

CHAPTER 3

Static Properties of Liquids: Thermodynamics and Structure

Liquids are homogeneous in the bulk, but inhomogeneities appear close to the confining walls or other physical boundaries and wherever different phases coexist. Although it might seem natural to develop the theory of uniform fluids first, it turns out to be equally convenient and in many ways more illuminating to treat uniform and non-uniform systems simultaneously from the outset. In the first six sections of this chapter we describe a general approach to the study of inhomogeneous fluids based on the formalism of the grand canonical ensemble.¹ The starting point is a hamiltonian that includes a term representing the interaction of the particles with some spatially varying, external field. The effect of this term is to break the translational symmetry of the system, but results for uniform fluids are easily recovered by taking the limit in which the external field vanishes. A key component of the theory is a variational principle for the grand potential, which is a classical version of a principle originally derived for the interacting electron gas.² The last three sections provide an introduction to the use of diagrammatic methods in the theory of liquids, with examples chosen to complement the work discussed in earlier parts of the chapter.

3.1 A FLUID IN AN EXTERNAL FIELD

We consider again a system of identical, spherical particles in a volume V . The hamiltonian of the system in the presence of an external potential $\phi(\mathbf{r})$ is given by (2.1.1), which for ease of reference we repeat here:

$$\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = K_N(\mathbf{p}^N) + V_N(\mathbf{r}^N) + \Phi_N(\mathbf{r}^N) \quad (3.1.1)$$

The external field is assumed to couple to the microscopic particle density $\rho(\mathbf{r})$, defined as a sum of δ -functions in the form already introduced implicitly in (2.5.11), i.e.

$$\rho(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (3.1.2)$$

Thus the total potential energy due to the field is

$$\Phi_N(\mathbf{r}^N) = \sum_{i=1}^N \phi(\mathbf{r}_i) = \int \rho(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r} \quad (3.1.3)$$

The average density at a point \mathbf{r} is the single-particle density, or *density profile*, $\rho^{(1)}(\mathbf{r})$:

$$\langle \rho(\mathbf{r}) \rangle = \rho^{(1)}(\mathbf{r}) \quad (3.1.4)$$

where the angular brackets denote an average over a grand canonical ensemble. Thus the average value of Φ_N is

$$\langle \Phi_N \rangle = \int \rho^{(1)}(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r} \quad (3.1.5)$$

Fluctuations in the local density about its average value are described by a density–density correlation function, $H^{(2)}(\mathbf{r}, \mathbf{r}')$, defined as

$$\begin{aligned} H^{(2)}(\mathbf{r}, \mathbf{r}') &= \langle [\rho(\mathbf{r}) - \langle \rho(\mathbf{r}) \rangle] [\rho(\mathbf{r}') - \langle \rho(\mathbf{r}') \rangle] \rangle \\ &= \rho^{(2)}(\mathbf{r}, \mathbf{r}') + \rho^{(1)}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') - \rho^{(1)}(\mathbf{r}) \rho^{(1)}(\mathbf{r}') \\ &= \rho^{(1)}(\mathbf{r}) \rho^{(1)}(\mathbf{r}') h^{(2)}(\mathbf{r}, \mathbf{r}') + \rho^{(1)}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \end{aligned} \quad (3.1.6)$$

where $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$ is given by the analogue of (2.5.13) in the grand canonical ensemble and $h^{(2)}(\mathbf{r}, \mathbf{r}')$ is the pair correlation function (2.6.8). The function $H^{(2)}(\mathbf{r}, \mathbf{r}')$ represents the first in a hierarchy of density correlation functions having the general form

$$H^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \langle [\rho(\mathbf{r}_1) - \rho^{(1)}(\mathbf{r}_1)] \cdots [\rho(\mathbf{r}_n) - \rho^{(1)}(\mathbf{r}_n)] \rangle \quad (3.1.7)$$

for $n \geq 2$. Each function $H^{(n)}$ is a linear combination of all particle densities up to and including $\rho^{(n)}$.

Inclusion of the external-field term in the hamiltonian requires some modification of earlier definitions. As before, the grand partition function is related to the grand potential by $\mathcal{E} = \exp(-\beta\Omega)$, but now has the form

$$\mathcal{E} = \sum_{N=0}^{\infty} \frac{1}{N!} \int \exp(-\beta V_N) \left(\prod_{i=1}^N z \exp[-\beta \phi(\mathbf{r}_i)] \right) d\mathbf{r}^N \quad (3.1.8)$$

and the definition of the particle densities in (2.6.1) is replaced by

$$\rho^{(n)}(\mathbf{r}^n) = \frac{1}{\mathcal{E}} \sum_{N=n}^{\infty} \frac{1}{(N-n)!} \int \exp(-\beta V_N) \left(\prod_{i=1}^N z \exp[-\beta \phi(\mathbf{r}_i)] \right) d\mathbf{r}^{(N-n)} \quad (3.1.9)$$

Equation (3.1.8) may be recast as

$$\mathcal{E} = \sum_{N=0}^{\infty} \frac{1}{N!} \int \cdots \int \exp(-\beta V_N) \left(\prod_{i=1}^N \frac{1}{\Lambda^3} \exp[\beta \psi(\mathbf{r}_i)] \right) d\mathbf{r}_1 \cdots d\mathbf{r}_N \quad (3.1.10)$$

where

$$\psi(\mathbf{r}) = \mu - \phi(\mathbf{r}) \quad (3.1.11)$$

The quantity $\psi(\mathbf{r})$ is called the *intrinsic chemical potential*. It is the contribution to μ that is not explicitly dependent on $\phi(\mathbf{r})$.

The intrinsic chemical potential arises naturally in a thermodynamic description of the system. We suppose that the definition of $\phi(\mathbf{r})$ includes the confining potential, i.e. the interaction between the particles and the containing walls.³ The usual thermodynamic variable V may then be replaced by $\phi(\mathbf{r})$, the volume accessible to the particles being that region of space in which $\phi(\mathbf{r})$ is finite. The change in U resulting from an infinitesimal change in equilibrium state is now

$$\delta U = T \delta S + \int \rho^{(1)}(\mathbf{r}) \delta \phi(\mathbf{r}) d\mathbf{r} + \mu \delta N \quad (3.1.12)$$

(cf. (2.3.5)), where the integral extends over all space rather than over a large but finite volume. The definition of the Helmholtz free energy remains $F = U - TS$ and the change in F in an infinitesimal process is therefore

$$\delta F = -S \delta T + \int \rho^{(1)}(\mathbf{r}) \delta \phi(\mathbf{r}) d\mathbf{r} + \mu \delta N \quad (3.1.13)$$

By analogy with (3.1.11), we can also define an *intrinsic free energy*, \mathcal{F} , as

$$\mathcal{F} = F - \int \rho^{(1)}(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r} \quad (3.1.14)$$

with

$$\begin{aligned} \delta \mathcal{F} &= -S \delta T - \int \delta \rho^{(1)}(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r} + \mu \delta N \\ &= -S \delta T + \int \delta \rho^{(1)}(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (3.1.15)$$

Thus $\psi(\mathbf{r})$ appears as the field variable conjugate to $\rho^{(1)}(\mathbf{r})$. Finally, the grand potential $\Omega = F - N\mu$, when expressed in terms of \mathcal{F} , is

$$\Omega = \mathcal{F} + \int \rho^{(1)}(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r} - N\mu \quad (3.1.16)$$

with a differential given by

$$\begin{aligned}\delta\Omega &= -S\delta T + \int \rho^{(1)}(\mathbf{r})\delta\phi(\mathbf{r}) - N\delta\mu \\ &= -S\delta T - \int \rho^{(1)}(\mathbf{r})\delta\psi(\mathbf{r}) \, d\mathbf{r}\end{aligned}\quad (3.1.17)$$

We see from (3.1.15) and (3.1.17) that it is natural to take \mathcal{F} and Ω as functions of T and *functionals*, respectively, of $\rho^{(1)}$ and ψ . These relationships are expressed by use of the notation $\mathcal{F}[\rho^{(1)}]$ and $\Omega[\psi]$. Hence the change, say, in \mathcal{F} created by a change in $\rho^{(1)}(\mathbf{r})$ is determined by the *functional derivative* of \mathcal{F} with respect to $\rho^{(1)}$. The calculation of such derivatives requires some familiarity with the rules of functional differentiation, which are summarised in the section that follows.

The intrinsic free energy can also be written as an ensemble average. The definition (2.4.5) of the grand canonical probability density $f_0(\mathbf{r}^N, \mathbf{p}^N; N)$ shows that in the presence of an external field:

$$\ln f_0 = \beta\Omega - \beta K_N - \beta V_N - \beta\Phi_N + N\beta\mu \quad (3.1.18)$$

Thus

$$\langle K_N + V_N + k_B T \ln f_0 \rangle = \Omega + \int \rho^{(1)}(\mathbf{r})\psi(\mathbf{r}) \, d\mathbf{r} = \mathcal{F} \quad (3.1.19)$$

If there are no correlations between particles, the intrinsic chemical potential at a point \mathbf{r} is given by the usual expression (2.3.17) for the chemical potential of a system of non-interacting particles, but with the overall number density ρ replaced by $\rho^{(1)}(\mathbf{r})$. Thus the chemical potential of an inhomogeneous, ideal gas is

$$\mu^{\text{id}} = k_B T \ln[\Lambda^3 \rho^{(1)}(\mathbf{r})] + \phi(\mathbf{r}) \quad (3.1.20)$$

where the first term on the right-hand side is the intrinsic part. Equation (3.1.20) can be rearranged to give the well-known *barometric law*:

$$\rho^{(1)}(\mathbf{r}) = z^{\text{id}} \exp[-\beta\phi(\mathbf{r})] \quad (3.1.21)$$

where the activity $z^{\text{id}} = \Lambda^{-3} \exp(\beta\mu^{\text{id}})$ is equal to the number density of the uniform gas at the same chemical potential. The intrinsic free energy of an ideal gas also has a purely “local” form, given by an integral over \mathbf{r} of the free energy per unit volume of a non-interacting system of density $\rho^{(1)}(\mathbf{r})$:

$$\mathcal{F}^{\text{id}} = k_B T \int \rho^{(1)}(\mathbf{r}) (\ln[\Lambda^3 \rho^{(1)}(\mathbf{r})] - 1) \, d\mathbf{r} \quad (3.1.22)$$

This expression reduces to (2.3.16) in the uniform case.

3.2 FUNCTIONALS AND FUNCTIONAL DIFFERENTIATION

A functional is a natural extension of the familiar mathematical concept of a function. The meaning of a function is that of a mapping from points in n -space to a real or complex number, n being the number of variables on which the function depends. A functional, by contrast, depends on all values of a function $u(x)$, say, in a range $a \leq x \leq b$. It can therefore be interpreted as a mapping from ∞ -space to a real or complex number, the points in ∞ -space being the values of $u(x)$ at the infinite number of points in the relevant range of the variable x . Functions of several variables and functionals are therefore conveniently treated as discrete and continuous versions of the same mathematical concept, making it possible to construct the rules of functional differentiation by analogy with those of elementary calculus. As usual, a sum in the discrete case is replaced by an integral in the limit in which the distribution of variables becomes continuous.

If f is a function of the n variables $\mathbf{z} \equiv z_1, \dots, z_N$ the change in f due to an infinitesimal change in \mathbf{z} is

$$df = f(\mathbf{z} + d\mathbf{z}) - f(\mathbf{z}) = \sum_{i=1}^n A_i(\mathbf{z}) dz_i \quad (3.2.1)$$

where

$$A_i(\mathbf{z}) \equiv \frac{\partial f}{\partial z_i} \quad (3.2.2)$$

Similarly, if F is a functional of $u(x)$, then

$$\delta F = F[u + \delta u] - F[u] = \int_a^b A[u; x] \delta u(x) dx \quad (3.2.3)$$

and the functional derivative

$$A[u; x] \equiv \frac{\delta F}{\delta u(x)} \quad (3.2.4)$$

is a functional of u and a function of x . The functional derivative determines the change in F resulting from a change in u at a particular value of x ; to calculate the change in F due to a variation in $u(x)$ throughout the range of x it is necessary to integrate over x , as in (3.2.3).

The rules of functional differentiation are most easily grasped by considering some specific examples. If f is a linear function of n variables we know that

$$f(\mathbf{z}) = \sum_{i=1}^n a_i z_i, \quad df = \sum_{i=1}^n a_i dz_i \quad (3.2.5)$$

and

$$\frac{\partial f}{\partial z_i} = a_i, \quad \text{independent of } \mathbf{z} \quad (3.2.6)$$

The analogue of (3.2.5) for a linear functional is

$$F[u] = \int a(x)u(x) dx, \quad \delta F = \int a(x)\delta u(x) dx \quad (3.2.7)$$

and comparison with (3.2.3) shows that

$$\frac{\delta F}{\delta u(x)} = a(x), \quad \text{independent of } u \quad (3.2.8)$$

A more general example of the same type is when

$$F = \int \cdots \int a(x_1, \dots, x_N)u(x_1)u(x_2) \cdots u(x_N) dx_1 \cdots dx_N \quad (3.2.9)$$

where the function $a(x_1, \dots, x_N)$ is symmetric with respect to permutation of the labels $1, \dots, N$. Then

$$\begin{aligned} \delta F = & \int \cdots \int a(x_1, \dots, x_N)\delta u(x_1)u(x_2) \cdots u(x_N) dx_2 \cdots dx_N \\ & + (N-1) \text{ other terms} \end{aligned} \quad (3.2.10)$$

The N terms on the right-hand side are all equivalent, so the change in F is N times the value of any one term. Thus

$$\frac{\delta F}{\delta u(x_1)} = N \int \cdots \int a(x_1, \dots, x_N)u(x_2) \cdots u(x_N) dx_2 \cdots dx_N \quad (3.2.11)$$

As a slightly more complicated example, consider the non-linear functional

$$F[u] = \int u(x) \ln u(x) dx \quad (3.2.12)$$

for which

$$\begin{aligned} \delta F &= \int [\delta u(x) \ln u(x) + u(x)\delta \ln u(x)] dx \\ &= \int [\ln u(x) + 1]\delta u(x) dx \end{aligned} \quad (3.2.13)$$

and hence

$$\frac{\delta F}{\delta u(x)} = \ln u(x) + 1 \quad (3.2.14)$$

This example shows how functional derivatives can be evaluated with the help of rules appropriate to ordinary differentiation.

An important special case is when

$$F[u] = u(x') = \int \delta(x - x') u(x) dx \quad (3.2.15)$$

Then

$$\delta F = \int \delta(x - x') \delta u(x) dx = \delta u(x') \quad (3.2.16)$$

and

$$\frac{\delta u(x')}{\delta u(x)} = \delta(x - x') \quad (3.2.17)$$

When u is a function of two variables the functional derivative is defined through the relation

$$\delta F = \iint \frac{\delta F}{\delta u(x_1, x_2)} \delta u(x_1, x_2) dx_1 dx_2 \quad (3.2.18)$$

In applications in statistical mechanics symmetry often leads to a simplification similar to that seen in the example (3.2.9). Consider the functional defined as

$$F[u] = \iiint a(x_1, x_2, x_3) u(x_1, x_2) u(x_2, x_3) u(x_3, x_1) dx_1 dx_2 dx_3 \quad (3.2.19)$$

where $a(x_1, x_2, x_3)$ is symmetrical with respect to permutation of the labels 1, 2 and 3. The change in F due to an infinitesimal change in the function u is now

$$\begin{aligned} \delta F &= \iiint a(x_1, x_2, x_3) \delta u(x_1, x_2) u(x_2, x_3) u(x_3, x_1) dx_1 dx_2 dx_3 \\ &\quad + \text{two equivalent terms} \end{aligned} \quad (3.2.20)$$

Thus

$$\frac{\delta F}{\delta u(x_1, x_2)} = 3 \int a(x_1, x_2, x_3) u(x_2, x_3) u(x_3, x_1) dx_3 \quad (3.2.21)$$

Higher-order derivatives are defined in a manner similar to (3.2.3). In particular, the second derivative is defined through the relation

$$\delta A[u; x] = \int \frac{\delta A[u; x]}{\delta u(x')} \delta u(x') dx' \quad (3.2.22)$$

The second derivative of the functional (3.2.9), for example, is

$$\frac{\delta^2 F}{\delta u(x_1) \delta u(x_2)} = N(N-1) \int \cdots \int a(x_1, \dots, x_N) u(x_3) \cdots u(x_N) dx_3 \cdots dx_N \quad (3.2.23)$$

and is a functional of u and a function of both x and x' . If the derivatives exist, a functional $F[u]$ can be expanded in a Taylor series around a function u_0 :

$$\begin{aligned} F[u] = & F[u_0] + \int \left. \frac{\delta F}{\delta u(x)} \right|_{u=u_0} [u(x) - u_0(x)] dx \\ & + \frac{1}{2!} \iint \left. \frac{\delta^2 F}{\delta u(x) \delta u(x')} \right|_{u=u_0} [u(x) - u_0(x)][u(x') - u_0(x')] dx dx' \\ & + \dots \end{aligned} \quad (3.2.24)$$

Finally, the equivalent of the chain rule of ordinary differentiation is

$$\frac{\delta F}{\delta u(x)} = \int \frac{\delta F}{\delta v(x')} \frac{\delta v(x')}{\delta u(x)} dx' \quad (3.2.25)$$

3.3 FUNCTIONAL DERIVATIVES OF THE GRAND POTENTIAL

The methods of the previous section can be used very straightforwardly to derive some important results involving derivatives of the grand potential. We saw in Section 3.1 that it is natural to treat the intrinsic free energy as a functional of the single-particle density. The manner in which the functional $\mathcal{F}[\rho^{(1)}]$ varies with $\rho^{(1)}$ is described by (3.1.15) and from that result, given the definition of a functional derivative, it follows immediately that

$$\frac{\delta \mathcal{F}}{\delta \rho^{(1)}(\mathbf{r})} = \psi(\mathbf{r}) \quad (3.3.1)$$

where the derivative is taken at constant T . The intrinsic free energy can be divided into ideal and excess parts in the form

$$\mathcal{F}[\rho^{(1)}] = \mathcal{F}^{\text{id}}[\rho^{(1)}] + \mathcal{F}^{\text{ex}}[\rho^{(1)}] \quad (3.3.2)$$

where the ideal part is given by (3.1.22). Use of example (3.2.14) confirms that the functional derivative of \mathcal{F}^{id} is

$$\frac{\delta \mathcal{F}^{\text{id}}}{\delta \rho^{(1)}(\mathbf{r})} = k_B T \ln[\Lambda^3 \rho^{(1)}(\mathbf{r})] \quad (3.3.3)$$

in agreement with (3.1.20). In the same way it follows from (3.1.17) that the functional derivative of $\Omega[\psi]$ with respect to ψ is

$$\frac{\delta \Omega}{\delta \psi(\mathbf{r})} = -\rho^{(1)}(\mathbf{r}) \quad (3.3.4)$$

From this result (or from (3.3.1)) it follows that the functionals $\Omega[\psi]$ and $\mathcal{F}[\rho^{(1)}]$ are related by a generalised Legendre transformation,⁴ i.e.

$$\Omega[\psi] - \int \psi(\mathbf{r}) \frac{\delta \Omega}{\delta \psi(\mathbf{r})} d\mathbf{r} \rightarrow \Omega[\psi] + \int \psi(\mathbf{r}) \rho^{(1)}(\mathbf{r}) d\mathbf{r} = \mathcal{F}[\rho^{(1)}] \quad (3.3.5)$$

In the limit $\phi \rightarrow 0$, ψ and $\rho^{(1)}$ can be replaced by μ and $\langle N \rangle / V$, respectively, and (3.3.1) and (3.3.4) reduce to standard thermodynamic results, $\partial F / \partial N = \mu$ and $\partial \Omega / \partial \mu = -N$.

The relationship that exists between Ω and \mathcal{E} means that it must also be possible to obtain (3.3.4) by differentiation of $\ln \mathcal{E}$. We already know the outcome of this calculation, but the exercise is nonetheless a useful one, since it points the way towards the calculation of higher-order derivatives. In carrying out the differentiation it proves helpful to introduce a *local activity*, z^* , defined as

$$z^*(\mathbf{r}) = \frac{\exp[\beta \psi(\mathbf{r})]}{\Lambda^3} = z \exp[-\beta \phi(\mathbf{r})] \quad (3.3.6)$$

If we also adopt a simplified notation in which a position vector \mathbf{r}_i is denoted by i , the grand partition function (3.1.10) can be rewritten in the form

$$\mathcal{E} = \sum_{N=0}^{\infty} \frac{1}{N!} \int \cdots \int \exp(-\beta V_N) \left(\prod_{i=1}^N z^*(i) \right) d1 \cdots dN \quad (3.3.7)$$

The derivative we require is

$$\frac{\delta \Omega}{\delta \psi(1)} = -k_B T \frac{\delta \ln \mathcal{E}}{\delta \psi(1)} = -\frac{z^*(1)}{\mathcal{E}} \frac{\delta \mathcal{E}}{\delta z^*(1)} \quad (3.3.8)$$

The term for $N = 0$ in (3.3.7) vanishes on differentiation. Higher-order terms are of the general form considered in example (3.2.9) and differentiation of each term therefore yields a factor N . Thus

$$\frac{\delta \mathcal{E}}{\delta z^*(1)} = \sum_{N=1}^{\infty} \frac{1}{(N-1)!} \int \cdots \int \exp(-\beta V_N) \left(\prod_{i=2}^N z^*(i) \right) d2 \cdots dN \quad (3.3.9)$$

and combination of (3.3.8) and (3.3.9) with the definition of the particle densities in (3.1.9) leads back to (3.3.4). By further differentiation of \mathcal{E} it is easy to show that

$$\rho^{(n)}(1, \dots, n) = \frac{z^*(1) \cdots z^*(n)}{\mathcal{E}} \frac{\delta^n \mathcal{E}}{\delta z^*(1) \cdots \delta z^*(n)} \quad (3.3.10)$$

The grand partition function is said to be the *generating functional* for the particle densities.

Calculation of the second derivative of Ω with respect to ψ is only slightly more complicated. The quantity to be determined is now

$$\frac{\delta^2 \Omega}{\delta \psi(1) \delta \psi(2)} = -\beta z^*(2) \frac{\delta}{\delta z^*(2)} \left(\frac{1}{\mathcal{E}} z^*(1) \frac{\delta \mathcal{E}}{\delta z^*(1)} \right) \quad (3.3.11)$$

Differentiation of successive factors in the product in brackets gives rise, respectively, to a term in $\rho^{(1)}(2)$, a term in $\delta(1, 2)$ (as in example (3.2.17)) and a term in $\rho^{(2)}(1, 2)$ (from (3.3.10)). On combining these results we find that

$$\begin{aligned} \frac{\delta^2 \Omega}{\delta \psi(1) \delta \psi(2)} &= \beta [\rho^{(1)}(1) \rho^{(1)}(2) - \rho^{(1)}(1) \delta(1, 2) - \rho^{(2)}(1, 2)] \\ &= -\beta H^{(2)}(1, 2) \end{aligned} \quad (3.3.12)$$

where $H^{(2)}(1, 2)$ is the density–density correlation function defined by (3.1.6). The process of differentiation can again be extended; although the algebra becomes increasingly tedious, the general result has a simple form:

$$\frac{\delta^n \beta \Omega}{\delta \beta \psi(1) \cdots \delta \beta \psi(n)} = -H^{(n)}(1, \dots, n), \quad n \geq 2 \quad (3.3.13)$$

The grand potential is therefore the generating functional for the n -fold density correlation functions.

3.4 DENSITY-FUNCTIONAL THEORY

The grand potential has temperature and intrinsic chemical potential as its natural variables. However, it turns out to be more profitable to treat $\rho^{(1)}$ rather than ψ as the fundamental field variable. The definition (3.1.9) shows that $\rho^{(1)}$ is a functional of ϕ . What is not obvious is the fact that for a given interparticle potential-energy function V_N and fixed values of T and μ , there is only one external potential that gives rise to a specific density profile. This result, the proof of which is given in Appendix B, has far-reaching implications. The grand canonical probability density f_0 defined by (2.4.5) is a functional of $\phi(\mathbf{r})$. Hence any quantity which, for given V_N , T and μ , is wholly determined by f_0 is necessarily a functional of $\rho^{(1)}$, and its functional dependence on $\rho^{(1)}$ is independent of the external potential. In particular, because the intrinsic free energy is the ensemble average of $(K_N + V_N + k_B T \ln f_0)$ (see (3.1.19)), it follows that $\mathcal{F}[\rho^{(1)}]$ is a unique functional of $\rho^{(1)}$.

Let $n(\mathbf{r})$ be some average of the microscopic density, not necessarily the equilibrium one, and let $\Omega_\phi[n]$ be a functional of n , defined for fixed external potential by

$$\Omega_\phi[n] = \mathcal{F}[n] + \int n(\mathbf{r}) \phi(\mathbf{r}) \, d\mathbf{r} - \mu \int n(\mathbf{r}) \, d\mathbf{r} \quad (3.4.1)$$

At equilibrium, $n(\mathbf{r}) = \rho^{(1)}(\mathbf{r})$, and Ω_ϕ reduces to the grand potential, i.e.

$$\Omega_\phi[\rho^{(1)}] = \Omega \quad (3.4.2)$$

while differentiation of (3.4.1) with respect to $n(\mathbf{r})$ gives

$$\left. \frac{\delta \Omega_\phi}{\delta n(\mathbf{r})} \right|_{n=\rho^{(1)}} = \left. \frac{\delta \mathcal{F}[n]}{\delta n(\mathbf{r})} \right|_{n=\rho^{(1)}} - \mu + \phi(\mathbf{r}) = 0 \quad (3.4.3)$$

where the right-hand side vanishes by virtue of (3.3.1). Thus Ω_ϕ is stationary with respect to variations in $n(\mathbf{r})$ around the equilibrium density. It is also straightforward to show that

$$\Omega_\phi[n] \geq \Omega \quad (3.4.4)$$

where the equality applies only when $n(\mathbf{r}) = \rho^{(1)}(\mathbf{r})$. In other words, the functional Ω_ϕ has a lower bound equal to the exact grand potential of the system. A proof of (3.4.4) is also given in Appendix B.

Equations (3.4.3) and (3.4.4) provide the ingredients for a variational calculation of the density profile and grand potential of an inhomogeneous fluid. What is required in order to make the theory tractable is a parametrisation of the free-energy functional $\mathcal{F}[n]$ in terms of $n(\mathbf{r})$. Since the ideal part is known exactly, the difficulty lies in finding a suitable form for $\mathcal{F}^{\text{ex}}[n]$. The best estimates of $\rho^{(1)}$ and Ω are then obtained by minimising the functional $\Omega_\phi[n]$ with respect to variations in $n(\mathbf{r})$. Minimisation of a functional such as $\Omega_\phi[n]$ is the central problem in the calculus of variations and normally requires the solution to a differential equation called the Euler or Euler–Lagrange equation. Computational schemes of this type are grouped together under the title *density-functional theory*. The theory has found application to a very wide range of problems, some of which are discussed in later chapters. As in any variational calculation, the success achieved depends on the skill with which the trial functional is constructed. Because \mathcal{F} is a unique functional of $\rho^{(1)}$, a good approximation would be one that was suitable for widely differing choices of external potential, but in practice most approximations are designed for use in specific physical situations.

If V_N is a sum of pair potentials, it is possible to derive an exact expression for \mathcal{F}^{ex} in terms of the pair density in a form that lends itself readily to approximation. The grand partition function can be written as

$$\mathcal{E} = \sum_{N=0}^{\infty} \frac{1}{N!} \int \cdots \int \left(\prod_{i < j}^N e(i, j) \right) \left(\prod_{i=1}^N z^*(i) \right) d1 \cdots dN \quad (3.4.5)$$

where $e(i, j) \equiv \exp[(-\beta v(i, j))]$. Then the functional derivative of Ω with respect to v at constant T and ψ is

$$\begin{aligned} \frac{\delta \Omega}{\delta v(1, 2)} &= \frac{\delta \ln \mathcal{E}}{\delta \ln e(1, 2)} = \frac{e(1, 2)}{\mathcal{E}} \frac{\delta \mathcal{E}}{\delta e(1, 2)} \\ &= \frac{1}{\mathcal{E}} \sum_{N=2}^{\infty} \frac{N(N-1)}{2N!} \int \cdots \int \left(\prod_{i < j}^N e(i, j) \right) \left(\prod_{i=1}^N z^*(i) \right) d3 \cdots dN \end{aligned} \quad (3.4.6)$$

where the factor $N(N - 1)/2$ is the number of equivalent terms resulting from the differentiation (cf. (3.2.20)). Comparison with the definition of $\rho^{(n)}$ in (3.1.9) shows that

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = 2 \frac{\delta \Omega}{\delta v(\mathbf{r}, \mathbf{r}')} \quad (3.4.7)$$

and hence that

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = 2 \frac{\delta \mathcal{F}^{\text{ex}}[\rho^{(1)}]}{\delta v(\mathbf{r}, \mathbf{r}')} \quad (3.4.8)$$

We now suppose that the pair potential can be expressed as the sum of a “reference” part, $v_0(\mathbf{r}, \mathbf{r}')$, and a “perturbation”, $w(\mathbf{r}, \mathbf{r}')$, and define a family of intermediate potentials by

$$v_\lambda(\mathbf{r}, \mathbf{r}') = v_0(\mathbf{r}, \mathbf{r}') + \lambda w(\mathbf{r}, \mathbf{r}'), \quad 0 \leq \lambda \leq 1 \quad (3.4.9)$$

The reference potential could, for example, be the hard-sphere interaction and the perturbation could be a weak, attractive tail, while the increase in λ from 0 to 1 would correspond to a gradual “switching on” of the perturbation. It follows from integration of (3.4.8) at constant single-particle density that the free-energy functional for the system of interest, characterised by the full potential $v(\mathbf{r}, \mathbf{r}')$, is related to that of the reference system by

$$\begin{aligned} \mathcal{F}^{\text{ex}}[\rho^{(1)}] &= \mathcal{F}_0^{\text{ex}}[\rho^{(1)}] + \frac{1}{2} \int_0^1 d\lambda \iint \rho^{(2)}(\mathbf{r}, \mathbf{r}'; \lambda) w(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &= \mathcal{F}_0^{\text{ex}}[\rho^{(1)}] + \frac{1}{2} \iint \rho^{(1)}(\mathbf{r}) \rho^{(1)}(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' + \mathcal{F}_{\text{corr}}[\rho^{(1)}] \end{aligned} \quad (3.4.10)$$

where $\rho^{(2)}(\mathbf{r}, \mathbf{r}'; \lambda)$ is the pair density for the system with potential v_λ and

$$\mathcal{F}_{\text{corr}}[\rho^{(1)}] = \frac{1}{2} \int_0^1 d\lambda \iint \rho^{(1)}(\mathbf{r}) \rho^{(1)}(\mathbf{r}') h^{(2)}(\mathbf{r}, \mathbf{r}'; \lambda) w(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (3.4.11)$$

is the contribution to \mathcal{F}^{ex} due to correlations induced by the perturbation. Equation (3.4.10) provides a basis for the perturbation theories of uniform fluids discussed in Chapter 5.

3.5 DIRECT CORRELATION FUNCTIONS

We saw in Section 3.3 that the grand potential is a generating functional for the density correlation functions $H^{(n)}(\mathbf{r}^n)$. In a similar way, the excess part of the free-energy functional acts as a generating functional for a parallel hierarchy of *direct correlation functions*, $c^{(n)}(\mathbf{r}^n)$. The single-particle function is defined as the first functional derivative of \mathcal{F}^{ex} with respect to $\rho^{(1)}$:

$$c^{(1)}(\mathbf{r}) = -\beta \frac{\delta \mathcal{F}^{\text{ex}}[\rho^{(1)}]}{\delta \rho^{(1)}(\mathbf{r})} \quad (3.5.1)$$

The pair function is defined as the functional derivative of $c^{(1)}$:

$$c^{(2)}(\mathbf{r}, \mathbf{r}') = \frac{\delta c^{(1)}(\mathbf{r})}{\delta \rho^{(1)}(\mathbf{r}')} = -\beta \frac{\delta^2 \mathcal{F}^{\text{ex}}[\rho^{(1)}]}{\delta \rho^{(1)}(\mathbf{r}) \delta \rho^{(1)}(\mathbf{r}')} \quad (3.5.2)$$

and similarly for higher-order functions: $c^{(n+1)}(\mathbf{r}^{n+1})$ is the derivative of $c^{(n)}(\mathbf{r}^n)$. It follows from (3.3.1), (3.3.3) and (3.5.1) that

$$\beta \psi(\mathbf{r}) = \beta \frac{\delta \mathcal{F}[\rho^{(1)}]}{\delta \rho^{(1)}(\mathbf{r})} = \ln[\Lambda^3 \rho^{(1)}(\mathbf{r})] - c^{(1)}(\mathbf{r}) \quad (3.5.3)$$

or, given that $\psi = \mu - \phi$ and $z = \exp(\beta\mu)/\Lambda^3$:

$$\rho^{(1)}(\mathbf{r}) = z \exp[-\beta\phi(\mathbf{r}) + c^{(1)}(\mathbf{r})] \quad (3.5.4)$$

Comparison with the corresponding ideal-gas result in (3.1.21) (the barometric law) shows that the effects of particle interactions on the density profile are wholly contained in the function $c^{(1)}(\mathbf{r})$. It is also clear from (3.5.3) that the quantity $-k_B T c^{(1)}(\mathbf{r})$, which acts in (3.5.4) as a self-consistent addition to the external potential, is the excess part of the intrinsic chemical potential. By appropriately adapting the argument of Section 2.4 it can be shown that $-k_B T c^{(1)}(\mathbf{r})$ is given by an expression identical to that on the right-hand side of (2.4.31), but where ε is now the energy of a test particle placed at \mathbf{r} that interacts with particles of the system but not with the external field.⁵ If $\phi = 0$, (3.5.4) can be rearranged to give

$$-k_B T c^{(1)} = \mu - k_B T \ln \Lambda^3 \rho = \mu^{\text{ex}} \quad (3.5.5)$$

To obtain a useful expression for $c^{(2)}(\mathbf{r}, \mathbf{r}')$ we must return to some earlier results. Equations (3.3.4) and (3.3.12) show that, apart from a constant factor, the density–density correlation function is the functional derivative of $\rho^{(1)}$ with respect to ψ :

$$H(\mathbf{r}, \mathbf{r}') = k_B T \frac{\delta \rho^{(1)}(\mathbf{r})}{\delta \psi(\mathbf{r}')} \quad (3.5.6)$$

where, for notational simplicity, we have temporarily omitted the superscript (2). It therefore follows from (3.2.17) and (3.2.25) that the functional inverse of H , defined through the relation

$$\int H(\mathbf{r}, \mathbf{r}'') H^{-1}(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' = \delta(\mathbf{r} - \mathbf{r}') \quad (3.5.7)$$

is

$$H^{-1}(\mathbf{r}, \mathbf{r}') = \beta \frac{\delta \psi(\mathbf{r})}{\delta \rho^{(1)}(\mathbf{r}')} \quad (3.5.8)$$

Functional differentiation of the expression for ψ in (3.5.3) gives

$$\beta \frac{\delta \psi(\mathbf{r})}{\delta \rho^{(1)}(\mathbf{r}')} = \frac{1}{\rho^{(1)}(\mathbf{r})} \delta(\mathbf{r} - \mathbf{r}') - c^{(2)}(\mathbf{r}, \mathbf{r}') = H^{-1}(\mathbf{r}, \mathbf{r}') \quad (3.5.9)$$

If we now substitute for H and H^{-1} in (3.5.7), integrate over \mathbf{r}'' and introduce the pair correlation function defined by (3.1.6), we obtain the *Ornstein–Zernike relation*:

$$h^{(2)}(\mathbf{r}, \mathbf{r}') = c^{(2)}(\mathbf{r}, \mathbf{r}') + \int c^{(2)}(\mathbf{r}, \mathbf{r}'') \rho^{(1)}(\mathbf{r}'') h^{(2)}(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' \quad (3.5.10)$$

This relation is often taken as the definition of $c^{(2)}$, but the definition as a derivative of the intrinsic free energy gives the function greater physical meaning. Equation (3.5.10) can be solved recursively to give

$$\begin{aligned} h^{(2)}(1, 2) = & c^{(2)}(1, 2) + \int c^{(2)}(1, 3) \rho^{(1)}(3) c^{(2)}(3, 2) d3 \\ & + \iint c^{(2)}(1, 3) \rho^{(1)}(3) c^{(2)}(3, 4) \rho^{(1)}(4) c^{(2)}(4, 2) d3 d4 + \dots \end{aligned} \quad (3.5.11)$$

This result has an obvious physical interpretation: the “total” correlation between particles 1 and 2, represented by $h^{(2)}(1, 2)$, is due in part to the “direct” correlation between 1 and 2 but also to the “indirect” correlation propagated via increasingly large numbers of intermediate particles. With this physical picture in mind it is plausible to suppose that the range of $c^{(2)}(1, 2)$ is comparable with that of the pair potential $v(1, 2)$ and to ascribe the fact that $h^{(2)}(1, 2)$ is generally much longer ranged than $v(1, 2)$ to the effects of indirect correlation. The differences between the two functions for the Lennard-Jones fluid at high density and low temperature are illustrated in Figure 3.1; $c(r)$ is not only shorter ranged than $h(r)$ but also simpler in structure.

If the fluid is uniform and isotropic, the Ornstein–Zernike relation becomes

$$h(r) = c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|) h(r') d\mathbf{r}' \quad (3.5.12)$$

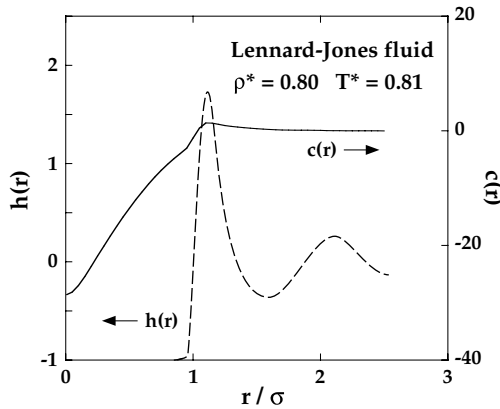


FIG. 3.1. The pair functions $h(r)$ (dashes) and $c(r)$ (full curve) obtained by Monte Carlo calculations for the Lennard-Jones fluid at a high density and low temperature. After Llano-Restrepo and Chapman.⁶

where the term representing the indirect correlation now appears as a convolution integral. We have also followed the convention adopted earlier for $g(r)$ by omitting the superscripts (2) when the system is homogeneous and shall continue to do so in circumstances where there is no risk of ambiguity. On taking the Fourier transform of both sides of (3.5.12) we obtain an algebraic relation between $\hat{h}(k)$ and $\hat{c}(k)$:

$$\hat{h}(k) = \frac{\hat{c}(k)}{1 - \rho \hat{c}(k)} \quad (3.5.13)$$

Equation (3.5.13) provides a link with thermodynamics via the compressibility equation (2.6.12). Since $h(r) = g(r) - 1$, it follows from (2.6.12) that the isothermal compressibility can be written in either of the two equivalent forms:

$$\rho k_B T \chi_T = 1 + \rho \hat{h}(0) \quad (3.5.14)$$

or

$$\frac{1}{\rho k_B T \chi_T} = 1 - \rho \hat{c}(0) \quad (3.5.15)$$

These results bring out particularly clearly the inverse relationship that exists between h and c .

The definitions of $c^{(1)}$ and $c^{(2)}$ in (3.5.1) and (3.5.2) are useful in characterising the nature of an approximate free-energy functional. As a simple example, consider the functional derived from the exact result (3.4.10) by discarding the term $\mathcal{F}_{\text{corr}}$, which amounts to treating the effects of the perturbation $w(\mathbf{r}, \mathbf{r}')$ in a mean-field approximation. Then

$$c^{(1)}(\mathbf{r}) \approx c_0^{(1)}(\mathbf{r}) - \beta \int \rho^{(1)}(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \quad (3.5.16)$$

$$c^{(2)}(\mathbf{r}, \mathbf{r}') \approx c_0^{(2)}(\mathbf{r}, \mathbf{r}') - \beta w(\mathbf{r}, \mathbf{r}') \quad (3.5.17)$$

where $c_0^{(1)}$ and $c_0^{(2)}$ are the direct correlation functions of the reference system. Substitution of (3.5.16) in (3.5.4) yields an integral equation for $\rho^{(1)}(\mathbf{r})$ that can be solved iteratively if the properties of the reference system are known or if some further approximation is made for $c_0^{(1)}$. Equation (3.5.17) is a well-known approximation in the theory of uniform fluids;⁷ for historical reasons it is called the *random-phase approximation* or RPA. It is generally accepted that $c^{(2)}(\mathbf{r}, \mathbf{r}')$ behaves asymptotically as $-\beta v(\mathbf{r}, \mathbf{r}')$. The RPA should therefore be exact when $|\mathbf{r} - \mathbf{r}'|$ is sufficiently large; this assumes that the perturbation contains the long-range part of the potential, which is almost invariably the case.

The formally exact expression for the intrinsic free energy given by (3.4.10) was obtained by thermodynamic integration with respect to the interparticle potential. Another exact expression can be derived from the definitions of $c^{(1)}$ and $c^{(2)}$ by integrating with respect to the single-particle density. Let $\rho_0^{(1)}(\mathbf{r})$ and $c_0^{(1)}(\mathbf{r})$ be the single-particle density and single-particle direct correlation function, respectively, in a reference state of the system of interest. We choose a linear integration path between the reference state and the

final state of density $\rho^{(1)}(\mathbf{r})$ such that

$$\rho^{(1)}(\mathbf{r}; \lambda) = \rho_0^{(1)}(\mathbf{r}) + \lambda \Delta \rho^{(1)}(\mathbf{r}) \quad (3.5.18)$$

where $\Delta \rho^{(1)} = \rho^{(1)} - \rho_0^{(1)}$. Then integration of (3.5.1) gives

$$\begin{aligned} \mathcal{F}^{\text{ex}}[\rho^{(1)}] &= \mathcal{F}_0^{\text{ex}}[\rho_0^{(1)}] - k_B T \int_0^1 d\lambda \int \frac{\partial \rho^{(1)}(\mathbf{r}; \lambda)}{\partial \lambda} c^{(1)}(\mathbf{r}; \lambda) d\mathbf{r} \\ &= \mathcal{F}_0^{\text{ex}}[\rho_0^{(1)}] - k_B T \int_0^1 d\lambda \int \Delta \rho^{(1)}(\mathbf{r}) c^{(1)}(\mathbf{r}; \lambda) d\mathbf{r} \end{aligned} \quad (3.5.19)$$

Similarly, from integration of (3.5.2):

$$c^{(1)}(\mathbf{r}; \lambda) = c_0^{(1)}(\mathbf{r}) + \int_0^\lambda d\lambda' \int \Delta \rho^{(1)}(\mathbf{r}') c^{(2)}(\mathbf{r}, \mathbf{r}'; \lambda') d\mathbf{r}' \quad (3.5.20)$$

and hence, after substitution of (3.5.20) in (3.5.19):

$$\begin{aligned} \mathcal{F}^{\text{ex}}[\rho^{(1)}] &= \mathcal{F}_0^{\text{ex}}[\rho_0^{(1)}] - k_B T \int \Delta \rho^{(1)}(\mathbf{r}) c_0^{(1)}(\mathbf{r}) d\mathbf{r} \\ &\quad - k_B T \int_0^1 d\lambda \int_0^\lambda d\lambda' \iint \Delta \rho^{(1)}(\mathbf{r}) \Delta \rho^{(1)}(\mathbf{r}') c^{(2)}(\mathbf{r}, \mathbf{r}'; \lambda) d\mathbf{r} d\mathbf{r}' \end{aligned} \quad (3.5.21)$$

The integration path defined by (3.5.18) is chosen for mathematical convenience, but the final result is independent of path, since \mathcal{F}^{ex} is a unique functional of $\rho^{(1)}$.

Some simplification of (3.5.21) is possible. An integration by parts shows that

$$\int_0^1 d\lambda \int_0^\lambda y(\lambda') d\lambda' = \int_0^1 (1 - \lambda) y(\lambda) d\lambda \quad (3.5.22)$$

for any function $y(\lambda)$. Thus

$$\begin{aligned} \mathcal{F}^{\text{ex}}[\rho^{(1)}] &= \mathcal{F}_0^{\text{ex}}[\rho_0^{(1)}] - k_B T \int \Delta \rho^{(1)}(\mathbf{r}) c_0^{(1)}(\mathbf{r}) d\mathbf{r} \\ &\quad - k_B T \int_0^1 d\lambda (1 - \lambda) \iint \Delta \rho^{(1)}(\mathbf{r}) \Delta \rho^{(1)}(\mathbf{r}') c^{(2)}(\mathbf{r}, \mathbf{r}'; \lambda) d\mathbf{r} d\mathbf{r}' \end{aligned} \quad (3.5.23)$$

In contrast to (3.4.10), use of this result in constructing a trial functional requires an approximation for $c^{(2)}(\mathbf{r}', \mathbf{r}'; \lambda)$ rather than $h^{(2)}(\mathbf{r}', \mathbf{r}'; \lambda)$, and its derivation does not rely on the assumption of pairwise additivity of the particle interactions. If we assume that the final state is homogeneous and that the initial state is one of zero density, (3.5.23) yields an expression for the excess free energy of a uniform fluid of density ρ :

$$F^{\text{ex}}(\rho) = \rho^2 k_B T \int_0^1 d\lambda (\lambda - 1) \int d\mathbf{r} \int c(|\mathbf{r}' - \mathbf{r}|; \lambda \rho) d(\mathbf{r}' - \mathbf{r}) \quad (3.5.24)$$

or, after integration over \mathbf{r} :

$$\frac{\beta F^{\text{ex}}(\rho)}{N} = \rho \int_0^1 d\lambda (\lambda - 1) \int c(r; \lambda \rho) d\mathbf{r} \quad (3.5.25)$$

3.6 THE DENSITY RESPONSE FUNCTION

Let us suppose that a uniform fluid of number density ρ_0 is exposed to a weak, external potential $\delta\phi(\mathbf{r})$. The hamiltonian of the system is

$$\mathcal{H} = \mathcal{H}_0 + \sum_{i=1}^N \delta\phi(\mathbf{r}_i) \quad (3.6.1)$$

where \mathcal{H}_0 is the hamiltonian of the uniform fluid. The external potential acts as a perturbation on the system and creates an inhomogeneity, measured by the deviation $\delta\rho^{(1)}(\mathbf{r})$ of the single-particle density from its value in the uniform state:

$$\delta\rho^{(1)}(\mathbf{r}) = \rho^{(1)}(\mathbf{r}) - \rho_0 \quad (3.6.2)$$

Because the perturbation is weak, it can be assumed that the response is a linear but non-local function of $\delta\phi(\mathbf{r})$, expressible in terms of a *linear response function* $\chi(\mathbf{r}, \mathbf{r}')$ in the form

$$\delta\rho^{(1)}(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') \delta\phi(\mathbf{r}') d\mathbf{r}' \quad (3.6.3)$$

It follows from the definition of a functional derivative that

$$\chi(\mathbf{r}, \mathbf{r}') = \left. \frac{\delta\rho^{(1)}(\mathbf{r})}{\delta\phi(\mathbf{r}')} \right|_{\phi=0} = - \left. \frac{\delta\rho^{(1)}(\mathbf{r})}{\delta\psi(\mathbf{r}')} \right|_{\phi=0} \quad (3.6.4)$$

and hence, from (3.5.6), that

$$\chi(\mathbf{r}, \mathbf{r}') = -\beta H^{(2)}(\mathbf{r}, \mathbf{r}') \quad (3.6.5)$$

where $H^{(2)}(\mathbf{r}, \mathbf{r}')$ is the density-density correlation function of the unperturbed system. Because the unperturbed system is homogeneous, the response function can be written as

$$\chi(|\mathbf{r} - \mathbf{r}'|) = -\beta [\rho_0^2 h(|\mathbf{r} - \mathbf{r}'|) + \rho_0 \delta(|\mathbf{r} - \mathbf{r}'|)] \quad (3.6.6)$$

and the change in density due to the perturbation divides into local and non-local terms:

$$\delta\rho^{(1)}(\mathbf{r}) = -\beta\rho_0\delta\phi(\mathbf{r}) - \beta\rho_0^2 \int h(|\mathbf{r} - \mathbf{r}'|) \delta\phi(\mathbf{r}') d\mathbf{r}' \quad (3.6.7)$$

This result is called the Yvon equation; it is equivalent to a first-order Taylor expansion of $\rho^{(1)}$ in powers of $\delta\phi$.

We now take the Fourier transform of (3.6.3) and relate the response $\delta\hat{\rho}^{(1)}(\mathbf{k})$ to the Fourier components of the external potential, defined as

$$\delta\hat{\phi}(\mathbf{k}) = \int \exp(-i\mathbf{k} \cdot \mathbf{r}) \delta\phi(\mathbf{r}) d\mathbf{r} \quad (3.6.8)$$

The result is

$$\delta\hat{\rho}^{(1)}(\mathbf{k}) = \chi(\mathbf{k})\hat{\phi}(\mathbf{k}) = -\beta\rho_0 S(\mathbf{k})\delta\hat{\phi}(\mathbf{k}) \quad (3.6.9)$$

where

$$S(\mathbf{k}) = 1 + \rho_0 \hat{h}(\mathbf{k}) = \frac{1}{1 - \rho_0 \hat{c}(k)} \quad (3.6.10)$$

is the *static structure factor* of the uniform fluid; the second equality in (3.6.10) follows from (3.5.13). The structure factor appears in (3.6.9) as a generalised response function, akin to the magnetic susceptibility of a spin system. The linear density response to an external field is therefore determined by the density–density correlation function in the absence of the field; this is an example of the *fluctuation–dissipation theorem*. More specifically, $S(\mathbf{k})$ is a measure of the density response of a system, initially in equilibrium, to a weak, external perturbation of wavelength $2\pi/k$. When the probe is a beam of neutrons, $S(\mathbf{k})$ is proportional to the total scattered intensity in a direction determined by the momentum transfer $\hbar\mathbf{k}$ between beam and sample. Use of such a probe provides an experimental means of determining the radial distribution function of a liquid, as in the example shown in Figure 2.1. Equations (3.5.14) and (3.6.10) together show that at long wavelengths $S(\mathbf{k})$ behaves as

$$\lim_{k \rightarrow 0} S(\mathbf{k}) = \rho k_B T \chi_T \quad (3.6.11)$$

and is therefore a measure of the response in one macroscopic quantity – the number density – to a change in another – the applied pressure. If the system is isotropic, the structure factor is a function only of the wavenumber k .

An example of an experimentally determined structure factor for liquid sodium near the triple point is pictured in Figure 3.2; the dominant feature is a pronounced peak at a wavenumber approximately equal to $2\pi/\Delta r$, where Δr is the spacing of the peaks in $g(r)$. As the figure shows, the experimental structure factor is very well fitted by Monte Carlo results for a purely repulsive potential that varies as r^{-4} . Since the r^{-4} potential is only a crude representation of the effective potential for liquid sodium, the good agreement seen in the figure strongly suggests that the structure factor is insensitive to details of the atomic interactions.

The discussion until now has been limited to one-component systems, but the ideas developed in this section and the preceding one can be extended to mixtures without major complications. Consider a system containing N_ν particles of species ν , with $\nu = 1$ to n . If $N = \sum_\nu N_\nu$ is the total number of particles, the number concentration of species ν is $x_\nu = N_\nu/N$. The partial microscopic density $\rho_\nu(\mathbf{r})$ and its average value $\rho_\nu^{(1)}(\mathbf{r})$ (the

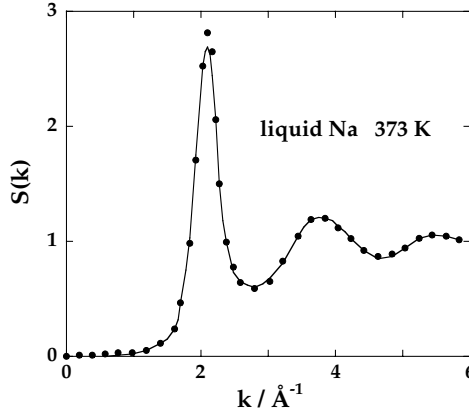


FIG. 3.2. Structure factor of liquid sodium near the normal melting temperature. The points are experimental x-ray scattering results⁸ and the curve is obtained from a Monte Carlo calculation⁹ for the r^{-4} potential under the same thermodynamic conditions.

single-particle density of species ν) are defined in a manner identical to (3.1.2) and (3.1.4), except that the sum on i is limited to particles of species ν . At the pair level, the structure of the fluid is described by $\frac{1}{2}n(n+1)$ partial pair correlation functions $h_{\nu\mu}^{(2)}(\mathbf{r}, \mathbf{r}')$ and $\frac{1}{2}n(n+1)$ direct correlation functions $c_{\nu\mu}^{(2)}(\mathbf{r}, \mathbf{r}')$. The two sets of functions are linked by a set of coupled equations, representing a generalisation of the Ornstein–Zernike relation (3.5.10), which in the homogeneous case becomes

$$h_{\nu\mu}(r) = c_{\nu\mu}(r) + \rho \sum_{\lambda} x_{\lambda} \int c_{\nu\lambda}(|\mathbf{r} - \mathbf{r}'|) h_{\lambda\mu}(r') d\mathbf{r}' \quad (3.6.12)$$

The change in the single-particle density of species ν induced by a weak external potential $\delta\phi_{\mu}(\mathbf{r})$ that couples to the density of species μ is given by a straightforward generalisation of (3.6.7):

$$\delta\rho_{\nu}^{(1)}(\mathbf{r}) = -x_{\nu}\delta_{\nu\mu}\beta\rho\delta\phi_{\mu}(\mathbf{r}) - x_{\nu}x_{\mu}\beta\rho^2 \int h_{\nu\mu}(|\mathbf{r} - \mathbf{r}'|)\delta\phi_{\mu}(\mathbf{r}') d\mathbf{r}' \quad (3.6.13)$$

or, after Fourier transformation:

$$\delta\hat{\rho}_{\nu}^{(1)}(\mathbf{k}) = \chi_{\nu\mu}(\mathbf{k})\delta\hat{\phi}_{\mu}(\mathbf{k}) = -\beta\rho S_{\nu\mu}(\mathbf{k})\delta\hat{\phi}_{\mu}(\mathbf{k}) \quad (3.6.14)$$

where $\chi_{\nu\mu}(\mathbf{k})$ is a linear response function and

$$S_{\nu\mu}(\mathbf{k}) = x_{\nu}\delta_{\nu\mu} + x_{\nu}x_{\mu}\rho\hat{h}_{\nu\mu}(\mathbf{k}) \quad (3.6.15)$$

is a partial structure factor of the uniform fluid. Note that the local contribution to $\delta\rho_{\nu}^{(1)}(\mathbf{r})$ in (3.6.13) disappears unless the labels ν, μ refer to the same species. Finally, the general-

isation to mixtures of the expression for the compressibility given by (3.5.15) is

$$\frac{1}{\rho k_B T \chi_T} = 1 - \rho \sum_v \sum_\mu \hat{c}_{v\mu}(0) \quad (3.6.16)$$

If the partial structure factors are represented as a matrix, $\mathbf{S}(k)$, combination of (3.6.12) and (3.6.15), together with a matrix inversion, shows that the corresponding generalisation of (3.6.11) is

$$\rho k_B T \chi_T = \frac{|\mathbf{S}(0)|}{\sum_v \sum_\mu x_v x_\mu |\mathbf{S}(0)|_{v\mu}} \quad (3.6.17)$$

where $|\mathbf{S}(0)|_{v\mu}$ is the cofactor of $S_{v\mu}(0)$ in the determinant $|\mathbf{S}(0)|$. Equation (3.6.17) is called the Kirkwood–Buff formula.¹⁰

3.7 DIAGRAMMATIC METHODS

The grand partition function and particle densities are defined as many-dimensional integrals over particle coordinates. Such integrals are conveniently represented by *diagrams* or *graphs*, which in turn can be manipulated by graph-theoretical methods. These methods include simple prescriptions for the evaluation of functional derivatives of the type encountered in earlier sections of this chapter. As we shall see, the diagrammatic approach leads naturally to expansions of thermodynamic properties and particle distribution functions in powers of either the activity or density. While such expansions are in general more appropriate to gases than to liquids, diagrammatic methods have played a prominent role in the development of the modern theory of dense fluids. The statistical mechanics of non-uniform fluids, for example, was originally formulated in diagrammatic terms.¹¹ The introductory account given here is based largely on the work of Morita and Hiroike,¹² de Dominicis¹³ and Stell.¹⁴ Although the discussion is self-contained, it is limited in scope, and no attempt is made at mathematical rigour.

We consider again the case when the interparticle potential energy is a sum of pair terms. As we shall see later, it is sometimes convenient to replace the Boltzmann factor $\exp(-\beta V_N)$ by a sum of products of *Mayer functions*, $f(i, j)$, defined as

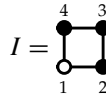
$$f(i, j) = \exp[-\beta v(i, j)] - 1 \equiv e(i, j) - 1 \quad (3.7.1)$$

Then, for example, in the definition of $\rho^{(1)}(1)$ given by (3.1.9) the term for $N = 4$ involves an integral of the form

$$I = \iiint \left(\prod_{i=1}^4 z^*(i) \right) f(1, 2) f(1, 4) f(2, 3) f(3, 4) d2 d3 d4 \quad (3.7.2)$$

To each such integral there corresponds a *labelled diagram* consisting of a number of *circles* linked by *bonds*. Circles represent particle coordinates and carry an appropriate label;

for that reason the diagrams are sometimes called “cluster” diagrams. The circles are of two types: *white circles* (or “root points”), which correspond to coordinates held constant in the integration, and *black circles* (or “field points”), which represent the variables of integration. With a circle labelled i we associate a function of coordinates, $\gamma(i)$, say. The circle is then referred to as a white or black γ -circle; a 1-circle is a circle for which $\gamma(i) = 1$. Bonds are drawn as lines between circles. With a bond between circles i and j we associate a function $\eta(i, j)$, say, and refer to it as an η -bond; a *simple* diagram is one in which no pair of circles is linked by more than one bond. The *value* of a labelled diagram is the value of the integral that the diagram represents; it is a function of the coordinates attached to the white circles and a functional of the functions associated with the black circles and bonds. Thus the integral in (3.7.2) is represented by a simple, labelled diagram consisting of z^* -circles (both white and black) and f -bonds:



The black circles in a diagram correspond to the dummy variables of integration. The manner in which the black circles are labelled is therefore irrelevant and the labels may conveniently be omitted altogether. The value of the resulting *unlabelled diagram* involves a combinatorial factor related to the topological structure of the diagram. Consider a labelled diagram containing m black γ -circles and any number of white circles. Each of the $m!$ possible permutations of labels of the black circles leaves the value of the diagram unchanged. There is, however, a subgroup of permutations which give rise to diagrams that are *topologically equivalent*. Two labelled diagrams are said to be topologically equivalent if they are characterised by the same set of *connections*, meaning that circles labelled i and j in one diagram are linked by an η -bond if and only if they are similarly linked in the other. In the case when all black circles are associated with the same function, the *symmetry number* of a simple diagram is the order of the subgroup of permutations that leave the connections unaltered. We adopt the convention that when the word “diagram” or the symbol for a diagram appears in an equation, the quantity to be inserted is the value of that diagram. Then the value of a simple diagram Γ consisting of n white circles labelled 1 to n and m unlabelled black circles is

$$\Gamma = (1/m!)[\text{the sum of all topologically inequivalent diagrams obtained by labelling the black circles}] \quad (3.7.3)$$

The number of labelled diagrams appearing on the right-hand side of this equation is equal to $m!/S$, where S is the symmetry number, and each of the diagrams has a value equal to that of the integral it represents. The definition (3.7.3) may therefore be reformulated as

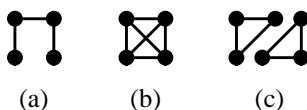
$$\begin{aligned} \Gamma &= (1/S)[\text{any diagram obtained by labelling the black circles}] \\ &= (1/S)[\text{the value of the corresponding integral}] \end{aligned} \quad (3.7.4)$$

In the example already pictured the symmetry number of the diagram is equal to two, since the connections are unaltered by interchange of the labels 2 and 4. Thus the unlabelled diagram obtained by removing the labels 2, 3 and 4 has a value equal to $\frac{1}{2}I$.

The definition of the value of a diagram can be extended to a wider class of diagrams than those we have discussed, but the definition of symmetry number may have to be modified. For example, if a diagram is *composite* rather than simple, the symmetry number is increased by a factor $n!$ for every pair of circles linked by n bonds of the same *species*. On the other hand, if the functions associated with the black circles are not all the same, the symmetry number is reduced.

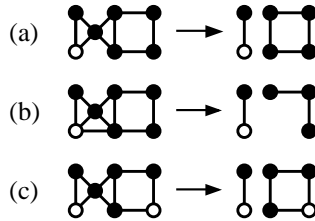
The difference in value of labelled and unlabelled diagrams is important because the greater ease with which unlabelled diagrams are manipulated is due precisely to the inclusion of the combinatorial factor S . In all that follows, use of the word “diagram” without qualification should be taken as referring to the unlabelled type, though the distinction will often be irrelevant. Two unlabelled diagrams are *topologically distinct* if it is impossible to find a permutation that converts a labelled version of one diagram into a labelled version of the other. Diagrams that are topologically distinct represent different integrals. Statistical mechanical quantities usefully discussed in diagrammatic terms are frequently obtained as “the sum of all topologically distinct diagrams” having certain properties. To avoid undue repetition we shall always replace the cumbersome phrase in quotation marks by the expression “all diagrams”. We also adopt the convention that any diagrams we discuss are simple unless they are otherwise described.

Two circles are *adjacent* if they are linked by a bond. A sequence of adjacent circles and the bonds that link them is called a *path*. Two paths between a given pair of circles are *independent* if they have no intermediate circle in common. A *connected* diagram is either *simply* or *multiply* connected; if there exist (at least) n independent paths between any pair of circles the diagram is (at least) n -*tuple* connected. In the examples shown below, diagram (a) is simply connected, (b) is triply connected and (c) is a *disconnected* diagram with two doubly-connected *components*.

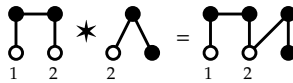


A bond is said to *intersect* the circles that it links. *Removal* of a circle from a diagram means that the circle and the bonds that intersect it are erased. A *connecting* circle is a circle whose removal from a connected diagram causes the diagram to become disconnected; the *multiplicity* of a connecting circle is the number of components into which the diagram separates when the circle is removed. Removal of an *articulation* circle from a connected diagram causes the diagram to separate into two or more components, of which at least one contains no white circle; an *articulation pair* is a pair of circles whose removal has the same effect. A diagram that is free of articulation circles is said to be *irreducible*; the absence of articulation pairs implies irreducibility but not vice versa. If a diagram contains at least two white circles, a *nodal* circle is one through which all paths between two particular white circles pass. Clearly there can be no nodal circle associated with a pair of white circles linked by a bond. A nodal circle is necessarily also a connecting circle and may also be

an articulation circle if its multiplicity is three or more. The examples below illustrate the effects of removing (a) an articulation circle, (b) an articulation pair and (c) a nodal circle.



A *subdiagram* of a diagram Γ is any diagram that can be obtained from Γ by some combination of the removal of circles and erasure of bonds. A subdiagram is *maximal* with respect to a given property if it is not embedded in another subdiagram with the same property; a particularly important class of maximal subdiagrams are those that are irreducible. The *star product* of two connected diagrams Γ_1 , Γ_2 is the diagram Γ_3 obtained by linking together the two diagrams in such a way that white circles carrying the same labels are superimposed, as in the example shown below:



The two diagrams are said to be *connected in parallel* at the n white circles having labels that are common to both Γ_1 and Γ_2 ; if the two diagrams are connected in parallel at white γ -circles, the corresponding circles in Γ_3 are γ^2 -circles. If Γ_1 and Γ_2 have no white circles in common, or if one or both contain only black circles, the star product is a disconnected diagram having Γ_1 and Γ_2 as its components. *Star-irreducible* diagrams are connected diagrams that cannot be expressed as the star product of two other diagrams except when one of the two is the diagram consisting of a single white circle. The definition of star-irreducibility excludes all diagrams containing white connecting circles or connecting subsets of white circles, all diagrams with adjacent white circles and, by convention, the diagram consisting of a single white circle. The star product of two star-irreducible diagrams can be uniquely decomposed into the factors that form the product; thus the properties of star-irreducible diagrams are analogous to those of prime numbers.

Diagrammatic expressions are manipulated with the aid of certain rules, the most important of which are contained in a series of lemmas derived by Morita and Hiroike.¹² The lemmas are stated here without proof and illustrated by simple examples;¹⁵ some details of the proofs are given in Appendix C.

Lemma 1. *Let G be a set of topologically distinct, star-irreducible diagrams and let H be the set of all diagrams in G and all possible star products of diagrams in G . Then*

$$[\text{all diagrams in } H] = \exp[\text{all diagrams in } G] - 1$$

Illustration. If G consists of a single diagram, Γ , where

$$\Gamma = \text{---}\bigcirc\text{---}\bullet$$

then

$$\exp(\Gamma) = 1 + \text{---}\bigcirc\text{---}\bullet + \begin{array}{c} \bigcirc \\ \diagup \quad \diagdown \\ \bullet \quad \bullet \end{array} + \begin{array}{c} \bigcirc \quad \bullet \\ \diagdown \quad \diagup \\ \bullet \quad \bullet \end{array} + \dots$$

Lemma 1 is called the “exponentiation theorem”. If the diagrams in G consist solely of black circles and bonds, use of the lemma makes it possible to express a sum of connected and disconnected diagrams in terms of the connected subset.

Lemmas 2 and 3 contain the diagrammatic prescriptions for the evaluation of two important types of functional derivative.

Lemma 2. *Let Γ be a diagram consisting of black γ -circles and bonds. Then*

$$\partial \Gamma / \partial \gamma(\mathbf{r}) = [\text{all diagrams obtained by replacing a black } \gamma\text{-circle of } \Gamma \text{ by a white 1-circle labelled } \mathbf{r}]$$

Illustration.

$$\Gamma = \begin{array}{c} \bullet \quad \bullet \\ \diagdown \quad \diagup \\ \bullet \quad \bullet \end{array} \quad \delta \Gamma / \delta \gamma = \begin{array}{c} \bullet \quad \bullet \\ \diagdown \quad \diagup \\ \bigcirc \quad \bullet \\ \mathbf{r} \end{array} + \begin{array}{c} \bullet \quad \bullet \\ \diagup \quad \diagdown \\ \bullet \quad \bigcirc \\ \mathbf{r} \end{array}$$

Lemma 3. *Let Γ be a diagram consisting of black circles and η -bonds. Then*

$$\partial \Gamma / \partial \eta(\mathbf{r}, \mathbf{r}') = \frac{1}{2} [\text{all diagrams obtained by erasing an } \eta\text{-bond of } \Gamma, \text{ whitening the circles that it linked and labelling the whitened circles } \mathbf{r} \text{ and } \mathbf{r}']]$$

Illustration.

$$\Gamma = \begin{array}{c} \bullet \\ \diagup \quad \diagdown \\ \bullet \quad \bullet \end{array} \quad \delta \Gamma / \delta \eta = \frac{1}{2} \begin{array}{c} \bullet \\ \diagdown \quad \diagup \\ \bigcirc \quad \bigcirc \\ \mathbf{r} \quad \mathbf{r}' \end{array}$$

The example illustrated is the diagrammatic representation of example (3.2.21) for the case when $a = 1$. The numerical factor present in (3.2.21) is taken care of by the different symmetry numbers before ($S = 6$) and after ($S = 1$) differentiation.

Lemmas 4 and 5 are useful in the process of *topological reduction*.

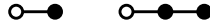
Lemma 4. *Let G be a set of topologically distinct, connected diagrams consisting of a white circle labelled \mathbf{r} , black γ -circles and bonds, and let $\mathcal{G}(\mathbf{r})$ be the sum of all diagrams in G . If Γ is a connected diagram, if H is the set of all topologically distinct diagrams*

obtained by decorating all black circles of Γ with diagrams in G , and if each diagram in H is uniquely decomposable, then

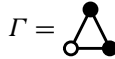
$$[\text{all diagrams in } H] = [\text{the diagram obtained from } \Gamma \text{ by replacing the black } \gamma\text{-circles by } \mathcal{G}\text{-circles}]$$

The process of *decorating* the diagram Γ consists of attaching one of the elements in G in such a way that its white circle is superimposed on a black circle of Γ and then blackened. For the diagrams in H to be *uniquely decomposable* it must be possible, given the structure of Γ , to determine by inspection which diagram in G has been used to decorate each black circle of Γ ; this is always possible if Γ is free of black articulation circles.

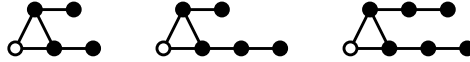
Illustration. If the set G consists of the two diagrams:



and if



then the set H consists of the three diagrams



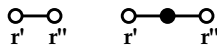
Although the example is a simple one, it illustrates the main ingredients of a topological reduction: the sum of a number of diagrams (here the diagrams in H , where the black circles are γ -circles) is replaced by a single diagram of simpler structure (here Γ , where the black circles are \mathcal{G} -circles).

Lemma 5. Let G be a set of topologically distinct, connected diagrams consisting of two white circles labelled \mathbf{r} and \mathbf{r}' , black circles and η -bonds, and let $\mathcal{G}(\mathbf{r}, \mathbf{r}')$ be the sum of all diagrams in G . If Γ is a connected diagram, if H is the set of all topologically distinct diagrams obtained by replacing all bonds of Γ by diagrams in G , and if each diagram in H is uniquely decomposable, then

$$[\text{all diagrams in } H] = [\text{the diagram obtained from } \Gamma \text{ by replacing the } \eta\text{-bonds by } \mathcal{G}\text{-bonds}]$$

Replacement of bonds in Γ involves superimposing the two white circles of the diagram drawn from G onto the circles of Γ and erasing the bond between them. The circles take the same colour and, if white, the same label as the corresponding circle in Γ .

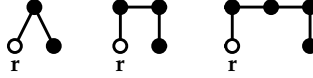
Illustration. If the set G consists of the two diagrams:



and if

$$\Gamma = \begin{array}{c} \bullet \\ \diagup \quad \diagdown \\ \circ \quad \bullet \\ \text{\textbf{r}} \end{array}$$

then the set H consists of the three diagrams



3.8 DIAGRAMMATIC EXPANSIONS OF THE DIRECT CORRELATION FUNCTIONS

We now give examples of how the definitions and lemmas of the previous section can be used to obtain results of physical interest. The examples we choose are ones that lead to series expansions of the direct correlation functions $c^{(1)}(\mathbf{r})$ and $c^{(2)}(\mathbf{r}, \mathbf{r}')$ introduced in Section 3.5. We assume again that the interparticle forces are pairwise additive and take as our starting point the expression for \mathcal{E} given by (3.4.5). It follows immediately that \mathcal{E} can be represented diagrammatically as

$$\begin{aligned} \mathcal{E} &= 1 + [\text{all diagrams consisting of black } z^*\text{-circles with an } e\text{-bond} \\ &\quad \text{linking each pair}] \\ &= 1 + \bullet + \bullet - \bullet + \begin{array}{c} \bullet \\ \diagup \quad \diagdown \\ \bullet \quad \bullet \end{array} + \begin{array}{c} \bullet \quad \bullet \\ \diagup \quad \diagdown \\ \bullet \quad \bullet \end{array} + \cdots \end{aligned} \quad (3.8.1)$$

Note that the definition of the value of a diagram takes care of the factors $1/N!$ in (3.4.5). Because $e(i, j) \rightarrow 1$ as $|\mathbf{r}_j - \mathbf{r}_i| \rightarrow \infty$, the contribution from the N th term in (3.8.1) is of order V^N , and problems arise in the thermodynamic limit. It is therefore better to reformulate the series in terms of Mayer functions by making the substitution $f(i, j) = e(i, j) - 1$, as in example (3.7.2). The series then becomes

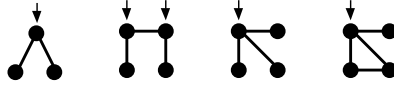
$$\begin{aligned} \mathcal{E} &= 1 + [\text{all diagrams consisting of black } z^*\text{-circles and } f\text{-bonds}] \\ &= 1 + \bullet + \bullet - \bullet + \begin{array}{c} \bullet \\ \diagup \quad \diagdown \\ \bullet \quad \bullet \end{array} + \begin{array}{c} \bullet \quad \bullet \\ \diagup \quad \diagdown \\ \bullet \quad \bullet \end{array} + \begin{array}{c} \bullet \quad \bullet \\ \diagup \quad \diagdown \\ \bullet \quad \bullet \end{array} + \begin{array}{c} \bullet \quad \bullet \\ \diagup \quad \diagdown \\ \bullet \quad \bullet \end{array} + \cdots \end{aligned} \quad (3.8.2)$$

The disconnected diagrams in (3.8.2) can be eliminated by taking the logarithm of \mathcal{E} and applying Lemma 1. This yields an expansion of the grand potential in the form

$$\begin{aligned} -\beta\Omega &= [\text{all connected diagrams consisting of black } z^*\text{-circles and } f\text{-bonds}] \\ &= \bullet + \bullet - \bullet + \begin{array}{c} \bullet \\ \diagup \quad \diagdown \\ \bullet \quad \bullet \end{array} + \begin{array}{c} \bullet \quad \bullet \\ \diagup \quad \diagdown \\ \bullet \quad \bullet \end{array} + \cdots \end{aligned} \quad (3.8.3)$$

Since there is no need to consider disconnected diagrams again, the requirement that diagrams must be connected will from now on be omitted.

At each order in z^* beyond the second, many of the diagrams in the series (3.8.3) contain articulation circles; those contributing at third and fourth orders are shown below, with the articulation circles marked by arrows:



If the system were translationally invariant, the articulation circles could be chosen as the origin of coordinates in the corresponding integrals. The integrals would then factorise as products of integrals that already appear at lower order in the expansion. While this is not possible in the general case, diagrams that contain articulation circles can be eliminated by switching from an activity to a density expansion. This requires, as an intermediate step, the activity expansion of $\rho^{(1)}(\mathbf{r})$. The single-particle density at a point \mathbf{r} is the functional derivative of the grand potential with respect to either $\psi(\mathbf{r})$ or, equivalently, $\ln z^*(\mathbf{r})$. From (3.3.10) and Lemma 2 it follows that

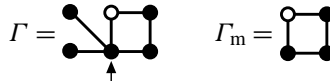
$$\rho^{(1)}(\mathbf{r})/z^*(\mathbf{r}) = 1 + [\text{all diagrams consisting of a white 1-circle labelled } \mathbf{r}, \text{ at least one black } z^*\text{-circle and } f\text{-bonds}] \quad (3.8.4)$$

The diagrams in (3.8.4) fall into two classes: those in which the articulation circle is a white circle and those in which it is not and are therefore star-irreducible. The first of these classes is just the set of all diagrams that can be expressed as star products of diagrams in the second class. Use of Lemma 1 therefore eliminates the diagrams with white articulation circles to give an expansion of $\ln[\rho^{(1)}(\mathbf{r})/z^*(\mathbf{r})]$ which, from (3.5.3), is equal to $c^{(1)}(\mathbf{r})$:

$$c^{(1)}(\mathbf{r}) = [\text{all diagrams consisting of a white 1-circle labelled } \mathbf{r}, \text{ at least one black } z^*\text{-circle and } f\text{-bonds, such that the white circle is not an articulation circle}] \quad (3.8.5)$$

The diagrams in (3.8.5) are all star-irreducible, but some contain black articulation circles. To eliminate the latter, we proceed as follows. For each diagram Γ in (3.8.5) we identify a maximal, irreducible subdiagram Γ_m that contains the single white circle.

Illustration.



In the example shown there is one articulation circle (marked by an arrow) and there are two maximal, irreducible subdiagrams, one of which contains the white circle. It is easily proved¹⁵ that for each Γ there is a unique choice of Γ_m ; if Γ itself is irreducible, Γ and Γ_m are the same. The set $\{\Gamma_m\}$ is a subset of the diagrams in (3.8.5). Given any Γ_m , the diagram from which it derives can be reconstructed by decorating the black circles with diagrams

taken from the set defined in (3.8.4). Lemma 4 can therefore be used in a topological reduction whereby the z^* -circles in (3.8.5) are replaced by $\rho^{(1)}$ -circles and diagrams with black articulation circles disappear. Thus

$$\begin{aligned}
 c^{(1)}(\mathbf{r}) &= [\text{all irreducible diagrams consisting of one white 1-circle} \\
 &\quad \text{labelled } \mathbf{r}, \text{ at least one black } \rho^{(1)}\text{-circle and } f\text{-bonds}] \\
 &= \text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \text{diagram 4} + \text{diagram 5} + \text{diagram 6} + \cdots
 \end{aligned} \tag{3.8.6}$$

The final step is to exploit the definition (3.5.2) of the two-particle direct correlation function as a functional derivative by applying Lemma 2 to the series (3.8.6). The diagrams in (3.8.6) are irreducible; since they contain only one white circle this is equivalent to saying that they are free of connecting circles. Clearly they remain free of connecting circles when a second black circle is whitened as a result of the functional differentiation. It follows that $c^{(2)}(\mathbf{r}, \mathbf{r}')$ can be expressed diagrammatically as

$$\begin{aligned}
 c^{(2)}(\mathbf{r}, \mathbf{r}') &= [\text{all diagrams consisting of two white 1-circles labelled } \mathbf{r} \\
 &\quad \text{and } \mathbf{r}', \text{ black } \rho^{(1)}\text{-circles and } f\text{-bonds, and which are free} \\
 &\quad \text{of connecting circles}] \\
 &= \text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \text{diagram 4} + \text{diagram 5} + \text{diagram 6} \\
 &\quad + \text{diagram 7} + \text{diagram 8} + \text{diagram 9} + \cdots
 \end{aligned} \tag{3.8.7}$$

When there is no external field, (3.8.7) becomes an expansion of $c(r)$ in powers of the number density.¹⁶

The form of (3.8.7) suggests that the range of the direct correlation function should be roughly the range of the pair potential, as anticipated in Section 3.5. To lowest order in ρ , $c(r) \approx f(r)$ or, at large r , $c(r) \approx -\beta v(r)$. Since all higher-order diagrams in (3.8.7) are at least doubly connected, the contributions they make to $c(r)$ decay at least as fast as $[f(r)]^2$, and are therefore negligible in comparison with the leading term in the limit $r \rightarrow \infty$. However, the effects of indirect correlations are such that $h(r)$ can be significantly different from zero even for distances at which the potential is very weak. The contrast in behaviour between $c(r)$ and $h(r)$ is particularly evident close to the critical point. As the critical point is approached the compressibility χ_T becomes very large. It follows from (3.5.14) that $\hat{h}(k)$, the Fourier transform of $h(r)$, acquires a strong peak at the origin, eventually diverging as $T \rightarrow T_c$, which implies that $h(r)$ becomes very long ranged. On the other hand, (3.5.15) shows that

$$\rho \hat{c}(0) = 1 - \beta / \rho \chi_T \tag{3.8.8}$$

Close to the critical point, $\rho \hat{c}(0) \approx 1$; $c(r)$ therefore remains short ranged.

The argument concerning the relative ranges of $h(r)$ and $c(r)$ does not apply to ionic fluids. The effect of screening in ionic systems is to cause $h(r)$ to decay exponentially at large r , whereas $c(r)$ still has the range of the potential and therefore decays as r^{-1} . In this situation $c(r)$ is of longer range than $h(r)$.

3.9 VIRIAL EXPANSION OF THE EQUATION OF STATE

The derivation of the series expansion of $c^{(1)}(\mathbf{r})$ yields as a valuable by-product the *virial expansion* of the equation of state of a homogeneous fluid. If there is no external field, $c^{(1)}$ can be replaced by $-\beta\mu^{\text{ex}}$ and $\rho^{(1)}$ by ρ . Equation (3.8.6) then becomes

$$\beta\mu = \beta\mu^{\text{id}} - \sum_{i=1}^{\infty} \beta_i \rho^i \quad (3.9.1)$$

where the coefficients β_i are the irreducible “cluster integrals”; $\beta_i \rho^i$ is the sum of all diagrams in (3.8.6) that contain precisely i black circles but with $\rho^{(1)}$ replaced by ρ . The first two coefficients are

$$\beta_1 = \int f(0, 1) d1 \quad (3.9.2)$$

$$\beta_2 = \frac{1}{2} \iint f(0, 1) f(0, 2) f(1, 2) d1 d2 \quad (3.9.3)$$

where, in each case, the white circle is labelled 0. Substitution of (3.9.1) in (2.4.21) and integration with respect to ρ gives

$$\beta P = \rho - \sum_{i=1}^{\infty} \frac{i}{i+1} \beta_i \rho^{i+1} \quad (3.9.4)$$

If the *virial coefficients* are defined as $B_1 = 1$,

$$B_{i+1} = -\frac{i}{i+1} \beta_i, \quad i \geq 1 \quad (3.9.5)$$

we recover the virial expansion in its standard form:

$$\frac{\beta P}{\rho} = 1 + \sum_{i=2}^{\infty} B_i(T) \rho^{i-1} \quad (3.9.6)$$

The coefficients B_2 and B_3 are given by

$$B_2 = -\frac{1}{2} \beta_1 = -\frac{1}{2} \int f(r) d\mathbf{r} \quad (3.9.7)$$

$$B_3 = -\frac{2}{3}\beta_2 = -\frac{1}{3} \iint f(r)f(r')f(|\mathbf{r}-\mathbf{r}'|) d\mathbf{r} d\mathbf{r}' \quad (3.9.8)$$

where the coordinates of the white circle have been taken as origin.

The expression for the second virial coefficient is more easily obtained by inserting in the virial equation (2.5.22) the low-density limit of $g(r)$ given by (2.6.10). Then

$$\frac{\beta P}{\rho} \approx 1 - \frac{2\pi\beta\rho}{3} \int_0^\infty v'(r)e(r)r^3 dr \quad (3.9.9)$$

If the pair potential decays faster than r^{-3} at large r , (3.9.9) can be integrated by parts to give

$$\frac{\beta P}{\rho} \approx 1 - 2\pi\rho \int_0^\infty f(r)r^2 dr \quad (3.9.10)$$

in agreement with (3.9.7). Measurements of the deviation of the equation of state of dilute gases from the ideal-gas law allow the second virial coefficient to be determined experimentally as a function of temperature. Such measurements are an important source of information on the nature of the force law between atoms or small molecules.

It is clear from the definition of the virial coefficients that the number of diagrams that contribute to the i th coefficient grows rapidly with i , while the associated integrals become increasingly more complicated. For example, the numbers of diagrams entering the expressions for B_3 , B_4 , B_5 and B_6 are, respectively, 1, 3, 10, 56 and 468, and the dimensions of the integrals increase each time by three. Not surprisingly, therefore, explicit calculations have been confined to the low-order coefficients. For hard spheres, B_2 , B_3 and B_4 are known analytically, and B_5 to B_8 have been evaluated numerically. If we define the *packing fraction*, η , as

$$\eta = \frac{\pi\rho d^3}{6} \quad (3.9.11)$$

the virial expansion for hard spheres can be rewritten as

$$\frac{\beta P}{\rho} = 1 + \sum_{i=1}^{\infty} \mathcal{B}_i \eta^i \quad (3.9.12)$$

with

$$\mathcal{B}_i = \left(\frac{6}{\pi d^3} \right)^i B_{i+1} \quad (3.9.13)$$

The eight-term series, based on tabulated values¹⁷ of the coefficients \mathcal{B}_i , is now

$$\begin{aligned} \frac{\beta P}{\rho} = & 1 + 4\eta + 10\eta^2 + 18.365\eta^3 + 28.225\eta^4 + 39.74\eta^5 \\ & + 53.5\eta^6 + 70.8\eta^7 + \dots \end{aligned} \quad (3.9.14)$$

Figure 3.3 shows that the pressures calculated from the truncated, eight-term series are in good agreement with the results of computer simulations at all densities up to the fluid–solid transition at $\eta \approx 0.49$.

Guided by the form of (3.9.14), Carnahan and Starling¹⁸ were able to construct a simple but very accurate hard-sphere equation of state. Noting that \mathcal{B}_1 and \mathcal{B}_2 are both integers, they chose to replace \mathcal{B}_3 by the nearest integer, 18, and supposed that \mathcal{B}_i for all i is given by

$$\mathcal{B}_i = a_1 i^2 + a_2 i + a_3 \quad (3.9.15)$$

With $\mathcal{B}_1 = 4$, $\mathcal{B}_2 = 10$ and $\mathcal{B}_3 = 18$, the solution to (3.9.15) is $a_1 = 1$, $a_2 = 3$ and $a_3 = 0$. The formula then predicts that $\mathcal{B}_4 = 28$, $\mathcal{B}_5 = 40$, $\mathcal{B}_6 = 54$ and $\mathcal{B}_7 = 70$, in close agreement with the coefficients in (3.9.14). The expression

$$\frac{\beta P}{\rho} = 1 + \sum_{i=1}^{\infty} (i^2 + 3i) \eta^i \quad (3.9.16)$$

may be written as a linear combination of the first and second derivatives of the geometric series $\sum_i \eta^i$. It can therefore be summed explicitly to give

$$\frac{\beta P}{\rho} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (3.9.17)$$

Equation (3.9.17) provides an excellent fit to the results of computer simulations over the entire fluid range; the largest discrepancies are of the order of 1%. Other equations of state

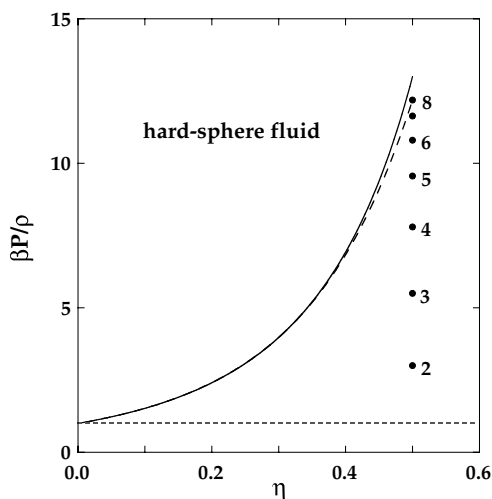


FIG. 3.3. Equation of state of hard spheres calculated from the virial series (3.9.14). The points are the values obtained for $\eta = 0.50$ when different numbers of virial coefficients are included and the full curve shows the nearly exact results given by (3.9.17).

have been devised,¹⁹ but the simple form of the Carnahan–Starling equation makes it very convenient for use in thermodynamic calculations.²⁰ In particular, a closed expression for the excess Helmholtz free energy is obtained by combining (3.9.17) with the second of the thermodynamic relations (2.3.8):

$$\frac{\beta F^{\text{ex}}}{N} = \int_0^\eta \left(\frac{\beta P}{\rho} - 1 \right) \frac{d\eta'}{\eta'} = \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} \quad (3.9.18)$$

The Carnahan–Starling equation of state is widely used in perturbation theories of the type discussed in Chapter 5.

NOTES AND REFERENCES

1. Our treatment draws freely on the classic review article by Evans, R., *Adv. Phys.* **28**, 143 (1979). See also Evans, R., *In* “Fundamentals of Inhomogeneous Fluids” (D. Henderson, ed.), Marcel Dekker, New York, 1991.
2. See Section 3.4. The principle was established for the ground state of the electron gas by Hohenberg, P. and Kohn, W., *Phys. Rev.* **136**, B864 (1964) and extended to finite temperatures by Mermin, N.D., *Phys. Rev.* **137**, A1441 (1964). It was first applied to classical systems by Ebner, C., Saam, W.F. and Stroud, D., *Phys. Rev. A* **14**, 226 (1976).
3. There may also be a contribution from an external source such as an electric or gravitational field.
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15. See also McDonald, I.R. and O’Gorman, S.P., *Phys. Chem. Liq.* **8**, 57 (1978).
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19. For a listing of many of the proposed equations and an assessment of their relative merits, see Mulero, A., Faúndez, C.A. and Cuadros, F., *Mol. Phys.* **97**, 453 (1999).
20. The Carnahan–Starling equation of state was later generalised to hard-sphere mixtures by Mansoori, G.A., Carnahan, N.F., Starling, K.E. and Leland, T.W., *J. Chem. Phys.* **54**, 1523 (1971).