansion for the ideal Fermi gas, do not converge (see Section 6.11.2).

8.3 The Second Virial Coefficient

We first find the form of the second virial coefficient B_2 by simple considerations. One way is to calculate the partition function for a small number of particles and to determine the effects of including the interactions between particles. For $N = 2$ particles we have

$$\frac{Z_2}{Z_{\text{ideal}}} = \frac{1}{V^2} \int e^{-\beta u_{12}} d\mathbf{r}_1 d\mathbf{r}_2, \quad (8.14)$$

where Z_{ideal} is the partition function for an ideal gas of two particles. We can simplify the integrals in (8.14) by choosing particle 1 as the origin and specifying the position of particle 2 relative to particle 1.⁵ This choice of coordinates gives a factor of V because particle 1 can be anywhere in the box. Hence, we can write (8.14) as

$$\frac{Z_2}{Z_{\text{ideal}}} = \frac{1}{V} \int e^{-\beta u(r)} d\mathbf{r}, \quad (8.15)$$

where $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ and $r = |\mathbf{r}|$.

Because we wish to describe a dilute gas, we might consider writing $e^{-\beta u} \approx 1 - \beta u$, thinking that u is small because the particles rarely interact. However, because $u(r) \gg 1$ for sufficiently small r , the integral $\int u(r) d\mathbf{r}$ diverges. That is, the particles rarely interact, but if they do, they interact strongly.

Another difficulty is that the function $e^{-\beta u(r)}$ in the integrand for Z_2 has the undesirable property that it approaches one rather than zero as $r \rightarrow \infty$. Because we want to obtain an expansion in the density, we want to write the integrand in (8.15) in terms of a function of r that is significant only if two particles are close to each other. Such a function is the Mayer function $f(r)$ defined in (8.11). Hence we write $e^{-\beta u(r)} = 1 + f(r)$ and express (8.15) as

$$\frac{Z_2}{Z_{\text{ideal}}} = \frac{1}{V} \int [1 + f(r)] d\mathbf{r}. \quad (8.16)$$

In Problem 8.3 we show that $f(r) \rightarrow 0$ for sufficiently large r for short-range potentials.

⁵This choice is equivalent to defining the coordinate system $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ and replacing $d\mathbf{r}_1 d\mathbf{r}_2$ by $d\mathbf{R} d\mathbf{r}$. Because the integrand is independent of \mathbf{R} , we can do the integral over \mathbf{R} and obtain a factor of V .

The first term in the integrand in (8.16) corresponds to no interactions and the second term corresponds to the second virial coefficient B_2 defined in (8.10a). To see this correspondence we choose particle 1 as the origin as before, and rewrite (8.10a) for B_2 as

$$B_2 = -\frac{1}{2} \int f(r) dr. \quad (8.17)$$

If we compare the form (8.16) and (8.17), we see that we can express Z_2/Z_{ideal} in terms of B_2 :

$$\frac{Z_2}{Z_{\text{ideal}}} = 1 - \frac{2}{V} B_2. \quad (8.18)$$

We next evaluate Z_N/Z_{ideal} for $N = 3$ particles. We have

$$\frac{Z_3}{Z_{\text{ideal}}} = \frac{1}{V^3} \int e^{-\beta \sum u_{ij}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \quad (8.19a)$$

$$= \frac{1}{V^3} \int \prod_{i<j} (1 + f_{ij}) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \quad (8.19b)$$

$$= \frac{1}{V^3} \int [(1 + f_{12})(1 + f_{13})(1 + f_{23})] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \quad (8.19c)$$

$$= \frac{1}{V^3} \int [1 + (f_{12} + f_{13} + f_{23}) + (f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23}) + f_{12}f_{13}f_{23}] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (8.19d)$$

If we keep only the first term in (8.19d), we recover the ideal gas result $Z/Z_{\text{ideal}} = 1$. It is plausible that only the second sum in (8.19d) involving pairs of particles is important for low densities. Hence, we ignore the remaining terms involving products of two and three products of f . Because the three terms f_{12} , f_{13} , and f_{23} give the same contribution, we have

$$\frac{Z_3}{Z_{\text{ideal}}} \approx 1 + \frac{3}{V} \int f(r) dr = 1 - \frac{6}{V} B_2. \quad (8.20)$$

From the form of Z_2/Z_{ideal} and Z_3/Z_{ideal} we can guess the form of Z_N/Z_{ideal} which includes only the second virial coefficient:

$$\frac{Z_N}{Z_{\text{ideal}}} \approx 1 - \frac{N(N-1)}{V} B_2. \quad (8.21)$$

Because $N-1 \approx N$ for $N \gg 1$ and $\rho = N/V$, we have

$$\frac{Z_N}{Z_{\text{ideal}}} \approx 1 - N\rho B_2, \quad (8.22)$$

which is the same form that we will now derive for large N . You might wish to skip to the discussion after (8.27).

For arbitrary N we have

$$\frac{Z_N}{Z_{\text{ideal}}} = \frac{1}{V^N} \int e^{-\beta \sum u_{ij}} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (8.23a)$$

$$= \frac{1}{V^N} \int \prod_{i<j} (1 + f_{ij}) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (8.23b)$$

We write

$$\prod_{i < j} (1 + f_{ij}) = 1 + \sum_{k < l} f_{kl} + \sum_{k < l, m < n} f_{kl} f_{mn} + \dots \quad (8.24)$$

We keep only the ideal gas contribution and the terms involving pairs of particles and ignore the remaining terms involving products of two or more f 's. There are a total of $\frac{1}{2}N(N-1)$ terms in the sum $\sum f_{kl}$ corresponding to the number of ways of choosing pairs of particles. These terms are all equal because they differ only in the way the variables of integration are labeled. Hence, we can express the integral of the second sum in (8.24) as

$$\frac{1}{V^N} \int \sum_{k < l} f_{kl} d\mathbf{r}_1 \dots d\mathbf{r}_N = \frac{1}{V^N} \frac{N(N-1)}{2} \int f(r_{12}) d\mathbf{r}_1 \dots d\mathbf{r}_N. \quad (8.25)$$

The integration with respect to $\mathbf{r}_3 \dots \mathbf{r}_N$ over the volume of the system gives a factor of V^{N-2} .

As before, we can simplify the remaining integration over \mathbf{r}_1 and \mathbf{r}_2 by choosing particle 1 as the origin and specifying particle 2 relative to particle 1. In this way we obtain an additional factor of V . Hence, we can write the right-hand side of (8.25) as

$$\frac{N(N-1)}{2} \frac{V^{N-2}V}{V^N} \int f(r) d\mathbf{r} \rightarrow \frac{N^2}{2V} \int f(r) d\mathbf{r}, \quad (8.26)$$

where we have again replaced $N-1$ by N . We identify the integral in (8.26) with B_2 and write

$$\frac{Z_N}{Z_{\text{ideal}}} \approx 1 - N\rho B_2, \quad (8.27)$$

as in (8.22).

If the interparticle potential $u(r) \approx 0$ for $r > r_0$, then $f(r)$ differs from zero only for $r < r_0$ and the integral B_2 is bounded and is order r_0^3 in three dimensions (see Problem 8.4). Hence B_2 is independent of V and is an intensive quantity. This well-behaved nature of B_2 implies that the second term in (8.27) is proportional to N and in the limit $N \rightarrow \infty$ (for fixed density), this term is larger than the first – not a good start for a perturbation theory.

The reason we have obtained an apparent divergence in the density expansion of Z_N/Z_{ideal} is that we have calculated the wrong quantity. The quantity of physical interest is the free energy F or $\ln Z$, not the partition function Z . Because F is an extensive quantity and is proportional to N , it follows from the relation $F = -kT \ln Z$ that Z_N must depend on the N th power of an intensive quantity. Hence, we expect the form of the density expansion of Z_N/Z_{ideal} to be

$$\frac{Z_N}{Z_{\text{ideal}}} = (1 + a_1\rho + a_2\rho^2 + \dots)^N, \quad (8.28)$$

where a_n are unknown coefficients. Hence we should rewrite (8.27)

$$\frac{Z_N}{Z_{\text{ideal}}} \approx 1 - N\rho B_2 \approx (1 - \rho B_2)^N, \quad (8.29)$$

so that F is proportional to N and the correct first-order dependence on ρ is obtained. The free energy is given by

$$F = F_{\text{ideal}} - NkT \ln(1 - \rho B_2) \approx F_{\text{ideal}} + NkT \rho B_2, \quad (8.30)$$

where we have used the fact that $\ln(1+x) \approx x$ for $x \ll 1$. The corresponding equation of state is given by

$$\frac{PV}{NkT} = 1 + \rho B_2, \quad (8.31)$$

where we have used the relation $P = -(\partial F/\partial V)_{T,N}$.

The second term in (8.31) represents the first-order density correction to the ideal gas equation of state. Because B_2 is order r_0^3 , the density expansion for a dilute gas is actually an expansion in powers of the dimensionless quantity ρr_0^3 (see Problem 8.5).

Problem 8.3. Qualitative behavior of the Mayer function

Plot the Mayer function $f(r)$ for the hard core interaction (8.3) and the Lennard-Jones potential (8.2). Does $f(r)$ depend on T for hard spheres? What is the qualitative behavior of $f(r)$ for large r ? \square

Problem 8.4. Second virial coefficient for hard spheres

- (a) To calculate B_2 in three dimensions we need to perform the angular integrations in (8.17). Show that because $u(r)$ depends only on r , B_2 can be written as

$$B_2(T) = -\frac{1}{2} \int f(r) d^3r = 2\pi \int_0^\infty [1 - e^{-\beta u(r)}] r^2 dr. \quad (8.32)$$

- (b) Show that $B_2 = 2\pi\sigma^3/3$ for a system of hard spheres of diameter σ .

- (c) Determine the form of B_2 for a system of hard disks. \square

Problem 8.5. Qualitative temperature behavior of $B_2(T)$

Suppose that $u(r)$ has the qualitative behavior shown in Figure 8.1; that is, $u(r)$ is repulsive for small r and weakly attractive for large r . Let r_0 equal the value of r at which $u(r)$ is a minimum (see Problem 8.1) and ϵ equal the value of u at its minimum. We can write (8.32) as

$$B_2(T) = 2\pi \int_0^{r_0} [1 - e^{-\beta u(r)}] r^2 dr + 2\pi \int_{r_0}^\infty [1 - e^{-\beta u(r)}] r^2 dr. \quad (8.33)$$

- (a) For high temperatures, $kT \gg \epsilon$, we have $u(r)/kT \ll 1$ for $r > r_0$. Explain why the second integral in (8.33) can be neglected in this limit (assuming that the integral $\int_{r_0}^\infty u(r)r^2 dr$ converges) and why the dominant contribution to B_2 is determined by the first integral, for which the integrand is approximately one because $u(r)/kT$ is large and positive for $r < r_0$. Hence for high temperatures show that $B_2(T) \approx b$, where

$$b = 2\pi r_0^3/3. \quad (8.34)$$

We can interpret r_0 as a measure of the effective diameter of the atoms. How is the parameter b related to the “volume” of a particle?

- (b) For low temperatures, $kT \ll \epsilon$, the dominant contribution to B_2 is determined by the second term in (8.33). What is the sign of $u(r)$ for $r > r_0$? Show that in this limit $B_2 \approx -a/kT$, where

$$a = -2\pi \int_{r_0}^{\infty} u(r) r^2 dr. \quad (8.35)$$

The parameter a is a measure of the strength of the attractive interaction between the particles.

- (c) The limits considered in parts (a) and (b) suggest that B_2 can be approximated as

$$B_2 = b - \frac{a}{kT}, \quad (8.36)$$

where b is given by (8.34) and a is given by (8.35). Why does $B_2(T)$ pass through zero at some intermediate temperature? The temperature at which $B_2(T) = 0$ is known as the Boyle temperature. The temperature dependence of B_2 is explored further in Problem 8.30. \square

Problem 8.6. The second-order virial coefficient for the van der Waals equation

Show that the van der Waals pressure equation of state (2.12) can be expressed as

$$\frac{PV}{NkT} = \frac{1}{1 - \rho b} - \frac{a\rho}{kT}. \quad (8.37)$$

Expand the right-hand side of (8.37) in powers of ρ and find the form of B_2 implied by the van der Waals equation of state. \square

Motivation of the van der Waals equation of state. In Problem 8.5 we found that B_2 can be written in the approximate form (8.36). This form of B_2 allows us to write the equation of state as (see (8.31))

$$P \approx \frac{NkT}{V} \left[1 + \rho b - \frac{\rho a}{kT} \right], \quad (8.38a)$$

or

$$P \approx \rho kT \left[\frac{1}{1 - \rho b} - \frac{\rho a}{kT} \right] = \frac{\rho kT}{1 - \rho b} - \rho^2 a. \quad (8.38b)$$

We have made the approximation that $1 + \rho b \approx 1/(1 - \rho b)$, which is consistent with our assumption that $\rho b \ll 1$. The approximate equation of state in (8.38b) is the van der Waals equation of state. A more systematic derivation of the van der Waals equation of state is given in Section 8.6.1.

Problem 8.7. Long-range interactions

Assume that $u(r)$ has the form $u(r) \sim r^{-n}$ for large r .

- (a) What is the r -dependence of $f(r)$ for large r ?
- (b) What is the condition on n such that the integral in (8.32) for B_2 exists? Consider the r -dependence of the integrand of B_2 for large r only.
- (c) Why is it plausible that the density expansion (8.8) is not applicable to a system of particles with a long-range interaction proportional to $1/r$ (the Coulomb potential)? \square

8.4 *Diagrammatic Expansions

In Section 8.3 we found that we had to make some ad hoc assumptions to obtain the form of B_2 from an expansion of Z/Z_{ideal} . To find the form of the higher order virial coefficients more systematically, we will introduce a formalism that allows us to obtain a density expansion of the free energy directly rather than first approximating the partition function. In Section 8.4.2 we first obtain the expansion of the free energy in powers of the inverse temperature β . We will find that it is convenient to represent the contributions to the free energy due to the interactions between particles in terms of diagrams. We rearrange this expansion in Section 8.4.3 so that it becomes an expansion in powers of the density ρ .

8.4.1 *Cumulants

The form (8.8) for F_c is similar to that frequently encountered in probability theory (see Section 3.11.2, page 157). We define the function $\phi(t)$ as

$$\phi(t) \equiv \langle e^{tx} \rangle, \quad (8.39)$$

where the random variable x occurs according to the probability distribution $p(x)$, that is, the average denoted by $\langle \dots \rangle$ is over $p(x)$. The function $\phi(t)$ is an example of a *moment generating function* because a power series expansion in t yields

$$\phi(t) = \langle [1 + tx + \frac{1}{2!}t^2x^2 + \dots] \rangle \quad (8.40a)$$

$$= 1 + t\langle x \rangle + \frac{t^2}{2!}\langle x^2 \rangle + \dots \quad (8.40b)$$

$$= \sum_{n=0}^{\infty} \frac{t^n \langle x^n \rangle}{n!}. \quad (8.40c)$$

In the present case the quantity of interest is proportional to $\ln Z$, so we want to consider the series expansion of $\ln \phi$ rather than ϕ . (The correspondence is $t \rightarrow -\beta$ and $x \rightarrow U$.) The series expansion of $\ln \phi(t)$ can be written in the form

$$\ln \phi = \ln \langle e^{tx} \rangle = \sum_{n=1}^{\infty} \frac{t^n M_n(x)}{n!}, \quad (8.41)$$

where the coefficients M_n are known as *cumulants*. The first four cumulants are

$$M_1 = \langle x \rangle, \quad (8.42a)$$

$$M_2 = \langle x^2 \rangle - \langle x \rangle^2, \quad (8.42b)$$

$$M_3 = \langle x^3 \rangle - 3\langle x^2 \rangle \langle x \rangle + 2\langle x \rangle^3, \quad (8.42c)$$

$$M_4 = \langle x^4 \rangle - 4\langle x^3 \rangle \langle x \rangle - 3\langle x^2 \rangle^2 + 12\langle x^2 \rangle \langle x \rangle^2 - 6\langle x \rangle^4. \quad (8.42d)$$

Problem 8.8. The first four cumulants

Expand $\ln(1+x)$ in a Taylor series (see (A.4)) and obtain the expressions for M_n given in (8.42). \square

The advantage of working with cumulants can be seen by considering two independent random variables, x and y . Because x and y are statistically independent, we have $\langle xy \rangle = \langle x \rangle \langle y \rangle$, and

$$\ln \langle e^{t(x+y)} \rangle = \ln \langle e^{tx} \rangle \langle e^{ty} \rangle = \ln \langle e^{tx} \rangle + \ln \langle e^{ty} \rangle. \quad (8.43)$$

From the relation

$$\ln \langle e^{t(x+y)} \rangle = \sum_{n=0}^{\infty} \frac{t^n}{n!} M_n(x+y), \quad (8.44)$$

we see that M_n satisfies the additive property:

$$M_n(x+y) = M_n(x) + M_n(y). \quad (8.45)$$

The relation (8.45) implies that all cross terms in M_n involving independent variables vanish, and hence $\ln \phi(x)$ is an extensive or additive quantity.

Example 8.1. Cancellation of cross terms in M_2

Show that the cross terms cancel in M_2 .

Solution. We have

$$M_2(x+y) = \langle (x+y)^2 \rangle - \langle (x+y) \rangle^2 \quad (8.46a)$$

$$= \langle x^2 \rangle + 2\langle x \rangle \langle y \rangle + \langle y^2 \rangle - \langle x \rangle^2 - 2\langle x \rangle \langle y \rangle + \langle y \rangle^2 \quad (8.46b)$$

$$= \langle x^2 \rangle - \langle x \rangle^2 + \langle y^2 \rangle - \langle y \rangle^2 \quad (8.46c)$$

$$= M_2(x) + M_2(y). \quad (8.46d)$$

\diamond

Problem 8.9. Cancellation of cross terms in M_3

As an example of the cancellation of cross terms, consider $M_3(x+y)$. From (8.42c) we see that $M_3(x+y)$ is given by

$$M_3(x+y) = \overline{(x+y)^3} - 3\overline{(x+y)^2} \overline{(x+y)} + 2\overline{(x+y)}^3 \quad (8.47)$$

Show explicitly that all cross terms cancel and hence that $M_3(x+y) = M_3(x) + M_3(y)$. \square

8.4.2 *High temperature expansion

Now that we have discussed the formal properties of the cumulants, we can use these properties to evaluate F_c . According to (8.8) and (8.41) we can write F_c as

$$-\beta F_c = \ln \langle e^{-\beta U} \rangle_0 = \sum_{n=1}^{\infty} \frac{(-\beta)^n}{n!} M_n. \quad (8.48)$$

The expansion (8.48) in powers of β is known as a *high temperature expansion*. Such an expansion is natural because β is the only parameter that appears explicitly in (8.48). The parameter β actually appears in the dimensionless combination βu_0 , where the energy u_0 is a measure of the strength of the interaction. Although we can choose β to be as small as we wish, the interparticle interaction for potentials such as the Lennard-Jones potential is strongly repulsive at short distances (see Figure 8.1), and hence ϵ is not well defined. For this reason a strategy based on expanding in the parameter β is not physically reasonable for an interaction such as the Lennard-Jones potential.

Because of these difficulties, we will first do what we can and then do what we want. Thus we will first determine the high temperature expansion coefficients M_n and assume that the potential is not strongly repulsive for small r . For example, we can choose $u(r)$ to have the form $u(r) = u_0 e^{-r^2/a^2}$ for small r . Then we will find that we can reorder the high temperature expansion to obtain a power series expansion in the density. Because it will be easy to become lost in the details, we emphasize that the main points of this section are the association of diagrams with the various contributions to the cumulants and the fact that only certain kinds of diagrams actually contribute to the free energy.

The first cumulant in the expansion (8.48) is the average of the total potential energy:

$$M_1 = \langle U \rangle = \frac{1}{V^N} \int \sum_{i < j} u_{ij} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (8.49)$$

Because every term in the sum gives the same contribution, we have

$$M_1 = \frac{1}{2} N(N-1) \frac{1}{V^N} \int u_{12} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (8.50a)$$

$$= \frac{1}{2} N(N-1) \frac{1}{V^N} V^{N-2} \int u_{12} d\mathbf{r}_1 d\mathbf{r}_2 \quad (8.50b)$$

$$= \frac{1}{2} N(N-1) \frac{1}{V^2} \int u_{12} d\mathbf{r}_1 d\mathbf{r}_2. \quad (8.50c)$$

The combinatorial factor $\frac{1}{2}N(N-1)$ is the number of terms in the sum. Because we are interested in the limit $N \rightarrow \infty$, we replace $N-1$ by N . We can simplify (8.50c) further by measuring the position of particle 2 from particle 1. We obtain

$$M_1 = \frac{N^2}{2V^2} V \int u(r) d\mathbf{r}, \quad (8.51a)$$

or

$$M_1 = \frac{\rho}{2} N \int u(r) d\mathbf{r}. \quad (8.51b)$$

Note that M_1 is an extensive quantity as is the free energy; that is, M_1 is proportional to N . Note that the integral in (8.51b) diverges for small r for the Lennard-Jones potential (8.2) and the hard core interaction (8.3), but converges for a Gaussian potential.

We next consider M_2 which is given by

$$M_2 = \langle U^2 \rangle - \langle U \rangle^2, \quad (8.52)$$

where

$$\langle U \rangle = \sum_{i < j} \sum_j \langle u_{ij} \rangle, \quad (8.53)$$

and

$$\langle U^2 \rangle = \sum_{i < j} \sum_j \sum_{k < l} \sum_l \langle u_{ij} u_{kl} \rangle, \quad (8.54)$$

The various terms in (8.54) and (8.53) may be classified according to the number of subscripts in common. As an example, consider a system of $N = 4$ particles. We have

$$U = \sum_{i < j=1}^{N=4} u_{ij} = u_{12} + u_{13} + u_{14} + u_{23} + u_{24} + u_{34}, \quad (8.55)$$

and

$$\begin{aligned} U^2 = & [u_{12}^2 + u_{13}^2 + u_{14}^2 + u_{23}^2 + u_{24}^2 + u_{34}^2] \\ & + 2[u_{12}u_{13} + u_{12}u_{14} + u_{12}u_{23} + u_{12}u_{24} + u_{13}u_{14} + u_{13}u_{23} \\ & + u_{13}u_{34} + u_{14}u_{24} + u_{14}u_{34} + u_{23}u_{24} + u_{23}u_{34} + u_{24}u_{34}] \\ & + 2[u_{12}u_{34} + u_{13}u_{24} + u_{14}u_{23}]. \end{aligned} \quad (8.56)$$

An inspection of (8.56) shows that the 36 terms in (8.56) can be grouped into three classes:

No indices in common (disconnected terms). A typical disconnected term is $\langle u_{12}u_{34} \rangle$. Because the variables \mathbf{r}_{12} and \mathbf{r}_{34} are independent, u_{12} and u_{34} are independent, and we can write

$$\langle u_{12}u_{34} \rangle = \langle u_{12} \rangle \langle u_{34} \rangle. \quad (8.57)$$

From (8.45) we know that every disconnected term such as the one in (8.57) is a cross term that is canceled if all terms in M_2 are included.

One index in common (reducible terms). An example of a reducible term is $\langle u_{12}u_{23} \rangle$. Such a term also factorizes because of the homogeneity of space. We choose particle 2 as the origin and integrate over \mathbf{r}_1 and \mathbf{r}_3 and find

$$\langle u_{12}u_{23} \rangle = \frac{1}{V^3} \int u_{12} u_{23} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \quad (8.58a)$$

$$= \frac{1}{V^2} \int u_{12} u_{23} d\mathbf{r}_{12} d\mathbf{r}_{23} \quad (8.58b)$$

$$= \langle u_{12} \rangle \langle u_{23} \rangle. \quad (8.58c)$$

A factor of V was obtained because particle 2 can be anywhere in the box of volume V . Again we find that the variables $u_{12}u_{23}$ are independent and hence are canceled by other terms in M_2 .

Both pairs of indices in common (irreducible terms). An example of an irreducible term is $\langle u_{12}^2 \rangle$. The corresponding contribution to M_2 is (see (8.52))

$$M_2 = \sum_{i < j=1}^N [\langle u_{ij}^2 \rangle - \langle u_{ij} \rangle^2]. \quad (8.59)$$

We can simplify (8.59) by comparing the magnitude of the two types of terms in the limit $N \rightarrow \infty$. We have that

$$\langle u_{ij}^2 \rangle = \frac{1}{V} \int u_{ij}^2 d\mathbf{r}_{ij} \propto \frac{1}{V} \propto O\left(\frac{1}{N}\right). \quad (8.60a)$$

$$\langle u_{ij} \rangle^2 = \left(\frac{1}{V} \int u_{ij} d\mathbf{r}_{ij} \right)^2 \propto O\left(\frac{1}{N^2}\right). \quad (8.60b)$$

We see that we can ignore the second term in comparison to the first.

These considerations lead us to the desired form of M_2 . Because there are $N(N-1)/2$ identical contributions such as (8.60a) to M_2 in (8.59), we obtain

$$M_2 = \frac{N(N-1)}{2V} \int u^2(\mathbf{r}) d\mathbf{r} \rightarrow \frac{\rho}{2} N \int u^2(\mathbf{r}) d\mathbf{r}. \quad (8.61)$$

The most important result of our evaluation of M_1 and M_2 is that the disconnected and reducible contributions do not contribute. The vanishing of the disconnected contributions is essential for M_n and thus for F_c to be an extensive quantity. For example, consider the contribution $\sum_{i < j, k < l} \langle u_{ij} \rangle \langle u_{kl} \rangle$ for $i \neq j \neq k \neq l$. As we saw in (8.60b), each $\langle u_{ij} \rangle$ is order $1/V$. Because each index is different, the number of terms is $\sim N^4$ and hence the order of magnitude of this type of contribution is $N^4/V^2 \sim N^2$. (Recall that $N/V = \rho$ is finite.) Because the presence of the disconnected terms in M_2 would imply that F_c would be proportional to N^2 rather than N , it is necessary that this spurious N dependence cancel exactly. The fact that the disconnected terms do not contribute to F_c was first shown for a classical system of particles by Joseph Mayer in 1937. The corresponding result was not established for a quantum system of particles until 1957.⁶

The reducible terms also vanish but do not lead to a spurious N -dependence. As an example, consider the term $\langle u_{ij} u_{jk} u_{kl} \rangle$ with four distinct indices. We can choose relative coordinates and show that $\langle u_{ij} u_{jk} u_{kl} \rangle = \langle u_{ij} \rangle \langle u_{jk} \rangle \langle u_{kl} \rangle$, and hence is canceled for a classical gas. The N -dependence of this term is $N^4/V^3 \sim N$. The reducible terms do not cancel for quantum systems.

Problem 8.10. The first two cumulants for a system of four particles

Consider a system of $N = 4$ particles and obtain the explicit form of M_2 . Show that the disconnected and reducible contributions cancel. \square

To simplify the calculation of the higher order cumulants and to understand the difference between the disconnected, reducible and irreducible terms, it is convenient to introduce a graphical notation that corresponds to the various contributions to M_n . As we have seen, we do not need to consider products of expectation values because they either cancel or are $O(1/N)$ relative to the irreducible terms arising from the first term in M_n . The rules for the calculation of M_n can be stated in graphical terms as follows:

- (1) For each particle (subscript on u) draw a vertex (a point).

⁶K. A. Brueckner, "Many-body problem for strongly interacting particles. II. Linked cluster expansion," Phys. Rev. **100**, 36–45 (1955) J. Goldstone, "Derivation of Brueckner many-body theory," Proc. Roy. Soc. A **239**, 267–279 (1957). The latter paper uses Feynman diagrams. A more accessible introduction to Feynman diagrams is by Richard D. Mattuck, *A Guide to Feynman Diagrams in the Many-Body Problem*, second edition, Dover Books (1992).

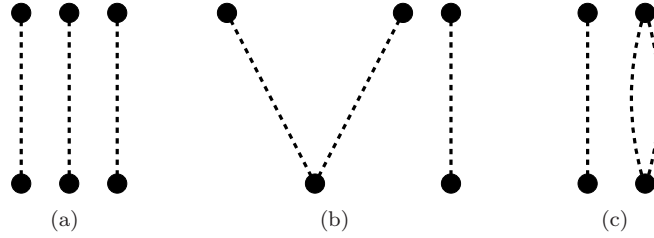


Figure 8.2: Examples of disconnected diagrams with three (potential) bonds. The potential (u) bonds are represented by dotted lines and the vertices are represented by filled circles.

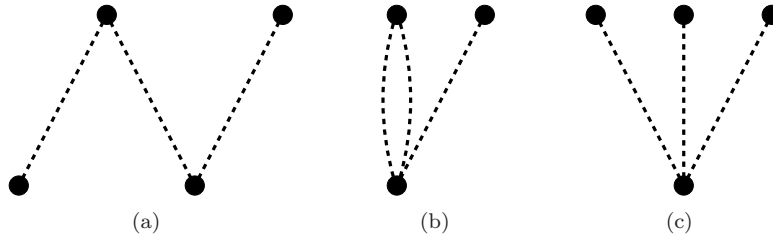


Figure 8.3: Examples of reducible diagrams with three (potential) bonds.

- (2) Draw a bond (a dotted line) between two vertices. There is a total of n bonds among p vertices, where $2 \leq p \leq n$.
- (3) If the diagram contains two or more pieces not joined by a bond, then the diagram is *disconnected*. If the diagram can be separated into two disconnected pieces by removing one vertex, then the diagram is *reducible*. The remaining diagrams are *irreducible* and are the only ones that need to be considered.

Examples of various types of disconnected and reducible diagrams are shown in Figs. 8.2–8.4 corresponding to M_3 .

It is now straightforward to find the contributions to M_3 corresponding to the two irreducible diagrams shown in Figure 8.4. There are $\frac{1}{2}N(N - 1)$ identical contributions of type shown in Figure 8.4(a) and $N(N - 1)(N - 2)$ of the type shown in Figure 8.4(b). Hence, the form of M_3 in the limit $N \rightarrow \infty$ is

$$\frac{M_3}{N} = \frac{\rho}{2} \int u^3(\mathbf{r}) d\mathbf{r} + \rho^2 \int u_{12} u_{23} u_{31} d\mathbf{r}_{12} d\mathbf{r}_{23}. \tag{8.62}$$

Problem 8.11. N and V dependence of the diagrams in Figures 8.2–8.4

Verify the N and V dependence of the diagrams in Figures 8.2–8.4 as summarized in Table 8.1. \square

Problem 8.12. Example of a high temperature expansion

Consider the potential $u(r) = u_0 e^{-\alpha r^2}$, which is finite for small r and goes to zero for large r . For this reason the various integrals for the cumulants are finite and a high temperature expansion is

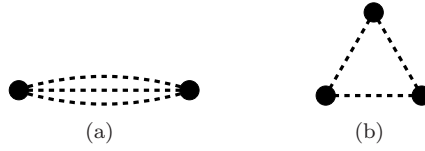


Figure 8.4: The two irreducible diagrams with three (potential) bonds.

Figure	V -dependence	number of terms in the sum	contribution
8.2(a)	V^{-3}	$O(N^6)$	$O(N^3)$
8.2(b)	V^{-3}	$O(N^5)$	$O(N^2)$
8.2(c)	V^{-2}	$O(N^4)$	$O(N^2)$
8.3(a)	V^{-3}	$O(N^4)$	$O(N)$
8.3(b)	V^{-2}	$O(N^3)$	$O(N)$
8.3(c)	V^{-3}	$O(N^4)$	$O(N)$
8.4(a)	V^{-1}	$O(N^2)$	$O(N)$
8.4(b)	V^{-2}	$O(N^3)$	$O(N)$

Table 8.1: Summary of the volume-dependence, the number of terms, and the contribution of each of the diagrams in Figures 8.2–8.4.

possible. The high temperature expansion of F_c for this potential is equivalent to expanding in the dimensionless ratio u_0/kT .

- (a) Explain why an expansion in powers of u_0/kT is equivalent to grouping the irreducible diagrams according to their number of bonds.
- (b) Draw the irreducible diagrams and give the corresponding integrals that contribute to F_c through order $(u_0/kT)^4$. Don't worry about the combinatorial factors.

8.4.3 *Density expansion

We saw in Section 8.4.2 that the calculation of M_n can be reduced to enumerating all irreducible diagrams with n bonds and p vertices, where $2 \leq p \leq n$. The expansion (8.48) is a high temperature expansion in powers of u_0/kT ; that is, the irreducible diagrams associated with M_n have n bonds. We now show how the high temperature expansion can be reordered so that we obtain an expansion in the density ρ or in the number of vertices p .

Consider an irreducible diagram of n bonds and p vertices. An example is shown in Figure 8.4(a) for $p = 2$ and $n = 3$. The p vertices correspond to p particles and yield a factor of N^p/V^p . One of the integrations can be performed immediately by choosing one of the vertices to be the origin. Hence an irreducible diagram with p vertices contributes a term that is order N^p/V^{p-1} , leading to an order ρ^{p-1} contribution to F_c/N . Hence, a classification of the diagrams according to the number of bonds corresponds to a high temperature expansion, and a classification according to the number of vertices is equivalent to a density expansion. That is, by summing all diagrams with a given number of vertices, the high temperature expansion (8.48) can be converted

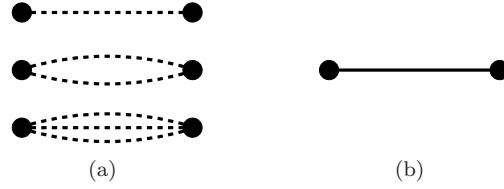


Figure 8.5: (a) The first several irreducible diagrams with two vertices and $n = 1, 2,$ and 3 potential bonds (dotted lines). (b) The equivalent diagram with one Mayer f bond (solid line).

to an expansion in the density. The result is traditionally written in the form (see (8.12))

$$-\beta \frac{F_c}{N} = \sum_{p=1}^{\infty} \frac{b_p \rho^p}{p+1}. \quad (8.63)$$

In the following we will find the form of the first few cluster integrals b_p .

We first add the contribution of all the two-vertex diagrams to find b_1 (see Figure 8.5(a)). From (8.48) we see that a factor of $-\beta$ is associated with each bond. The contribution to $-\beta F_c$ from all two vertex irreducible diagrams is

$$\sum_{n=1}^{\infty} \frac{(-\beta)^n}{n!} M_n = N \frac{\rho}{2} \sum_{n=1}^{\infty} \frac{(-\beta)^n}{n!} \int u^n(\mathbf{r}) \, d\mathbf{r} = N \frac{\rho}{2} \int (e^{-\beta u(\mathbf{r})} - 1) \, d\mathbf{r}. \quad (8.64)$$

Because $B_2 = -\frac{1}{2}b_1$ (see (8.13), we recover the result (8.32) that we found in Section 8.2 by a plausibility argument. Note the appearance of the Mayer f function in (8.64) and that f emerges by summing an infinite number of potential bonds between two particles.

We can now simplify the diagrammatic expansion by replacing the infinite sum of u (potential) bonds between any two particles by f . For example, b_1 corresponds to the single diagram shown in Figure 8.5(b), where the solid line represents the Mayer f function.

To find b_2 we consider the set of all irreducible diagrams with $n = 3$ vertices. Some of the diagrams with u bonds are shown in Figure 8.6(a). By considering all the possible combinations of the u bonds, we can sum up all the irreducible diagrams with three vertices with l_{12} , l_{23} , and l_{31} bonds. Instead, we will use our intuition and replace the various combinations of u bonds between two vertices by a single f bond between any two vertices as shown in Figure 8.6(b). The corresponding contribution to b_2 is

$$b_2 = \frac{1}{2!} \int f_{12} f_{23} f_{31} \, d\mathbf{r}_{12} \, d\mathbf{r}_{23}. \quad (8.65)$$

It can be shown that b_p is the sum over all topologically distinct irreducible diagrams among $p+1$ vertices. For example, b_3 corresponds to the four-vertex diagrams shown in Figure 8.7. The corresponding result for b_3 is

$$b_3 = \frac{1}{3!} \int (3f_{12}f_{23}f_{34}f_{41} + 6f_{12}f_{23}f_{34}f_{41}f_{13} + f_{12}f_{23}f_{34}f_{41}f_{13}f_{24}) \, d\mathbf{r}_2 \, d\mathbf{r}_3 \, d\mathbf{r}_4. \quad (8.66)$$

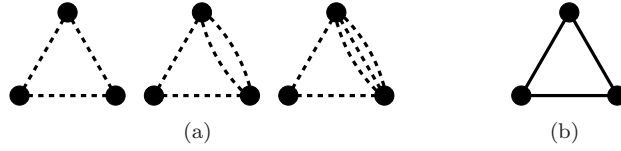


Figure 8.6: (a) The first several irreducible diagrams with three vertices and various numbers of u bonds (dotted lines). (b) The corresponding diagram with f -bonds (solid lines).

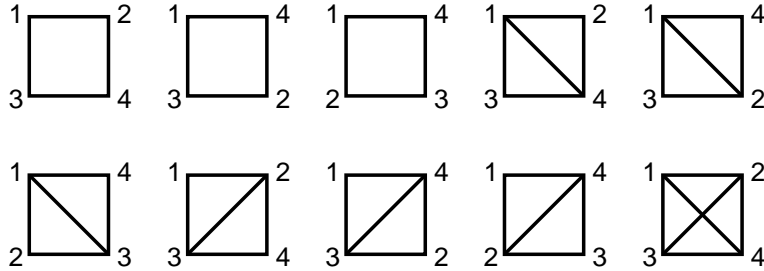


Figure 8.7: The four-vertex diagrams with all the possible different labelings. Note that the bonds are f bonds.

We see that we have converted the original high temperature expansion to a density expansion for the free energy and by summing what are known as *ladder diagrams*. These diagrams corresponding to all the possible u bonds between any two particles (vertices). The result of this sum is the Mayer f function.

The procedure for finding higher order terms in the density expansion of the free energy is straightforward in principle. To find the contribution of order ρ^{p-1} we enumerate all the irreducible diagrams with p vertices and various numbers of f bonds. There is only one f bond between any two vertices. The enumeration of the cluster integrals b_p becomes more and more tedious for larger p , and it becomes increasingly difficult to determine the combinatorial factors such as the factors of 3, 6, and 1 in (8.66).

8.4.4 Higher order virial coefficients for hard spheres

The values of the first six virial coefficients (not counting $B_1 = 1$) for hard spheres are given in Table 8.2 in terms of the dimensionless parameter

$$\eta = \pi\rho\sigma^3/6, \tag{8.67}$$

where σ is the diameter of the spheres. The parameter η can be expressed as

$$\eta = \frac{N\frac{4\pi}{3}\left(\frac{\sigma}{2}\right)^3}{V} = \rho\frac{4\pi}{3}\left(\frac{\sigma}{2}\right)^3. \tag{8.68}$$

The form of (8.68) shows that η is the fraction of the space occupied by N spheres. For this reason η is called the *packing fraction*. The second virial coefficient B_2 was calculated in Problem 8.4 for hard

virial coefficient	magnitude
ρB_2	$\frac{2}{3}\pi\rho\sigma^3 = 4\eta$
$\rho^2 B_3$	$\frac{5}{18}\pi^2\rho^2\sigma^6 = 10\eta^2$
$\rho^3 B_4$	$18.365\eta^3$
$\rho^4 B_5$	$28.24\eta^4$
$\rho^5 B_6$	$39.5\eta^5$
$\rho^6 B_7$	$56.5\eta^6$

Table 8.2: The values of the first six virial coefficients for hard spheres.

spheres, and the third virial coefficient B_3 is calculated analytically in Section 8.9.1. Boltzmann calculated the fourth order virial coefficient B_4 in 1899 by considering the excluded volume due to the finite size of the hard spheres. Because formal expressions for the virial coefficients did not exist then, his calculation was based on physical insight and was not confirmed until 1952. Calculations of the hard sphere virial coefficients for $n > 4$ must be done numerically and are now known through B_{12} .

Problem 8.13. Density of close packing

Because a system of hard disks and hard spheres cannot overlap, there is a well defined density of close packing.

- (a) The maximum packing density of a system of hard disks corresponds to a hexagonal lattice with each disk touching its six nearest neighbors. Show that in this arrangement $\rho_{\max}\sigma^2 = 2/3^{1/2} \approx 1.1547$ and the corresponding value of η is $\eta_{\max} = \frac{1}{6}\sqrt{3}\pi \approx 0.9069$. This number follows from the ratio of the area of the disc of diameter σ to the area of the circumscribing hexagon whose side equals $\sigma/\sqrt{3}$.⁷
- (b) *Show that the maximum packing density of a system of hard spheres is equal to $\rho_{\max} = \sigma^3/\sqrt{2}$, assuming a face centered cubic lattice. What is the corresponding maximum value of η ? \square

Problem 8.14. Carnahan-Starling equation of state

From the results shown in Table 8.2 we can write the equation of state of a system of hard spheres as

$$\frac{PV}{NkT} = 1 + \sum_{s=1}^6 C_s \eta^s \quad (8.69a)$$

$$= 1 + 4\eta + 10\eta^2 + 18.365\eta^3 + 28.24\eta^4 + 39.5\eta^5 + 56.5\eta^6. \quad (8.69b)$$

- (a) Show that the coefficients C_s can be written in the approximate form $C_s = 3s + s^2$ and that this form of C_s implies that

$$\frac{PV}{NkT} = 1 + \sum_{s=1}^{\infty} (3s + s^2)\eta^s. \quad (8.70)$$

⁷See for example, C. A. Rogers, *Packing and Covering*, Cambridge University Press (1964), Chapter 1.

(b) Do the sum in (8.70) and show that

$$\frac{PV}{NkT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \quad (8.71)$$

(Hint: start with the infinite sum $\sum_{s=0}^{\infty} \eta^s = (1 - \eta)^{-1}$ and take derivatives of both sides with respect to η .) The form (8.71) is known as the Carnahan-Starling equation of state and is a good approximation to the equation of state found by Monte Carlo simulations.

(c) Use the Carnahan-Starling equation of state (8.71) to derive analytical expressions for the entropy S , energy E , and the Helmholtz free energy F for a hard sphere fluid. \square

The virial coefficients for a gas of particles interacting via the Lennard-Jones potential can be done numerically (see Problem 8.30 for a calculation of B_2).

8.5 The Radial Distribution Function

Now that we know how to include the interactions between particles to obtain the equation of state of a dilute gas, we consider how these interactions lead to correlations between the particles. We know that if the interactions are neglected, the positions of the particles are uncorrelated, and the probability of finding a particle a distance r away from a particular particle is proportional to the density ρ . In the following, we will introduce the *radial distribution function* $g(r)$ as a measure of the correlations between particles due to their interactions. This function is analogous to the spin-spin correlation function introduced in Section 5.5.2.

Suppose that we choose the origin of our coordinate system at a particular particle (say particle one). Then the quantity $\rho g(r) d\mathbf{r}$ is defined as the mean number of particles that are within the distance \mathbf{r} and $\mathbf{r} + d\mathbf{r}$ from the origin. That is,

$$\rho g(r) = \text{mean local density a distance } r \text{ from a given particle.} \quad (8.72)$$

If the gas is dilute, we need to consider only the effect of the interactions between particle one and any other particle and ignore the effects of all the other particles. Because the energy of interaction between two particles is $u(r)$, the form of $g(r)$ for a dilute gas is given by

$$g(r) = e^{-\beta u(r)}, \quad (\text{dilute gas}) \quad (8.73)$$

where $e^{-\beta u(r)}$ is the probability that another particle is a distance r away. We will derive the low density limit (8.73) in the following. Note that if $u(r) = 0$, then $g(r) = 1$, and the mean local density equals the mean density ρ .

The radial distribution function $g(r)$ is important because it can be measured experimentally and in simulations and because the mean energy and mean pressure can be calculated from $g(r)$. We will show that the mean energy is given by

$$E = \frac{3}{2}NkT + \frac{\rho}{2}N \int_0^{\infty} u(r)g(r) 4\pi r^2 dr, \quad (8.74)$$

and the mean pressure is given by

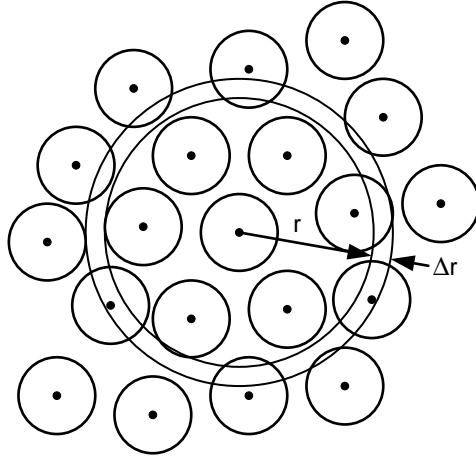


Figure 8.8: The radial distribution function is determined by counting how many particles are within a distance r and $r + \Delta r$ from a given particle.

$$\frac{PV}{NkT} = 1 - \frac{\rho}{6kT} \int_0^\infty r \frac{du(r)}{dr} g(r) 4\pi r^2 dr. \quad (8.75)$$

The two terms in (8.74) are the mean kinetic energy and the mean potential energy, respectively. To understand the interpretation of the second term we note that the interaction energy between a particular particle and all other particles between r and $r + dr$ is $u(r)\rho g(r)4\pi r^2 dr$ (in three dimensions), where $\rho g(r)dr$ is the local number of particles. The total potential energy is found by integrating over all r and multiplying by $N/2$. The factor of N is included because any of the N particles can be chosen as the particle at the origin; the factor of $1/2$ accounts for the fact that each pair interaction is counted only once.

We can gain more insight into the meaning of the radial distribution function by considering how to compute it for a given configuration of particles in two dimensions. Choose a particle as the origin and draw two concentric circles (spheres in three dimensions), one of radius r and the other of radius $r + \Delta r$ (see Figure 8.8). Count the number of atoms $n(r)$ between r and $r + \Delta r$. Then divide $n(r)$ by the area (volume) $\pi(r + \Delta r)^2 - \pi r^2 \approx 2\pi r \Delta r$ between r and $r + \Delta r$ and the average density of particles. The result is $g(r)$ for one configuration.

$$g(r) = \frac{n(r)}{\rho 2\pi r \Delta r}. \quad (\text{two dimensions}) \quad (8.76)$$

We obtain better statistics by choosing each particle as the origin for a given configuration of particles and by averaging over many configurations.

The qualitative features of $g(r)$ for a Lennard-Jones fluid are shown in Figure 8.9. We see that $g \rightarrow 0$ as $r \rightarrow 0$ because the repulsive part of the interaction between the particles does not allow the particles to become too close. At large r the other particles are not correlated with the fixed particle at the origin and $g(r) \rightarrow 1$ as $r \rightarrow \infty$. The properties of $g(r)$ for a system of hard disks at various densities and a Lennard-Jones system of particles at various densities and temperatures are explored in Problem 8.15.

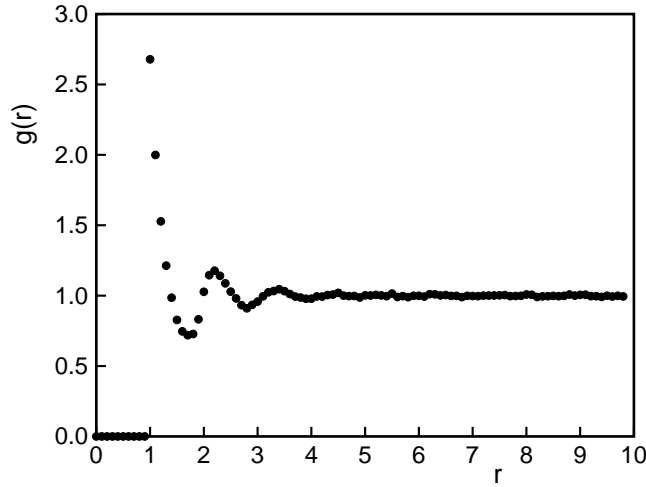


Figure 8.9: Dependence of $g(r)$ on r for a system of $N = 256$ hard disks at a density of $\rho\sigma^2 = 0.64$. What is the meaning of the peaks of $g(r)$?

Problem 8.15. Qualitative behavior of $g(r)$

Use either molecular dynamics (Programs `LJ2DMD` and `HardDisksMD`) or Monte Carlo (Programs `LJ2DMetropolis` and `HardDisksMetropolis`) methods to simulate the static properties of a system of hard disks and particles interacting with the Lennard-Jones potential to determine the behavior of $g(r)$ for various densities and temperatures. We consider two-dimensional systems because they are easier to visualize.

- (a) Consider a system of hard disks and describe how $g(r)$ changes with the density ρ . Both the Monte Carlo and molecular dynamics programs use units such that the hard core diameter $\sigma = 1$. Is the temperature of the system relevant?
- (b) Consider a system of particles interacting with the Lennard-Jones potential (8.2) at the same densities (and number of particles) as you considered in part (a). How does $g(r)$ for the two systems compare at the same density? How does $g(r)$ change with temperature for a given ρ ?
- (c) Choose either interaction and describe how $g(r)$ changes as the density is increased. What is the meaning of the peaks in $g(r)$? □

**More formal considerations.* To define $g(r)$ more formally⁸ we introduce the probability of a configuration of N particles in a volume V in equilibrium with a heat bath at temperature T :

$$P_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N = \frac{e^{-\beta U} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N}{\int e^{-\beta U} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N} \tag{8.77a}$$

$$= \frac{e^{-\beta U} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N}{Q_N}, \tag{8.77b}$$

⁸An alternative way of defining $g(r)$ in terms of the spatial correlations of the density fluctuations is given in Section 8.9.2.

where U is the total potential energy of the configuration. The quantity $P_N d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N$ is the probability that particle 1 is in the range $d\mathbf{r}_1$ about \mathbf{r}_1 , particle 2 is in the range $d\mathbf{r}_2$ about \mathbf{r}_2 , etc. Note that the probability density $P_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is properly normalized.

It is convenient to define the *configuration integral* Q_N as

$$Q_N = \int e^{-\beta U} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (8.78)$$

The configuration integral Q_N is related to the partition function Z_N by

$$Q_N = Z_N / (N! \lambda^{3N}). \quad (8.79)$$

Q_N is defined so that $Q_N = V^N$ for an ideal gas.

The probability that particle 1 is in the range $d\mathbf{r}_1$ about \mathbf{r}_1 and particle 2 is in the range $d\mathbf{r}_2$ about \mathbf{r}_2 is obtained by integrating (8.77) over the positions of particles 3 through N :

$$P_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \frac{\int e^{-\beta U} d\mathbf{r}_3 \dots d\mathbf{r}_N}{Q_N} d\mathbf{r}_1 d\mathbf{r}_2. \quad (8.80)$$

The probability that *any* particle is in the range $d\mathbf{r}_1$ about \mathbf{r}_1 and any other particle is in the range $d\mathbf{r}_2$ about \mathbf{r}_2 is $N(N-1)P_2 d\mathbf{r}_1 d\mathbf{r}_2$. The *pair distribution function* $g(\mathbf{r}_1, \mathbf{r}_2)$ is defined as

$$\rho^2 g(\mathbf{r}_1, \mathbf{r}_2) = N(N-1)P_2 = N(N-1) \frac{\int e^{-\beta U} d\mathbf{r}_3 \dots d\mathbf{r}_N}{Q_N}. \quad (8.81)$$

We use $\rho = N/V$ to write g as

$$g(\mathbf{r}_1, \mathbf{r}_2) = \left(1 - \frac{1}{N}\right) \frac{V^2 \int e^{-\beta U} d\mathbf{r}_3 \dots d\mathbf{r}_N}{Q_N}. \quad (8.82)$$

If the interparticle interaction is spherically symmetric and the system is a fluid (a liquid or a gas), then $g(\mathbf{r}_1, \mathbf{r}_2)$ depends only on the distance $r = |\mathbf{r}_1 - \mathbf{r}_2|$ between particles 1 and 2. We adopt the notation $g(r) = g(r_{12})$ and define the *radial distribution function* $g(r)$ as

$$\boxed{g(r) = \left(1 - \frac{1}{N}\right) \frac{V^2 \int e^{-\beta U} d\mathbf{r}_3 \dots d\mathbf{r}_N}{Q_N}}. \quad (8.83)$$

Note that (8.83) implies that $g(r) = 1 - 1/N$ for an ideal gas. We can ignore the $1/N$ correction in the thermodynamic limit so that $g(r) = 1$. From (8.83) we see that the normalization of $\rho g(r)$ is given by (for $d = 3$)

$$\rho \int g(r) 4\pi r^2 dr = \rho \left(1 - \frac{1}{N}\right) V^2 \frac{1}{V} = N - 1 \approx N. \quad (8.84)$$

To determine $g(r)$ for a dilute gas we write $g(r)$ as (see (8.83))

$$g(r) = \frac{V^2 \int e^{-\beta U} d\mathbf{r}_3 \dots d\mathbf{r}_N}{Q_N}, \quad (8.85)$$

where we have taken the limit $N \rightarrow \infty$. At low densities, we can integrate over particles 3, 4, \dots , N , assuming that these particles are distant from particles 1 and 2 and also distant from each other. Also for almost all configurations we can replace U by u_{12} in the numerator. Similarly, the denominator can be approximated by V^N . Hence (8.85) reduces to

$$g(r) \approx \frac{V^2 e^{-\beta u_{12}} V^{N-2}}{V^N} = e^{-\beta u(r)}, \quad (8.86)$$

as given in (8.73).

To obtain the relation (8.74) for the mean total energy E in terms of $g(r)$ we write

$$E = \frac{3}{2} N k T + \bar{U}, \quad (8.87)$$

where

$$\bar{U} = \frac{1}{Q_N} \int \dots \int U e^{-\beta U} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (8.88)$$

We assume that U is given by (8.1) and write \bar{U} as

$$\bar{U} = \frac{N(N-1)}{2} \frac{1}{Q_N} \int e^{-\beta U} u(r_{12}) d\mathbf{r}_1 \dots d\mathbf{r}_N \quad (8.89a)$$

$$= \frac{N(N-1)}{2} \int u(r_{12}) \left[\frac{\int e^{-\beta U} d\mathbf{r}_3 \dots d\mathbf{r}_N}{Q_N} \right] d\mathbf{r}_1 d\mathbf{r}_2. \quad (8.89b)$$

From (8.82) we see that the term in brackets is related to $\rho^2 g(\mathbf{r}_1, \mathbf{r}_2)$. Hence we can write \bar{U} as

$$\bar{U} = \frac{1}{2} \int u(r_{12}) \rho^2 g(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \frac{N^2}{2V} \int u(r) g(r) dr \quad (8.90a)$$

$$= N \frac{\rho}{2} \int u(r) g(r) 4\pi r^2 dr. \quad (8.90b)$$

We assumed three dimensions to obtain (8.90b).

The derivation of the relation (8.75) between the mean pressure and $g(r)$ is more involved. We write the pressure in terms of Q_N :

$$P = -\frac{\partial F}{\partial V} = kT \frac{\partial \ln Q_N}{\partial V}. \quad (8.91)$$

Recall that $Q_N = V^N$ for an ideal gas. For large V the pressure is independent of the shape of the container. For convenience, we assume that the container is a cube of linear dimension L , and we write Q_N as

$$Q_N = \int_0^L \dots \int_0^L e^{-\beta U} dx_1 dy_1 dz_1 \dots dx_N dy_N dz_N. \quad (8.92)$$

We first change variables so that the limits of integration are independent of L and let $\tilde{x}_i = x_i/L$, etc. This change of variables allows us to take the derivative of Q_N with respect to V . We have

$$Q_N = V^N \int_0^1 \dots \int_0^1 e^{-\beta U} d\tilde{x}_1 d\tilde{y}_1 d\tilde{z}_1 \dots d\tilde{x}_N d\tilde{y}_N d\tilde{z}_N, \quad (8.93)$$

where U depends on the separation $\tilde{r}_{ij} = L[(\tilde{x}_i - \tilde{x}_j)^2 + (\tilde{y}_i - \tilde{y}_j)^2 + (\tilde{x}_i - \tilde{z}_j)^2]^{1/2}$. We now take the derivative

$$\begin{aligned} \frac{\partial Q_N}{\partial V} &= NV^{N-1} \int_0^1 \cdots \int_0^1 e^{-\beta U} d\tilde{x}_1 \cdots d\tilde{z}_N \\ &\quad - \frac{V^N}{kT} \int_0^1 \cdots \int_0^1 e^{-\beta U} \frac{\partial U}{\partial V} d\tilde{x}_1 \cdots d\tilde{z}_N, \end{aligned} \quad (8.94)$$

where

$$\frac{\partial U}{\partial V} = \sum_{i < j} \frac{du(r_{ij})}{dr_{ij}} \frac{dr_{ij}}{dL} \frac{dL}{dV} = \sum_{i < j} \frac{du(r_{ij})}{dr_{ij}} \frac{r_{ij}}{L} \frac{1}{3L^2}. \quad (8.95)$$

Now that we have differentiated Q_N with respect to V , we transform back to the original variables x_1, \dots, z_N . In the second term of (8.95) we also use the fact that there are $N(N-1)/2$ identical contributions. In this way we obtain

$$\frac{\partial \ln Q_N}{\partial V} = \frac{1}{Q_N} \frac{\partial Q_N}{\partial V} = \frac{N}{V} - \frac{\rho^2}{6VkT} \int r_{12} \frac{du(r_{12})}{dr_{12}} g(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2, \quad (8.96)$$

and hence

$$\frac{PV}{NkT} = 1 - \frac{\rho}{6kT} \int_0^\infty r \frac{du(r)}{dr} g(r) 4\pi r^2 dr. \quad (\text{virial equation of state}) \quad (8.97)$$

The integrand in (8.97) is related to the virial in classical mechanics and is the mean value of the product $\mathbf{r} \cdot \mathbf{F}$ (cf. Goldstein).

**Density expansion of $g(r)$.* The density expansion of $g(r)$ is closely related to the density expansion of the free energy. Instead of deriving the relation here, we show only the diagrams corresponding to the first two density contributions. We write

$$g(r) = e^{-\beta u(r)} y(r), \quad (8.98)$$

and

$$y(r) = \sum_{n=0}^{\infty} \rho^n y_n(r), \quad (8.99)$$

with $y_0(r) = 1$. It is convenient to consider the function $y(r)$ defined by (8.98) instead of the function $g(r)$ because $y(r)$ is more slowly varying. The diagrams for $y(r)$ have two fixed points represented by open circles corresponding to particles 1 and 2. The other particles are integrated over the volume of the system. The diagrams for $y_1(r)$ and $y_2(r)$ are shown in Figure 8.10. The corresponding integrals are

$$y_1(r) = \int f(r_{13}) f(r_{23}) d\mathbf{r}_3, \quad (8.100)$$

and

$$\begin{aligned} y_2(r) &= \frac{1}{2} \int [2f_{13}f_{34}f_{42} + 4f_{13}f_{34}f_{42}f_{32} + f_{13}f_{42}f_{32}f_{14} \\ &\quad + f_{13}f_{34}f_{42}f_{32}f_{14}] d\mathbf{r}_3 d\mathbf{r}_4. \end{aligned} \quad (8.101)$$

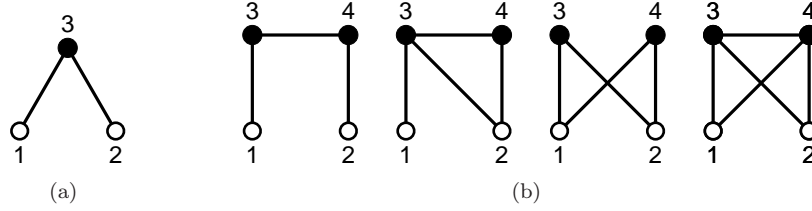


Figure 8.10: The diagrams contributing to (a) $y_1(r)$ and (b) $y_2(r)$. Particles one and two are represented by open circles and the other particles (filled circles) are integrated over the volume of the system. The bonds correspond to Mayer f functions.

Note that the diagrams in Figure 8.10 and hence the integrals in (8.100) and (8.101) are closely related to the diagrams for the virial coefficients.

Pressure equation for hard spheres. Because the relation (8.97) involves the derivative of the pair potential $u(r)$, it is not directly applicable to a system of hard spheres. To find the desired relation we write $g(r)$ as in (8.98) and assume that $y(r)$ is a continuous function of r even when $u(r)$ has discontinuities. We substitute this form of $g(r)$ in (8.97) and write

$$\frac{PV}{NkT} = 1 - \frac{2\pi\beta\rho}{3} \int_0^\infty u'(r) e^{-\beta u(r)} y(r) r^3 dr \quad (8.102a)$$

$$= 1 + \frac{2\pi\rho}{3} \int_0^\infty \frac{d(e^{-\beta u(r)})}{dr} y(r) r^3 dr, \quad (8.102b)$$

where we have used the fact that $d(e^{-\beta u(r)})/dr = -\beta u'(r) e^{-\beta u(r)}$. For hard spheres $e^{\beta u(r)} = 0$ for $r < \sigma$, $e^{\beta u(r)} = 1$ for $r > \sigma$ and $d(e^{-\beta u(r)})/dr = \delta(r - \sigma)$. Hence

$$\frac{PV}{NkT} = 1 + \frac{2\pi\rho}{3} \lim_{r \rightarrow \sigma^+} r^3 y(r) = 1 + \frac{2\pi\rho}{3} \sigma^3 g(r = \sigma^+). \quad (8.103)$$

We see that the pressure of a hard sphere fluid is determined by the value of $g(r)$ at contact. Note that $g(r)$ goes discontinuously to zero; that is $g(r = \sigma^-) = 0$.

Problem 8.16. Pressure equation for hard disks

Derive the expression analogous to (8.103) for hard disks. □

8.6 Perturbation Theory of Liquids

So far we have discussed several models that can be solved analytically and that add to our understanding of gases and crystalline solids. For example, we have seen that the ideal gas can be used as the starting point for the density expansion of a dilute gas, and the harmonic model is an idealized model of a solid (see Section 6.9, page 333). The development of a microscopic theory of fluids (dense gases and liquids) was hampered for many years by the lack of a convenient small expansion parameter or a simple model.

Simulations of simple liquids have led to the realization that the details of the weak attractive part of the interparticle interaction and the details of the repulsive part of the interaction also are unimportant. As you found in Problem 8.15, the radial distribution function $g(r)$ of a dense fluid does not depend strongly on the temperature, and the radial distribution function $g(r)$ for a system of hard spheres is a good approximation to $g(r)$ for a Lennard-Jones system at the same density. Moreover, we can simulate hard sphere systems relatively easily and obtain essentially exact solutions for $g(r)$ and the equation of state.

The picture of a dense fluid that is suggested by simulations suggests that the repulsive part of the interaction dominates its structure, and the attractive part of the interaction can be treated as a perturbation. In the following we will develop a perturbation theory of liquids in which the unperturbed or reference system is taken to be a system of hard spheres (or disks) rather than an ideal gas. The idea is that the difference between the hard sphere interaction and a more realistic interaction can be used as an effective expansion parameter.

We begin by writing the potential energy as

$$U = U_0 + \tilde{U}, \quad (8.104)$$

where U_0 is the potential energy of the reference system, and \tilde{U} will be treated as a perturbation. The configurational integral Q_N is given by

$$Q_N = \int \dots \int e^{-\beta(U_0 + \tilde{U})} d\mathbf{r}_1 \dots d\mathbf{r}_N. \quad (8.105)$$

We multiply and divide the right-hand side of (8.105) by

$$Q_0 = \int \dots \int e^{-\beta U_0} d\mathbf{r}_1 \dots d\mathbf{r}_N, \quad (8.106)$$

and write

$$Q_N = \int \dots \int e^{-\beta U_0} d\mathbf{r}_1 \dots d\mathbf{r}_N \frac{\int \dots \int e^{-\beta(U_0 + \tilde{U})} d\mathbf{r}_1 \dots d\mathbf{r}_N}{Q_0} \quad (8.107a)$$

$$= Q_0 \int \dots \int P_0 e^{-\beta \tilde{U}} d\mathbf{r}_1 \dots d\mathbf{r}_N, \quad (8.107b)$$

where

$$P_0 = \frac{e^{-\beta U_0}}{Q_0}. \quad (8.108)$$

We see that we can express Q_N in (8.107b) as the average of $\exp(-\beta \tilde{U})$ over the reference system. We write

$$Q_N = Q_0 \langle e^{-\beta \tilde{U}} \rangle_0, \quad (8.109)$$

and

$$-\beta \tilde{F} = \ln \langle e^{-\beta \tilde{U}} \rangle_0 = \sum_{n=1}^{\infty} \frac{(-\beta)^n \tilde{M}_n}{n!}. \quad (8.110)$$

The brackets $\langle \dots \rangle_0$ denote an average over the microstates of the reference system weighted by the probability P_0 . We have written \tilde{M} rather than M to distinguish the cumulants for an arbitrary

reference system from the cumulants defined in Section 8.4.2 for the ideal gas reference system. Note the formal similarity between (8.110) and the expression for F_c in (8.8) and the cumulant expansion in (8.48).

Problem 8.17. Ideal gas as a reference system

- (a) Compare the form of (8.109) and (8.110) for an arbitrary reference system to the form of (8.7) and (8.8), respectively.
- (b) Show that if we choose the reference system to be an ideal gas, the expressions (8.109) and (8.110) reduce to (8.7) and (8.8). \square

We now evaluate the first cumulant \tilde{M}_1 in a manner similar to that done to evaluate M_1 in (8.49) for a dilute gas. The leading term in (8.110) is

$$\tilde{M}_1 = \langle \tilde{U} \rangle_0 = \sum_{i < j=1}^N \langle \tilde{u}(r_{ij}) \rangle_0, \quad (8.111a)$$

$$= \frac{N(N-1)}{2} \frac{1}{Q_0} \int \dots \int e^{-\beta U_0} \tilde{u}(r_{12}) d\mathbf{r}_1 \dots d\mathbf{r}_N. \quad (8.111b)$$

The radial distribution function of the reference system is given by (see (8.81))

$$\rho^2 g_0(r_{12}) = N(N-1) \frac{\int e^{-\beta U_0} d\mathbf{r}_3 \dots d\mathbf{r}_N}{Q_0}. \quad (8.112)$$

Hence, we can write \tilde{M}_1 as

$$\tilde{M}_1 = \frac{\rho^2}{2} \int \tilde{u}(r_{12}) g_0(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 \quad (8.113a)$$

$$= \frac{\rho N}{2} \int \tilde{u}(r) g_0(r) d\mathbf{r}, \quad (8.113b)$$

and

$$\tilde{F} = \tilde{F}_0 + \frac{\rho N}{2} \int \tilde{u}(r) g_0(r) d\mathbf{r}, \quad (8.114)$$

where \tilde{F}_0 in (8.114) is the free energy of the reference system. Note that the form of \tilde{M}_1 in (8.113b) is similar to the form of M_1 in (8.51b). The difference is that we have included the correlation between the particles due to their interaction in (8.113b).

8.6.1 The van der Waals equation

The idea that the structure of a simple liquid is determined primarily by the repulsive part of the potential is not new and is the basis of the van der Waals equation of state. We now show how the van der Waals equation of state can be derived from the perturbation theory we have developed by choosing the reference system to be a system of hard spheres and making some simple approximations.

We first assume that g_0 has the simple form

$$g_0(r) = \begin{cases} 0 & r < \sigma \\ 1 & r \geq \sigma. \end{cases} \quad (8.115)$$

This approximate form for $g_0(r)$ gives

$$\tilde{M}_1 = 2\pi\rho N \int_{\sigma}^{\infty} \tilde{u}(r) r^2 dr = -\rho a N, \quad (8.116)$$

where (see (8.35))

$$a = -2\pi \int_{\sigma}^{\infty} \tilde{u}(r) r^2 dr. \quad (8.117)$$

The simplest approximation for \tilde{F}_0 is to assume that the effective volume available to a particle in a fluid is smaller than the volume available in an ideal gas. In this spirit we assume that \tilde{F}_0 has the same form as it does for an ideal gas (see ((6.26), page 299) with V replaced by V_{eff} . We write

$$\frac{\tilde{F}_0}{NkT} = -\left[\ln \frac{V_{\text{eff}}}{N} + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + 1 \right], \quad (8.118)$$

where

$$V_{\text{eff}} = V - V_0, \quad (8.119)$$

and

$$V_0 = Nb = \frac{1}{2} N \frac{4\pi\sigma^3}{3}. \quad (8.120)$$

In (8.120) we have accounted for the fact that only half of the volume of a sphere can be assigned to a given particle. The corresponding equation of state with these approximations for \tilde{M}_1 , \tilde{F}_0 , and V_{eff} is given by

$$\frac{PV}{NkT} = \frac{1}{1 - b\rho} - \frac{a\rho}{kT}. \quad (8.121)$$

Equation (8.121) is the familiar van der Waals equation of state. The latter gives results that are in qualitative, but not quantitative agreement with experiment. From the simple approximations we have made for $g_0(r)$ and \tilde{F}_0 we can do better.

A much more accurate approximation for the equation of state of liquids is known as the Weeks-Chandler-Andersen theory (see the references). In this approach the interparticle potential is separated into a reference part and a perturbative part. One way is to separate the potential into positive and negative contributions. This choice implies that we should separate the Lennard-Jones potential at $r = \sigma$. Another way is to separate the potential at $r = 2^{1/6}\sigma$ so that the force is separated into positive and negative contributions. This choice is the one adopted by the Weeks-Chandler-Andersen theory. The Lennard-Jones potential is expressed as

$$u_{\text{LJ}}(r) = u_0(r) + \tilde{u}(r), \quad (8.122)$$

where

$$u_0(r) = \begin{cases} u_{\text{LJ}}(r) + \epsilon & r < 2^{1/6}\sigma \\ 0 & r \geq 2^{1/6}\sigma \end{cases} \quad (8.123a)$$

$$\tilde{u}(r) = \begin{cases} -\epsilon & r < 2^{1/6}\sigma \\ u_{\text{LJ}}(r) & r \geq 2^{1/6}\sigma \end{cases} \quad (8.123b)$$

We have added and subtracted ϵ to $u_{\text{LJ}}(r)$ for $r < 2^{1/6}\sigma$ so that $u_0(r)$ and $\tilde{u}(r)$ are continuous.

Problem 8.18. Qualitative behavior of $\tilde{u}(r)$

Plot the dependence of $\tilde{u}(r)$ on r and confirm that $\tilde{u}(r)$ is a slowly varying function of r . \square

Because the reference system in the Weeks-Chandler-Andersen theory is not a system of hard spheres, further approximations are necessary, and the reference system is approximated by hard spheres with a temperature and density-dependent diameter. One way to determine the effective diameter is to require that the function $y(r)$ defined in (8.98) be the same for hard spheres and for the repulsive part (8.123a) of the potential. The details will not be given here. What is important to understand is that a successful perturbation theory of dense gases and liquids now exists based on the use of a hard sphere reference system.

8.7 *The Ornstein-Zernicke Equation and Integral Equations for $g(\mathbf{r})$

As mentioned in Section 8.5, we can derive a density expansion for the function $y(r)$, which is related to $g(r)$ by (8.98). However, a better approach is to expand a related function that is shorter range. Such a function is the *direct correlation function* $c(r)$.

To define $c(r)$ it is convenient to first define the pair correlation function $h(r)$ by the relation

$$h(r) = g(r) - 1. \quad (8.124)$$

Because $g(r) \rightarrow 1$ for $r \gg 1$, $h(r) \rightarrow 0$ for sufficiently large r . Also $h(r) = 0$ for an ideal gas. These two properties makes it easier to interpret $h(r)$ rather than $g(r)$ in terms of the correlations between the particles due to their interaction.

We define $c(r)$ by the relation (for a homogeneous and isotropic system):

$$h(r) = c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|) h(r') d\mathbf{r}'. \quad (\text{Ornstein-Zernicke equation}) \quad (8.125)$$

The relation (8.125) is known as the *Ornstein-Zernicke equation*. Equation (8.125) can be solved recursively by first substituting $h(r) = c(r)$ on the right-hand side and then repeatedly substituting the resultant solution for $h(r)$ on the right-hand side to obtain

$$\begin{aligned} h(r) = & c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|) c(r') d\mathbf{r}' \\ & + \rho^2 \iint c(|\mathbf{r} - \mathbf{r}'|) c(|\mathbf{r}' - \mathbf{r}''|) c(|\mathbf{r}'' - \mathbf{r}'|) d\mathbf{r}' d\mathbf{r}'' + \dots \end{aligned} \quad (8.126)$$

The interpretation is that the correlation $h(r)$ between particles 1 and 2 is due to the direct correlation between 1 and 2 and the indirect correlation due to increasing numbers of intermediate particles. This interpretation suggests that the range of $c(r)$ is comparable to the range of the potential $u(r)$, and that $h(r)$ is longer ranged than $u(r)$ due to the effects of the indirect correlations. That is, $c(r)$ usually has a much shorter range than $h(r)$ and hence $g(r)$.⁹

Because the right-hand side of the Ornstein-Zernicke equation involves a convolution integral (see (A.11), page 476), we know that we can find $c(r)$ from $h(r)$ by introducing the Fourier transforms

$$c(k) = \int c(r) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}, \quad (8.127)$$

and

$$h(k) = \int h(r) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}. \quad (8.128)$$

We take the Fourier transform of both sides of (8.125) and find that

$$h(k) = c(k) + \rho c(k)h(k), \quad (8.129)$$

or

$$c(k) = \frac{h(k)}{1 + \rho h(k)}, \quad (8.130)$$

and

$$h(k) = \frac{c(k)}{1 - \rho c(k)}. \quad (8.131)$$

***Problem 8.19.** Properties of $c(r)$

- (a) Write $c(r) = c_0(r) + \rho c_1(r) + \dots$, and show that $c_0(r) = f(r)$ and $c_1(r) = f(r)y_1(r)$, where $y_1(r)$ is given in (8.100).
- (b) We know that $g(r) \approx -\beta u(r)$ for $\beta u(r) \ll 1$, as is the case for large r . Show that $c(r) = -\beta u(r)$ for large r . Hence in this limit the range of $c(r)$ is comparable to the range of the potential. \square

The Ornstein-Zernicke equation can be used to obtain several approximate integral equations for $g(r)$ that are applicable to dense fluids. The most useful of these equations for systems with short-range interactions is the *Percus-Yevick* equation. This equation corresponds to ignoring an (infinite) subset of diagrams (and including another subset), but a discussion of these diagrams does not add much physical insight.

One way to motivate the Percus-Yevick equation is to note that the lowest order density contributions to $c(r)$ are $c_0(r) = f(r)y_0(r)$ and $c_1(r) = f(r)y_1(r)$ (see Problem 8.19), where $y_0(r) = 1$. We assume that this relation between $c(r)$ and $y(r)$ holds for all densities:

$$c(r) \approx f(r)y(r) = [1 - e^{\beta u(r)}]g(r). \quad (8.132)$$

⁹This assumption does not hold near the critical point.

Equation (8.132) is correct to first order in the density. If we substitute the approximation (8.132) into the Ornstein-Zernicke equation (8.125), we obtain the Percus-Yevick equation:

$$y(r) = 1 + \rho \int f(r')y(r')h(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}'. \quad (\text{Percus-Yevick equation}) \quad (8.133)$$

We can alternatively express (8.133) as

$$e^{\beta u(r)}g(r) = 1 + \rho \int [1 - e^{\beta u(r')}]g(r')[g(|\mathbf{r} - \mathbf{r}'|) - 1] d\mathbf{r}'. \quad (8.134)$$

Equations (8.133) and (8.134) are examples of nonlinear integral equations.

In general, the Percus-Yevick must be solved numerically. However, it can be solved analytically for hard spheres (but not for hard disks). The analytical solution of the Percus-Yevick equation for hard spheres can be expressed as

$$c(r) = \begin{cases} -\frac{1}{(1-\eta)^4}[(1-2\eta)^2 - 6\eta(1+\frac{1}{2}\eta)^2(r/\sigma) + \frac{1}{2}\eta(1+2\eta)^2(r/\sigma)^2] & (r < \sigma) \\ 0, & (r > \sigma). \end{cases} \quad (8.135)$$

Note that the range of $c(r)$ is equal to σ and is much less than the range of $g(r)$.

Given $c(r)$, we can find $g(r)$ by solving the Ornstein-Zernicke equation. The derivation is tedious, and we give only the result for $g(r)$ at contact:

$$g(r = \sigma^+) = \frac{1 + \frac{1}{2}\eta}{(1-\eta)^2}. \quad (8.136)$$

We can use (8.136) and (8.103) to obtain the corresponding approximate virial equation of state for hard spheres. The result is

$$\frac{PV}{NkT} = \frac{1 + 2\eta + 3\eta^2}{(1-\eta)^2}. \quad (\text{virial equation of state}) \quad (8.137)$$

An alternative way of calculating the pressure is to use the compressibility relation (see (8.200))

$$1 + \rho \int [g(r) - 1] d\mathbf{r} = \rho kT\kappa, \quad (8.138)$$

which can be expressed as (see Section 8.9.3)

$$\left(kT \frac{\partial \rho}{\partial P}\right)^{-1} = 1 - \rho \int c(r) d\mathbf{r}. \quad (8.139)$$

If we substitute the Percus-Yevick result (8.135) into (8.139) and integrate, we find

$$\frac{PV}{NkT} = \frac{1 + \eta + \eta^2}{(1-\eta)^3}. \quad (\text{compressibility equation of state}) \quad (8.140)$$

If the Percus-Yevick equation were exact, the two ways of obtaining the equation of state would yield identical results. That is, the Percus-Yevick equation is not thermodynamically consistent.

It is interesting that the Carnahan-Starling equation of state for hard spheres (8.71) can be found by a weighted average of the two approximate equations of state:

$$\frac{PV}{NkT} = \frac{1}{\rho kT} \left[\frac{1}{3} P_v + \frac{2}{3} P_c \right], \quad (8.141)$$

where P_v and P_c are given by (8.137) and (8.140), respectively. The Carnahan-Starling equation of state gives better results than either (8.137) or (8.140).

The Percus-Yevick equation gives reasonable results for $g(r)$ and the equation of state for fluid densities. However, it predicts finite pressures for $\eta_{\max} \leq \eta < 1$, even though the maximum packing fraction $\eta_{\max} = \sqrt{2}\pi/6 \approx 0.74$ (see Problem 8.13).

Problem 8.20. Virial equation of state

Use the form of $g(r = \sigma^+)$ given in (8.136) and the relation (8.103) to derive (8.137) for the pressure equation of state as given by the Percus-Yevick equation.

Another simple closure approximation for the Ornstein-Zernicke equation can be motivated by the following considerations. Consider a fluid whose particles interact via a pair potential of the form

$$u(r) = \begin{cases} \infty & (r < \sigma) \\ v(r) & (r > \sigma), \end{cases} \quad (8.142)$$

where $v(r)$ is a continuous function of r . Because $u(r) = \infty$ for $r < \sigma$, $g(r) = 0$ for $r < \sigma$. For large r the Percus-Yevick approximation for $c(r)$ reduces to

$$c(r) = -\beta v(r). \quad (8.143)$$

The *mean spherical approximation* is based on the assumption that (8.143) holds not just for large r , but for all r . The mean spherical approximation is

$$c(r) = -\beta v(r) \quad (r > \sigma) \quad (8.144a)$$

and

$$g(r) = 0, \quad (r < \sigma) \quad (8.144b)$$

together with the Ornstein-Zernicke equation.

The *hypernetted-netted chain approximation* is another useful integral equation for $g(r)$. It is equivalent to setting

$$c(r) = f(r)y(r) + y(r) - 1 - \ln y(r). \quad (\text{hypernetted chain equation}) \quad (8.145)$$

If we analyze the Percus-Yevick and the hypernetted-chain approximations in terms of a diagrammatic expansion (see Problem 8.34), we find that the hypernetted-chain approximation includes more diagrams than the Percus-Yevick approximation. However, it turns out that the Percus-Yevick approximation is more accurate for hard spheres and other short-range potentials. In contrast, the hypernetted-chain approximation is more accurate for systems with long-range interactions.

8.8 *One-Component Plasma

We found in Problem 8.7 that the second virial coefficient does not exist if the interparticle potential $u(r)$ decreases less rapidly than $1/r^3$ for large r . For this reason we expect that a density expansion of the free energy and other thermodynamic quantities is not applicable to a gas consisting of charged particles interacting via the Coulomb potential $u(r) \propto 1/r$. We say that the Coulomb potential is long-range because its second moment $\int r^2 u(r) r^2 dr$ diverges for large r . The divergence of the second virial coefficient for the Coulomb potential divergence is symptomatic of the fact that a density expansion is not physically meaningful for a system of particles interacting via a long-range potential.

The simplest model of a system of particles interacting via the Coulomb potential is a gas of mobile electrons moving in a fixed, uniform, positive background. The charge density of the positive background is chosen to make the system overall neutral. Such a system is known as an electron gas or a *one-component plasma* (OCP in the literature).

Problem 8.21. Fourier transform of the Coulomb potential

The interaction potential between two particles of charge q is $u(r) = q^2/r$. Show that the Fourier transform of $u(r)$ is given by

$$u(k) = \frac{4\pi q^2}{k^2}. \quad (8.146)$$

First find the Fourier transform of $\frac{1}{r}e^{r/\lambda}$ and then take the limit $\lambda \rightarrow 0$. \square

Debye-Hückel theory. Debye and Hückel developed a mean-field theory that includes the interactions between charged particles in very clever, but approximate way. Consider an electron at $\mathbf{r} = 0$ of charge $-q$. The average electric potential $\phi(\mathbf{r})$ in the neighborhood of $\mathbf{r} = 0$ is given by Poisson's equation:

$$\begin{aligned} \nabla^2 \phi(\mathbf{r}) = & -4\pi [(\text{negative point charge at origin}) + (\text{density of positive uniform background}) \\ & + (\text{density of other electrons})]. \end{aligned} \quad (8.147a)$$

That is,

$$\nabla^2 \phi(\mathbf{r}) = -4\pi [-q\delta(\mathbf{r}) + q\rho - q\rho g(\mathbf{r})], \quad (8.147b)$$

where ρ is the mean number density of the electrons and the uniform positive background, and $\rho g(\mathbf{r})$ is the density of the electrons in the vicinity of $\mathbf{r} = 0$. Equation (8.147b) is exact, but we have not specified $g(\mathbf{r})$. The key idea is that $g(\mathbf{r})$ is approximately given by the Boltzmann factor (see (8.73))

$$g(\mathbf{r}) \approx e^{\beta q \phi(\mathbf{r})}. \quad (8.148)$$

If we combine (8.147b) and (8.148), we obtain the Poisson-Boltzmann equation for $\phi(\mathbf{r})$:

$$\nabla^2 \phi(\mathbf{r}) = -4\pi q [-\delta(\mathbf{r}) + \rho - \rho e^{\beta q \phi(\mathbf{r})}]. \quad (8.149)$$

For $\beta q \phi \ll 1$, we may write $e^{-\beta q \phi(\mathbf{r})} \approx 1 - \beta q \phi(\mathbf{r})$ and obtain the linearized Poisson-Boltzmann equation

$$(\nabla^2 - \kappa_D^2)\phi(r) = 4\pi q \delta(r), \quad (8.150)$$

where κ_D^2 is given by

$$\kappa_D^2 = 4\pi\beta\rho q^2. \quad (8.151)$$

The solution to (8.150) that is spherically symmetric can be shown to be (see (9.22), page 440)

$$\phi(r) = -q \frac{e^{-r/\lambda_D}}{r}, \quad (8.152)$$

where $\lambda_D = 1/\kappa_D$. The energy of the other electrons in the potential $\phi(r)$ is $u_{\text{eff}}(r) = -q\phi(r)$ so that the effective energy of interaction between two electrons is given by

$$u_{\text{eff}}(r) = q^2 \frac{e^{-r/\lambda_D}}{r}. \quad (8.153)$$

The result (8.153) shows that the electrons collaborate in such a way as to screen the potential of a given electron over a distance λ_D . The quantity λ_D is called the *Debye screening length* and is the radius of the cloud of the electrons about any one electron that act to screen the Coulomb potential. The screening of the charge of the electrons is another example of a cooperative effect.

Note that to use statistical arguments, it is necessary that many particles have approximately the same potential energy, that is, many particles need to be within the range λ_D of ϕ . This requirement can be written as $\rho\lambda_D^3 \gg 1$. This condition holds in the limit of low density and high temperature.

Problem 8.22. Range of validity of the Debye-Hückel theory

Show that the condition $\rho\lambda_D^3 \gg 1$ is equivalent to the condition that the mean interaction energy between two electrons $e^2/(r = \lambda_D)$ be much smaller than the mean kinetic energy. \square

We now determine the radial distribution function $g(r)$ and the thermodynamic properties of the one-component plasma. From (8.148) we have

$$g(r) = e^{\beta q\phi(r)} \approx 1 - \beta q\phi(r) = 1 - \frac{\beta q^2}{r} e^{-r/\lambda_D}. \quad (8.154)$$

Problem 8.23. Thermodynamic properties of the Debye-Hückel theory

(a) The total energy per particle of the one-component plasma is given by

$$\frac{E}{N} = \frac{3}{2}NkT + \frac{\rho}{2} \int [g(r) - 1] u(r) d\mathbf{r}. \quad (8.155)$$

The factor of $g - 1$ rather than g in the integrand is due to the uniform positive background. Use the approximation (8.154) to show that the mean energy per particle can be expressed as

$$\frac{E}{N} = \frac{3}{2}kT - \frac{1}{2} \frac{e^2}{\lambda_D} = kT \left[\frac{3}{2} - \frac{1}{2} \frac{e^2}{\lambda_D kT} \right] = kT \left[\frac{3}{2} - \frac{\epsilon}{2} \right], \quad (8.156)$$

where the dimensionless parameter ϵ is defined as

$$\epsilon \equiv \frac{e^2}{\lambda_D kT}. \quad (8.157)$$

(b) Find an expression similar to (8.156) for the mean pressure. \square

The form of the right-hand side of (8.156) suggests that the Debye-Hückel theory is equivalent to keeping the first term in an expansion in powers of ϵ , in analogy to the expansion in powers of the density for systems with short-range interactions. However, the expansion is more complicated and involves logarithmic terms in ϵ . For example, the next order terms are proportional to ϵ^2 and $\epsilon^2 \ln \epsilon$.

Problem 8.24. The Debye-Hückel approximation of the direct correlation function

Use the form (8.154) to find the corresponding Fourier transform $h(k)$. Then use (8.130) to show that the direct correlation function $c(k)$ in the Debye-Hückel approximation is given by

$$c(k) = -\beta u(k). \quad (8.158)$$

Hence the Debye-Hückel approximation is equivalent to approximating the direct correlation function $c(r)$ by $-\beta u(r)$, the result for $c(r)$ to lowest order in the potential (see Problem 8.19b). \square

**Diagrammatic expansion.* We derived the density expansion of the free energy by first doing a high temperature expansion (see Section 8.4.2). Although individual terms in this expansion diverge at short separations for systems with a strongly repulsive interaction, we found that the divergence was removed by rearranging the expansion so that all terms of a given density are grouped together and summed.

As we have discussed, an expansion in terms of the density and the interaction of small numbers of particles makes no sense if the interaction is long range. We now discuss how to group individual terms in the high temperature expansion so that the divergence at large separations due to the long-range nature of the Coulomb potential is removed.¹⁰

Instead of considering the diagrammatic expansion for the free energy, we consider the high temperature expansion for $g(r)$, because the latter is easier to interpret physically. It is convenient to write $g(r)$ in the form

$$g(r) = e^{-\beta\psi(r)}, \quad (8.159)$$

where $\psi(r)$ is the *potential of mean force*. Note that $\psi(r)$ reduces to $u(r)$ in the limit of low densities. Recall that we obtained the low density expansion by first summing all possible potential (u) bonds between two particles. That is, we summed the infinite class of diagrams with the maximum number of bonds for a given number of particles. Because the Coulomb interaction is long-range, it is plausible that we should first sum the infinite class of diagrams corresponding to the maximum number of particles for a given number of bonds. These diagrams are called *ring diagrams*. The first several ring diagrams are shown in Figure 8.11. Because we know that the Coulomb interaction is screened, we expect that we should add up the contributions of all the ring diagrams before we include the contributions of other diagrams.

The contribution of the ring diagrams to $\psi(r)$ is given by

$$\begin{aligned} -\beta\psi(r) = & -\beta u(r) + \rho \int [-\beta u(r_{13})][-\beta u(r_{32})] d\mathbf{r}_3 \\ & + \rho^2 \int [-\beta u(r_{13})][-\beta u(r_{34})][-\beta u(r_{42})] d\mathbf{r}_3 d\mathbf{r}_4 + \dots, \end{aligned} \quad (8.160)$$

¹⁰Important early work was done by J. E. Mayer, "The theory of ionic solutions," J. Chem. Phys. **18**, 1426–1436 (1950).

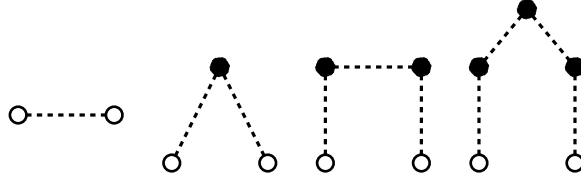


Figure 8.11: The first several ring diagrams for $\psi(r)$. The bonds represent the Coulomb interaction $u(r) = e^2/r$.

where $r = |\mathbf{r}_1 - \mathbf{r}_2|$. The structure of the integrals in (8.160) is the same as the convolution integral discussed in Section 8.9.1. We follow the same procedure and take the spatial Fourier transform of both sides of (8.160). The result can be written as

$$-\beta\psi(k) = -\beta u(k) + \rho[-\beta u(k)]^2 + \rho^2[-\beta u(k)]^3 + \dots, \quad (8.161)$$

where $u(k)$ is the Fourier transform of $u(r) = e^2/r$ (see Problem 8.146). Because the terms in (8.161) form a geometric series, we obtain

$$-\beta\psi(k) = \frac{-\beta u(k)}{1 + \rho\beta u(k)} = \frac{-\beta 4\pi e^2}{k^2 + \beta\rho 4\pi e^2} \quad (8.162a)$$

$$= -\beta \frac{4\pi e^2}{k^2 + \kappa_D^2}, \quad (8.162b)$$

where κ_D is given by (8.151). Hence

$$\psi(k) = \frac{4\pi e^2}{k^2 + \kappa_D^2} \quad (8.163)$$

and

$$\psi(r) = \frac{\beta e^2}{r} \epsilon^{-\kappa_D r}. \quad (8.164)$$

From (8.164) we see that the effective interaction is the Debye-Hückel screened potential as expected.

8.9 Supplementary Notes

8.9.1 The third virial coefficient for hard spheres

The third virial coefficient B_3 is given by (see (8.10b))

$$B_3 = -\frac{1}{3V} \int f(|\mathbf{r}_1 - \mathbf{r}_2|) f(|\mathbf{r}_1 - \mathbf{r}_3|) f(|\mathbf{r}_2 - \mathbf{r}_3|) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (8.165)$$

B_3 can be calculated for hard spheres by geometrical considerations, but these considerations test one's geometrical intuition. An easier way is to take advantage of the fact that (8.165) is an

example of a convolution integral (see Section A.11) and can be expressed in terms of the Fourier transform of $f(r)$.

Problem 8.25. Evaluation of B_3 for hard spheres

- (a) Read Appendix A.11 on convolution integrals and show that B_3 in (8.165) can be expressed as

$$B_3 = -\frac{1}{3} \int \frac{d^3 k}{(2\pi)^3} f(k)^3, \quad (8.166)$$

where $f(k)$ is the Fourier transform of $f(r)$.

- (b) Use (A.46) and the form of $f(r)$ for hard spheres,

$$f(r) = \begin{cases} -1 & (0 < r < \sigma) \\ = 0 & (r > \sigma), \end{cases} \quad (8.167)$$

to show that

$$f(k) = 4\pi\sigma^3 \left[\frac{\cos k\sigma}{(k\sigma)^2} - \frac{\sin k\sigma}{(k\sigma)^3} \right]. \quad (8.168)$$

- (c) *The integral in (8.166) with (8.168) for $f(k)$ can be evaluated numerically or calculated analytically. The result is

$$B_3 = \frac{5\pi^2}{18} \sigma^6. \quad (\text{hard spheres}) \quad (8.169)$$

□

B_4 can also be evaluated analytically for hard spheres, but higher order virial coefficients have to be evaluated by Monte Carlo methods.

8.9.2 Definition of $g(\mathbf{r})$ in terms of the local particle density

Another way of defining $g(r)$ is in terms of the local particle density. Given the properties of the delta function $\delta(x - x_0)$ (see Section A.10), we have that

$$\int_{x_0 - \epsilon}^{x_0 + \epsilon} \delta(x - x_0) dx = 1, \quad (8.170)$$

and the integral over any other values of x gives zero. Hence, the integral of the sum $\sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$ about \mathbf{r} over the volume element $d\mathbf{r}$ gives the number of particles in the volume element. We define the *local particle density*

$$\rho(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i), \quad (8.171)$$

and the single particle density function

$$\rho_1(\mathbf{r}) = \left\langle \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle, \quad (8.172)$$

where $\langle \delta(\mathbf{r} - \mathbf{r}_1) \rangle$ is given by

$$\langle \delta(\mathbf{r} - \mathbf{r}_1) \rangle = \frac{1}{Q_N} \int \delta(\mathbf{r} - \mathbf{r}_1) e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)} d\mathbf{r}_1 \dots d\mathbf{r}_N \quad (8.173a)$$

$$= \frac{1}{Q_N} \int e^{-\beta U(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)} d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (8.173b)$$

Similarly, the two-particle distribution function $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ is defined as

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i \neq j=1}^N \langle \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) \rangle. \quad (8.174)$$

We can use the same reasoning as in (8.173) to show that ρ_2 as defined in (8.174) can be written as

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \frac{\int e^{-\beta U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)} d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N}{\int e^{-\beta U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N}. \quad (8.175)$$

If we compare (8.175) and (8.81), we see that we can also express $g(\mathbf{r}_1, \mathbf{r}_2)$ as

$$\rho^2 g(\mathbf{r}_1, \mathbf{r}_2) = \rho_2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i \neq j} \langle \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) \rangle. \quad (8.176)$$

Hence, we see that $g(r)$ is related to the spatial correlations of the density fluctuations in the system.

Problem 8.26. One particle distribution function

Use the definition (8.172) and the result (8.173b) to show that $\rho_1(\mathbf{r}_1) = \rho$ for a homogeneous system. Hint: let $\mathbf{r}_j = \mathbf{r}_1 + \mathbf{x}_j$ for $j \neq 1$. Note that the denominator becomes independent of \mathbf{r}_1 . \square

8.9.3 X-ray scattering and the static structure function

The mean distance between particles in a typical fluid or solid is the order of 10^{-10} m. These wavelengths are available using neutrons or X-rays. To understand how an elastic scattering experiment can probe the static correlations between particles we consider X-ray scattering. A photon of wavelength of 10^{-10} m has an energy of $\hbar\omega = hc/\lambda \approx 10^4$ eV. This energy is very large in comparison to the typical energy of the particles in a liquid which is the order of kT or approximately 0.1 eV at room temperatures. Hence, the collisions of photons with the particles in a liquid and a solid will leave the photon energies almost unchanged and to a good approximation, the scattering can be treated as elastic.

In the following we will show that the scattered intensity $I(\theta)$ of the X-rays is given by

$$I(\theta) \propto NI_0 S(k), \quad (8.177)$$

where the wave vector k is related to the scattering angle θ and I_0 is the intensity of the incoming beam. The *static structure function* $S(k)$ is defined as

$$S(k) = \frac{1}{N} \left\langle \sum_{i,j=1}^N e^{i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)} \right\rangle. \quad (8.178)$$

In the following we will derive (8.177) and show that the radial distribution function $g(r)$ is related to the Fourier transform of $S(k)$.

To obtain (8.177) we assume that the incoming beam is a plane wave of wave vector \mathbf{q} . For simplicity we assume that the incident beam is scattered from an atom at the origin. The scattered signal is measured as a function of θ , the angle between the incident and scattered beams (see Figure 8.12). The detector receives a (spherical) wave of amplitude $f(\theta)/R$, where R is the distance of the detector from the origin. The form factor $f(\theta)$ depends on the detailed physics of the scattering process. Because the scattering is elastic, we have $|\mathbf{q}'| = |\mathbf{q}|$.

The amplitude of the wave scattered by an atom at \mathbf{r}_i has a phase difference of $(\mathbf{q}' - \mathbf{q}) \cdot \mathbf{r}_i$ relative to the wave scattered by the atom at the origin. Hence the scattering amplitude from atom i at \mathbf{r}_i is proportional to

$$\frac{f(\theta)}{R} e^{i\mathbf{k}\cdot\mathbf{r}_i}, \quad (8.179)$$

where

$$\mathbf{k} = \mathbf{q}' - \mathbf{q}. \quad (8.180)$$

Because the form factor $f(\theta)$ is the same for all atoms, the total scattering amplitude is the sum

$$A(\theta) = \frac{f(\theta)}{R} \sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i}. \quad (8.181)$$

The detector measures the thermal average of the scattering intensity:

$$I(\theta) = \langle |A(\theta)|^2 \rangle = \frac{|f(\theta)|^2}{R^2} \left\langle \sum_{i,j} e^{i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)} \right\rangle = \frac{|f(\theta)|^2}{R^2} N S(\mathbf{k}), \quad (8.182)$$

where the static structure function $S(k)$ is defined in (8.178).

The static structure function $S(k)$ is a measure of the correlations between the positions of the atoms in the liquid. We now show that $S(k)$ is related to the Fourier transform of $g(r)$. We first divide the sum over i and j in (8.178) into self, $i = j$, and distinct, $i \neq j$, contributions. There are N of the former and $N(N - 1)$ of the latter. We have

$$S(k) = 1 + \frac{1}{N} N(N - 1) \langle e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)} \rangle \quad (8.183a)$$

$$= 1 + \frac{N(N - 1)}{N} \frac{\int e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)} e^{-\beta U} d\mathbf{r}_1 \dots d\mathbf{r}_N}{\int e^{-\beta U} d\mathbf{r}_1 \dots d\mathbf{r}_N}. \quad (8.183b)$$

If we use the definition (8.81) of $g(\mathbf{r}_1, \mathbf{r}_2)$, we can write (8.183b) as

$$S(k) = 1 + \frac{1}{N} \int \rho^2 g(\mathbf{r}_1, \mathbf{r}_2) e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)} d\mathbf{r}_1 d\mathbf{r}_2. \quad (8.184)$$

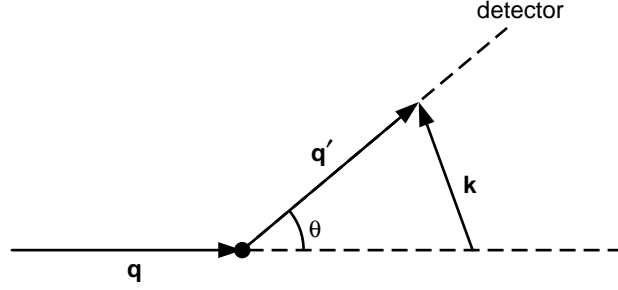


Figure 8.12: The geometry of the elastic scattering of a photon.

For a homogeneous liquid, $g(\mathbf{r}_1, \mathbf{r}_2)$ depends only on $|\mathbf{r}_1 - \mathbf{r}_2|$, and we obtain

$$S(k) = 1 + \rho \int g(r) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}. \quad (8.185)$$

It is customary to rewrite (8.185) as

$$S(k) - 1 = \rho \int [g(r) - 1] e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} + \rho \int e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \quad (8.186a)$$

$$= \rho \int [g(r) - 1] e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} + \rho(2\pi)^3 \delta(\mathbf{k}). \quad (8.186b)$$

The contribution of the $\delta(\mathbf{k})$ term in (8.186b) is unimportant because it is identically zero except when $\mathbf{k} = 0$, that is, for radiation not scattered by the atoms in the fluid. Hence, we can rewrite (8.186b) in the desired form:

$$\boxed{S(k) - 1 = \rho \int [g(r) - 1] e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}}. \quad (8.187)$$

From (8.187) we see that $S(k) - 1$ is the Fourier transform of $g(r) - 1$, and a measurement of the intensity of the elastically scattered radiation yields the Fourier transform of the radial distribution function.

Problem 8.27. Alternative form of $S(k)$

(a) Use the fact that the Fourier transform of the density $\rho(\mathbf{r})$ is

$$\rho_{\mathbf{k}} = \int e^{-i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r}) d\mathbf{r} = \sum_{i=1}^N e^{-i\mathbf{k}\cdot\mathbf{r}_i} \quad (8.188)$$

to show that $S(\mathbf{k})$ can be expressed as

$$S(\mathbf{k}) = \frac{1}{N} \langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle. \quad (8.189)$$

(b) Use (8.189) to show that $S(\mathbf{k})$ can be written as

$$S(\mathbf{k}) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N e^{-i\mathbf{k}\cdot\mathbf{r}_i} e^{i\mathbf{k}\cdot\mathbf{r}_j} \right\rangle \quad (8.190)$$

$$= \frac{1}{N} \left\langle \left| \sum_{i=1}^N e^{-i\mathbf{k}\cdot\mathbf{r}_i} \right|^2 \right\rangle. \quad (8.191)$$

□

Compressibility equation. In a scattering experiment the beam samples a subset of the total volume. Because the number of particles in the subset fluctuates, we need to use the grand canonical ensemble to describe the measured value of $S(k)$. The energy and pressure equations (8.74) and (8.97) are identical in both ensembles, but the *compressibility equation* holds only in the grand canonical ensemble because it relates the integral of $g(r) - 1$ and hence $S(k = 0)$ to fluctuations in the density.

In Section 6.11 we derived the relation between the isothermal compressibility and the density (number) fluctuations (see (6.238), page 343):

$$\rho\kappa = \frac{1}{kT} \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}. \quad (8.192)$$

We now relate the integral over $g(r)$ to the density fluctuations. In the grand canonical ensemble the probability density of finding n particular particles with positions $\mathbf{r}_1, \dots, \mathbf{r}_n$ in the range $d\mathbf{r}_1, \dots, d\mathbf{r}_n$ is given by

$$P_n(\mathbf{r}_1, \dots, \mathbf{r}_n) = \sum_{N=0}^{\infty} \frac{z^N}{N! Z_G} \int e^{-\beta U_N} d\mathbf{r}_{n+1} \dots d\mathbf{r}_N, \quad (8.193)$$

where $z = e^{\beta\mu}$. There are $N(N-1)\dots(N-n+1) = N!/(N-n)!$ different sets of particles which can correspond to the n particles. Hence, the total probability that any n particles occupy these volume elements is given by

$$P_n(\mathbf{r}_1, \dots, \mathbf{r}_n) \equiv \rho^n g(\mathbf{r}_1, \dots, \mathbf{r}_n), \quad (8.194a)$$

$$= \sum_{N=0}^{\infty} \frac{z^N}{N-n)! Z_G} \int \dots \int e^{-\beta U_N} d\mathbf{r}_{N+1}, \dots, d\mathbf{r}_N. \quad (8.194b)$$

From the definition of P_1 and P_2 , it follows that

$$\int P_1(\mathbf{r}_1) d\mathbf{r}_1 = \langle N \rangle, \quad (8.195)$$

and

$$\iint P_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \langle N(N-1) \rangle. \quad (8.196)$$

We can use (8.196) and (8.195) to obtain

$$\iint [P_2(\mathbf{r}_1, \mathbf{r}_2) - P_1(\mathbf{r}_1)P_1(\mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2 = \langle N^2 \rangle - \langle N \rangle^2 - \langle N \rangle. \quad (8.197)$$

The left-hand side of (8.197) is equal to $V\rho^2 \int [g(r) - 1] d\mathbf{r}$ for a homogeneous system. Hence we obtain

$$N\rho \int [g(r) - 1] d\mathbf{r} = \langle N^2 \rangle - \langle N \rangle^2 - \langle N \rangle, \quad (8.198)$$

or

$$1 + \rho \int [g(r) - 1] d\mathbf{r} = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}. \quad (8.199)$$

If we use the relation (8.192), we find the desired relation

$$1 + \rho \int [g(r) - 1] d\mathbf{r} = \rho k T \kappa. \quad (\text{compressibility equation}) \quad (8.200)$$

The relation (8.200), known as the *compressibility equation*, expresses the isothermal compressibility κ as an integral over $g(r)$ and holds only in the grand canonical ensemble. From the relation (8.187) we have

$$S(k=0) - 1 = \rho \int [g(r) - 1] d\mathbf{r}, \quad (8.201)$$

and hence

$$S(k=0) = \rho k T \kappa. \quad (8.202)$$

Problem 8.28. Value of $S(k=0)$ in different ensembles

As mentioned, the condition (8.202) on $S(k=0)$ only applies in the grand canonical ensemble. What is $S(k=0)$ in the canonical ensemble? Why is the value of $S(k=0)$ different in these two ensembles? \square

Alternative form of the compressibility relation. Finally, we express the compressibility relation (8.138) in terms of $c(r)$ rather than $h(r) = g(r) - 1$ by using the Ornstein-Zernicke equation (8.125). We write the latter as

$$g(r) - 1 = c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|) [g(\mathbf{r}') - 1] d\mathbf{r}'. \quad (8.203)$$

and multiply both sides by $d\mathbf{r}$ and integrate noting that $\int c(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r} = \int c(r) d\mathbf{r}$. We then rearrange the results to find

$$\int [g(r) - 1] d\mathbf{r} = \frac{\int c(r) d\mathbf{r}}{1 - \rho \int c(r) d\mathbf{r}}. \quad (8.204)$$

Finally we combine (8.204) with (8.138) to find (8.139).

8.10 Vocabulary

density expansion, virial coefficients, cluster integrals
 Mayer f function
 cumulant, high temperature expansion
 disconnected, reducible, and irreducible diagrams
 ladder diagrams, ring diagrams
 radial distribution function $g(r)$
 static structure function $S(k)$
 reference theory of liquids
 Debye-Hückel theory

Additional Problems

Problem 8.29. Why is the method that we have used to obtain the virial expansion for a classical fluid not applicable to a quantum system? \square

Problem 8.30. Temperature dependence of B_2

- (a) A simpler potential that captures some of the properties of the Lennard-Jones potential is the square well potential which is defined as

$$u(r) = \begin{cases} \infty & (r < \sigma) \\ -\epsilon & (0 < r < \lambda\sigma) \\ 0 & (r > \lambda\sigma), \end{cases} \quad (8.205)$$

where σ is the diameter of the hard core part, $\lambda\sigma$ is the range of the attractive well, and ϵ is the well depth. Show that for this potential the Mayer function $f(r)$ is given by

$$f(r) = \begin{cases} -1 & (r < \sigma) \\ g = e^{\beta\epsilon} - 1 & (0 < r < \lambda\sigma) \\ 0 & (r > \lambda\sigma), \end{cases} \quad (8.206)$$

and

$$B_2(T) = \frac{\pi}{2} [1 - (\lambda^2 - 1)g]. \quad (8.207)$$

- (b) Make a plot of the temperature dependence of $B_2(T)$ as given by (8.207) and compare it to the approximate temperature dependence given by (8.36).
- (c) Program `SecondVirialCoefficient` evaluates the integral over r in (8.32) numerically using a simple numerical method (Simpson's rule) to determine the T -dependence of B_2 for the Lennard-Jones potential. Compare the numerical results for the Lennard-Jones potential with the approximate result in (8.36). At what temperature does B_2 vanish? How does this temperature compare with that predicted by (8.36)? \square

Problem 8.31. Inversion temperature of argon

In Section 2.23.2, page 86, we discussed the porous plug or Joule-Thomson process in which a gas is forced from a high pressure chamber through a porous plug into a lower pressure chamber. The process occurs at constant enthalpy and the change in temperature of the gas is given by $dT = (\partial T/\partial P)_H dP$ for small changes in pressure. We know that (see (2.218), page 87)

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T}\right)_{P,N} - V \right]. \quad (8.208)$$

The locus of points $(\partial T/\partial P)_H = 0$ is called the Joule-Thomson inversion curve. Assume the approximate equation of state $V = NkT/P + NB_2$ and use your numerical results for B_2 from Problem 8.30 for the Lennard-Jones potential to compute the inversion temperature at which the inversion curve is a maximum. Use $\sigma = 3.4 \text{ \AA}$ and $\epsilon/k = 120 \text{ K}$ and compare your result with the experimental value of 780 K. \square

Problem 8.32. Alternative form of B_2

(a) Show that the virial coefficient B_2 given in (8.32) can be written in the form

$$B_2 = -\frac{1}{6kT} \int_0^\infty r \frac{du(r)}{dr} e^{-\beta u(r)} 4\pi r^2 dr. \quad (8.209)$$

(b) Assume that $g(r)$ can be written in the form

$$g(r) = g_0 + \rho g_1(r) + \rho^2 g_2(r) + \dots \quad (8.210)$$

Use the virial equation of state (8.97) to obtain

$$\frac{PV}{NkT} = 1 - \frac{\rho}{6kT} \sum_{n=0}^{\infty} \rho^n \int_0^\infty r \frac{du}{dr} g_n(r) 4\pi r^2 dr. \quad (8.211)$$

Compare the density expansion (8.9) of PV/NkT with (8.210) and show that

$$B_{n+2} = -\frac{1}{6kT} \int_0^\infty r \frac{du}{dr} g_n(r) 4\pi r^2 dr. \quad (8.212)$$

(c) From the result of part (a) show that

$$g_0(r) = e^{-\beta u(r)}. \quad (8.213)$$

(d) Use the relation (8.97) to find the form of B_2 implied by (8.213). \square

Problem 8.33. Exact equation of state for hard rods

Consider a one-dimensional system of particles confined to a box of length L . The interparticle interaction is given by

$$u(x) = \begin{cases} \infty & (x < \sigma) \\ 0 & (x \geq \sigma) \end{cases} \quad (8.214)$$

This system of hard rods is also known as a Tonks gas.

- (a) Evaluate the virial coefficients B_2 and B_3 . It is possible to do the integrals analytically.
- (b) Note that the form of the interaction (8.214) prevents particles from exchanging places, that is, from changing their order. What is the available “volume” in which the particles can move? Use this consideration to guess the form of the equation of state.
- (c) *Calculate the partition function and show that the exact equation of state of a system of hard rods is given by

$$\frac{P}{\rho kT} = \frac{1}{1 - \eta}, \quad (8.215)$$

where $\eta = \rho\sigma$ and $\rho = N/L$.

- (d) What is the value of the n th virial coefficient that is implied by the form (8.215) of the hard rod equation of state? \square

***Problem 8.34.** Virial coefficients implied by the Percus-Yevick approximation

Use the approximate results (8.137) and (8.140) for the Percus-Yevick equation of state for hard spheres to determine the virial coefficients implied by the Percus-Yevick equation. How do these virial coefficients compare with the exact coefficients given in Table 8.2? \square

Suggestions for Further Reading

Early work on hard disks was done by B. J. Alder and T. E. Wainwright, “Phase transition in elastic disks,” *Phys. Rev.* **127**, 349–361 (1962). See also A. C. Mitus, H. Weber, and D. Marx, “Local structure analysis of the hard-disk fluid near melting,” *Phys. Rev. E* **55**, 6855–6859 (1997).

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- Stanislav Labík, Jiří Kolafa, and Anatol Malijevský, “Virial coefficients of hard spheres and hard disks up to the ninth,” *Phys. Rev. E* **71**, 021105-1–8 (2005).
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