Chapter 2

Statistical mechanics of fluids

In this chapter we consider classical fluids as an (important) example of an interacting system of particles. We present two theoretical techniques that incorporate the effect of interactions. One technique is suitable for weaklyinteracting systems, and builds upon the idealgas approximation; it is based on expansions about the ideal gas, using the density as expansion parameter. The other is a completely different approach, suitable for strongly-interacting systems: the *mean-field approximation*. At the end of the chapter we briefly discuss quantum fluids.

To make things simple, we restrict ourselves to the case of classical fluids. Obviously the criterion that must be satised for this restriction to be valid is that quantum effects are not important. A simple way to check this condition is to focus on the de Broglie wavelength of the particles making up the fluid; this wavelength λ gives a measure of the localisation of a particle in terms of the width of its associated wavepacket. According to quantum theory the momentum p of a free particle is related to the wavevector k (and hence to the de Broglie wavelength $\lambda = 2\pi/k$) by $p = hk$, where $\hbar = h/2\pi$. Then $\lambda = 2\pi\hbar/p = h/mv$, where v is the typical particle velocity. Let a be the mean distance between particles, which is related to the density; we can write $a = (V/N)^{1/3} = 1/\rho^{1/3}$, with V the volume, N the number of particles and ρ the mean density. If wave functions do not overlap, i.e. if the condition

$$\lambda \ll a = \frac{1}{\rho^{1/3}} \tag{2.1}$$

holds, we can be sure that quantum effects can be neglected and that the classical approximation is valid. Most liquids at normal temperatures do satisfy this condition. Notable exceptions are liquid He and, in general, light atomic fluids at low temperatures and/or high densities. The following table gives typical values of the dimensionless parameter $\lambda\rho^{1/3} = \lambda/a$ at the triple point. We begin by considering fluids at low density. The reason is that, starting at the ideal gas, the effect of interactions can be added in a systematic fashion provided the density is not too high. The latter case, which will be considered later, requires completely different approaches.

Liquid	λ (Å)	λ/a
Ne	0.78	0.26
Li	0.31	0.11
Ar	0.30	0.083
Na	0.19	0.054
Kr	0.18	0.046

2.1   Canonical partition function

Let us start with an ideal classical gas made of identical particles. We introduce interactions between the particles assuming that these interactions are pairwise, i.e. the potential energy can be written as a sum over distinct pairs of particles of a pair potential $\phi(r)$ depending only on the distance r between two particles (this is valid only for particles with spherical symmetry; for anisotropic molecules one has to consider not only the centreofmass distance but also the molecular Euler angles):

$$U = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}\phi\left(|\mathbf{r}_j - \mathbf{r}_i|\right) = \sum_{i=1}^{N}\sum_{j>i}\phi\left(|\mathbf{r}_j - \mathbf{r}_i|\right). \tag{2.2}$$

The pair potential $\phi(r)$ depends on the type of interactions being considered. The simplest interaction is the dispersion or van der Waals interactions, due to the isotropic (non-directional) interaction between the fluctuating electronic charges of the atomic shells. Dispersion forces are the most important interactions in atomic noble gases (Ar, Xe, Ne, etc.) A simple mathematical model to represent these interactions is the Lennard-Jones potential:

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{2.3}$$

where ϵ is an energy parameter (the depth of the potential well) and σ is a length parameter (the distance at which the potential is zero). Fig. 2.1 represents the Lennard-Jones potential; it exhibits a repulsive region at short distances (due to overlap of electronic shells leading to repulsion because of Paulis exclusion principle) followed by an attractive region at longer distances (due to van der Waals forces). As a result of these two different components, the potential presents an energy minimum at a distance $r = 2^{1/6}\sigma$.
The complete Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{N}\frac{|\mathbf{p}_i|^2}{2m} + U(\{\mathbf{r}_i\}) = \sum_{i=1}^{N}\frac{|\mathbf{p}_i|^2}{2m} + \sum_{i=1}^{N}\sum_{j>i}\phi\left(|\mathbf{r}_j - \mathbf{r}_i|\right). \tag{2.4}$$

The partition function in the canonical ensemble is

$$Q = \frac{1}{h^{3N}N!}\int d\mathbf{p}_1\cdots\int d\mathbf{p}_N\int d\mathbf{r}_1\cdots\int d\mathbf{r}_N e^{-\beta\sum_i|\mathbf{p}_i|^2/2m - \beta\sum_i\sum_{j>i}\phi(|\mathbf{r}_j-\mathbf{r}_i|)}$$

$$= \frac{1}{h^{3N}N!}\left(\int d\mathbf{p}\,e^{-\beta|\mathbf{p}|^2/2m}\right)^N\int d\mathbf{r}_1\cdots\int d\mathbf{r}_N e^{-\beta\sum_i\sum_{j>i}\phi(|\mathbf{r}_j-\mathbf{r}_i|)} = \frac{Z_N}{N!\Lambda^{3N}}, \tag{2.5}$$
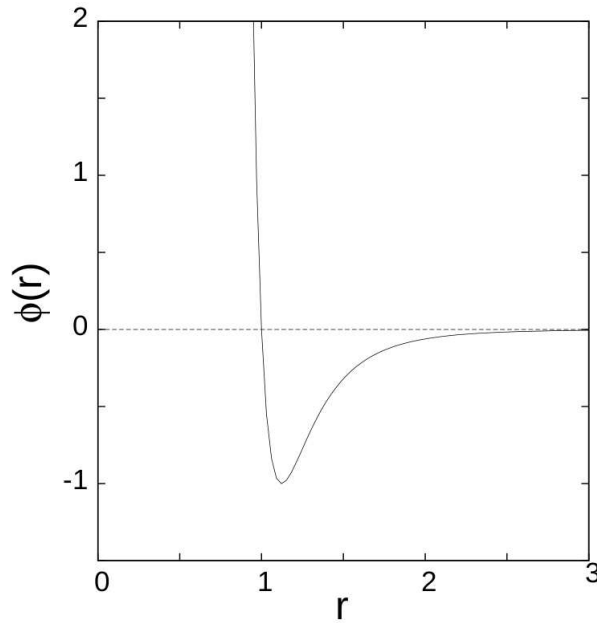
Figure 2.1: Lennard-Jones potential (r in units of σ and $\phi(r)$ in units of ϵ).

where Λ is the thermal wavelength and Z_N the configurational partition function:

$$Z_N(V,T) = \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N e^{-\beta U(\{\mathbf{r}_i\})}. \tag{2.6}$$

For the ideal gas $U = 0$, so that $Z_N = V^N$. The so-called *real gas* is a model that includes the effect of interactions on Q beyond the ideal gas; in other words, it involves a correction factor χ in $Z_N = V^N \chi$ which is unity for an ideal gas. All thermodynamic functions will be affected by this correction, in particular the free energy, which can be written $F = F_{\text{ideal}} - kT \log \chi$.

Corrections due to interactions are intimately related to the gas density: when low, particles do not feel the presence of each other, and the ideal-gas approximation is good. As density increases the typical distance between particles decreases so that particles will feel more and more the presence of the rest, so that a correction is necessary. This correction will become more important as the gas density gets larger.

2.2   Virial expansion

There is a systematic methodology to incorporate corrections due to interactions. This is the virial expansion, an expansion in powers of the density ρ. Every thermodynamic quantity can be written as a virial expansion. For example, for the pressure:

$$\frac{pV}{NkT} = 1 + B_2(T)\rho + B_3(T)\rho^2 + \cdots \tag{2.7}$$

where $B_n(T)$ are the *virial coefficients* which will in general be temperature dependent. The unit term in the right-hand side comes from the ideal-gas contribution. The remaining terms are corrections due to the density (i.e. to the interactions). The virial expansion

is used to fit experimental data for the equation of state, but it can be obtained in a rigorous way from the partition function. We will not go into too many details, just showing how the most important correction is obtained and then writing the general result.

We start with the congurational partition function:

$$Z_N = \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N e^{-\beta U(\{\mathbf{r}_i\})}. \tag{2.8}$$

A very useful auxiliary function is the *Mayer function*, $f(r)$:

$$f(r) = e^{-\beta\phi(r)} - 1. \tag{2.9}$$

Using the notation $\phi_{ij} \equiv \phi(|\mathbf{r}_j - \mathbf{r}_i|)$, $f_{ij} \equiv f(|\mathbf{r}_j - \mathbf{r}_i|)$, we have

$$e^{-\beta\sum_i\sum_{j>i}\phi_{ij}} = \prod_i\prod_{j>i}(1 + f_{ij}) = (1 + f_{12})(1 + f_{13})...(1 + f_{23})\cdots$$

$$= 1 + \sum_i\sum_{j>i} f_{ij} + \cdots \tag{2.10}$$

Terms represented by dots come from products of two, three or more Mayer functions. This is just an expansion in which the expansion parameter is the Mayer function, a legitimate expansion parameter for low density (i.e. the distance between two particles i and j, $|\mathbf{r}_j - \mathbf{r}_i|$, is large, so that $\phi_{ij} \to 0$) and/or high temperature; in both limits $\exp(\beta\phi_{ij}) \to 1$ and $f_{ij} \to 0$. Then:

$$Z_N = \int d\mathbf{r}_1... \int d\mathbf{r}_N \left(1 + \sum_i\sum_{j>i} f_{ij} + \cdots\right) = V^N + \sum_i\sum_{j>i} \int d\mathbf{r}_1... \int d\mathbf{r}_N f_{ij} + \cdots$$

$$= V^N + V^{N-2}\sum_i\sum_{j>i} \int d\mathbf{r}_i \int d\mathbf{r}_j f_{ij} + \cdots \tag{2.11}$$

Integrals can be calculated first defining $\mathbf{r} \equiv \mathbf{r}_j - \mathbf{r}_i$:

$$\int d\mathbf{r}_i \int d\mathbf{r}_j f(|\mathbf{r}_j - \mathbf{r}_i|) = \int d\mathbf{r}_i \int d\mathbf{r} f(r) = V \int d\mathbf{r} f(r) \equiv -2V B_2. \tag{2.12}$$

For the time being let us define the second virial coefficient as

$$B_2 = -\frac{1}{2}\int d\mathbf{r} f(r). \tag{2.13}$$

We then have

$$Z_N = V^N - V^{N-1}N(N-1)B_2 + \cdots \tag{2.14}$$

[since there are $N(N1)/2$ distinct pairs of atoms -the sum over i and j-, all of which give the same contribution], and taking $N1 \simeq N$:

$$Q = \left(\frac{V^N}{N!\Lambda^{3N}}\right)\left(1 - \frac{N^2}{V}B_2 + \cdots\right), \tag{2.15}$$

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which is the final expression. The Helmholtz free energy is (we neglect higher-order terms, since we only look for the leading correction):

$$F = F_{\text{ideal}} - kT \log \left(1 - \frac{N^2}{V} B_2 \right), \tag{2.16}$$

and the pressure is

$$p = -\left(\frac{\partial F}{\partial V} \right)_{N,T} = \frac{NkT}{V} + kT \frac{\frac{N^2}{V^2} B_2}{1 - \frac{N^2}{V} B_2} = \frac{NkT}{V} \left(1 + \frac{\frac{N}{V} B_2}{1 - \frac{N^2}{V} B_2} \right)$$

$$= \frac{NkT}{V} \left(1 + \frac{N}{V} B_2 + \cdots \right) \tag{2.17}$$

(we used the expansion $(1+x)^{-1} = 1 - x + \cdots$ and $B_2 \sim f$, with f small). Finally:

$$\frac{pV}{NkT} = 1 + B_2 \rho + \cdots, \qquad B_2 = -\frac{1}{2} \int d\mathbf{r} f(r). \tag{2.18}$$

This result confirms the validity of the virial expansion. This is a very important result since it relates an experimentally measurable quantity, such as the pressure p (and hence B_2), with the microscopic quantity $f(r)$ and then with the intermolecular interaction potential $\phi(r)$.

It turns out that all virial coefficients can be expressed in terms of integrals over products of Mayer functions. The first two coefficients are:

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

$$B_3 = -\frac{1}{3} \int d\mathbf{r} \int d\mathbf{r}' f(r) f(r') f(|\mathbf{r} - \mathbf{r}'|). \tag{2.19}$$

Higher-order coefficients are given by considerably more complicated integrals. These integrals can be given a short-hand notation by means of the so-called graphs.

Note that Eqn. (2.18) only includes corrections to first order in density and, consequently, is strictly valid only at low density. However, we can use a trick that extends its range of applicability. Writing:

$$\frac{pV}{NkT} = 1 + B_2 \rho + \cdots \simeq \frac{1}{1 - B_2 \rho}, \qquad \rho \text{ small} \tag{2.20}$$

(here use has been made of the expansion $(1 - x)^{-1} = 1 + x + \cdots$). This is the *Clausius equation of state*. It is equivalent to approximating the virial coefficients of high order in terms of B_2:

$$\frac{1}{1 - B_2 \rho} = 1 + B_2 \rho + (B_2)^2 \rho^2 + (B_2)^3 \rho^3 + \cdots \quad \rightarrow \quad B_3 \approx (B_2)^2, \ B_4 \approx (B_2)^4, \ \cdots \tag{2.21}$$

Note that the (dimensionless) scaled virial coefficients turn out to be approximated by unity:

$$\frac{B_3}{(B_2)^2} \approx 1, \qquad \frac{B_4}{(B_2)^3} \approx 1, \qquad \cdots \tag{2.22}$$

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2.3 Interaction models

We already introduced the LennardJones potential as a realistic mathematical model for the dispersion interactions. Other, even more simplified, interaction models are frequently used in the statistical mechanics of fluids. Let us review two of the most popular.

2.3.1 The hard-sphere model

It can be considered as the simplest non-trivial model pair potential. Nevertheless, it captures the important repulsive region, and explains many features of real matter. The hard-sphere model assumes particles to be spherical hard balls of diameter σ that collide elastically:

$$\phi(r) = \begin{cases} \infty, & r < \sigma, \\ 0, & r > \sigma. \end{cases} \tag{2.23}$$

This is a completely repulsive potential (no attraction); however, a fluid of hard spheres presents a phase transition between a fluid phase and a crystalline phase. Since the associated Boltzmann factor $\exp[-\beta\phi(r)]$, does not depend on temperature (since it is zero or unity), Z_N is temperature-independent and the only thermal dependence comes from the kinetic part.

The first seven virial coefficients of the hard-sphere potential are known, either exactly (the first three) of approximately by means of computer evaluation. The first are:

$$B_2^{\mathrm{HS}} = \frac{2\pi\sigma^3}{3}, \quad \frac{B_3^{\mathrm{HS}}}{(B_2^{\mathrm{HS}})^2} = 0.625, \quad \frac{B_4^{\mathrm{HS}}}{(B_2^{\mathrm{HS}})^3} \simeq 0.287, \quad \frac{B_5^{\mathrm{HS}}}{(B_2^{\mathrm{HS}})^4} \simeq 0.110. \tag{2.24}$$

As can be seen the Clausius approximation severely overestimates the value of the virial coefficients. Now, writing

$$B_2^{\mathrm{HS}}\rho = \frac{2\pi}{3}\rho\sigma^3 = 4\eta, \quad \eta \equiv \rho v, \tag{2.25}$$

where η is the *packing fraction* and v the volume of a sphere,

$$v = \frac{4\pi}{3}\left(\frac{\sigma}{2}\right)^3 = \frac{\pi}{6}\sigma^3, \quad \eta = \rho v = \frac{Nv}{V} = \frac{\text{volume occupied by spheres}}{\text{total volume}}, \tag{2.26}$$

we can write the Clausius equation as

$$\frac{pV}{NkT} = \frac{1}{1 - 4\eta}. \tag{2.27}$$

This equation is only valid for $\eta < 1/4$ (i.e. when the occupied volume is less than 25%); this is obviously a severe limitation of the model, which arises from the too simplistic assumptions that we have made.

The hard-sphere model played a very important role in the understanding of liquids and of crystallisation in the '50 of last century. J. G. Kirkwood, using integral-equation theory

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(see later) for the hard-sphere fluid, had made the prediction that the fluid should crystallise at high density. His prediction was based on the absence of a solution to the liquid theory, a feature he identified with the beginning of crystallisation. But this conclusion was not widely accepted, as people found it hard to believe that purely repulsive particles could form a stable crystal. The application of the then incipient computer simulation methods to statistical physics and, specifically, to the hard-sphere model by Alder and Wainwright and by Wood and Jacobson finally settled the question.

2.3.2 The square-well model

This model is given mathematically as follows:

$$
\phi(r) = \begin{cases} \infty, & r < \sigma, \\ -\epsilon, & \sigma < r < \sigma + \delta, \\ 0, & r > \sigma + \delta. \end{cases} \tag{2.28}
$$

In essence, the model consists of a hard-sphere model where each sphere has an attractive 'skin of width $\delta/2$. The model has three parameters: σ, the diameter of the spheres, ϵ, the depth of the attractive potential well, and δ, the range of the attraction. The presence of the attractive part is responsible for the liquid-vapour condensation, and the associated critical point, that the model exhibits; in this sense, the model is more realistic than the hard-sphere model.

The (approximate) Clausius equation of state for the hard-sphere potential implies that, at constant temperature, pressure increases with density. In fact this is the correct behaviour expected in a gas: as the gas is compressed (p increases) its density ρ increases. But this is a more general behaviour. From thermodynamics we know that the isothermal compressibility is positive, which means that $\partial p / \partial \rho > 0$:

$$
\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{N,T} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_{N,T} > 0. \tag{2.29}
$$

We will now see that, in some circumstances, this condition is violated. By examining the equation of state of the square-well model it is possible to understand why this is so. The second virial coefficient B_2 is:

$$
\begin{aligned}
B_2 &= -\frac{1}{2}\int d\mathbf{r}f(r) = -2\pi\int_0^\infty dr r^2\left[e^{-\beta\phi(r)} - 1\right] \\
&= -2\pi\left\{\int_0^\sigma dr r^2(-1) + \int_\sigma^{\sigma+\delta} dr r^2\left(e^{\beta\epsilon} - 1\right)\right\} \\
&= B_2^{\text{HS}} - \frac{2\pi}{3}\left(e^{\beta\epsilon} - 1\right)\left[(\sigma + \delta)^3 - \sigma^3\right].
\end{aligned} \tag{2.30}
$$

If the temperature is high enough with respect to ϵ, i.e. $\beta\epsilon \ll 1$, we can write

$$
e^{\beta\epsilon} - 1 \simeq \beta\epsilon, \tag{2.31}
$$

so that

$$B_2 = B_2^{\text{HS}} - \frac{2\pi\epsilon\sigma^3\lambda}{3kT}, \quad \lambda \equiv \left(1 + \frac{\delta}{\sigma}\right)^3 - 1. \tag{2.32}$$

The pressure is then

$$\frac{pV}{NkT} = 1 + B_2\rho = 1 + B_2^{\text{HS}}\rho - \frac{2\pi\epsilon\rho\sigma^3\lambda}{3kT} \simeq \frac{1}{1 - 4\eta} - \frac{4\epsilon\lambda\eta}{kT}. \tag{2.33}$$

This equation is known as the *van der Waals equation of state*[1]. The equation can also be written as a dimensionless pressure in terms of the volume of the spheres v:

$$\frac{pv}{kT} = \frac{\eta}{1 - 4\eta} - \frac{4\epsilon\lambda\eta^2}{kT}. \tag{2.34}$$

Note that the term due to the attractive well is negative, which implies the possibility of the compressibility becoming negative; this phenomenon would be associated to an instability due to the liquid-vapour phase transition. We will examine this phenomenon in more detail later on.

2.4 Dense fluids: distribution and correlation functions

The problem with any truncated virial expansion is that it rapidly fails to account for the fluid properties as the density increases. Any attempt to use expansions in a small parameter such as the density is bound to failure, simply because in dense fluids there is no such small parameter. This is in contrast with the theory of solids, where one can use expansions in the particle displacements about the lattice sites, which gives a well defined and accurate model: the harmonic solid. There is no equivalent reference model in the theory of liquids (dense fluids). Therefore, a radically different method is used, and this method is based on probabilistic arguments, mathematically expressed in terms of distribution and correlation functions.

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[1]This equation can also be obtained from the well-known van der Waals equation of state:

$$(p + a\rho^2)(V - Nb) = NkT,$$

where a and b are constants. a is related to the pressure reduction coming from molecular attraction, whereas b has to do with the reduction in the volume accessible to a molecule due to the volume occupied by the other molecules, i.e. the volume *excluded* to the centre of mass of a sphere due to the rest. Solving for the pressure:

$$p = \frac{NkT}{V - Nb} - a\rho^2 \quad \rightarrow \quad \frac{pV}{NkT} = \frac{1}{1 - b\rho} - \frac{a\rho}{kT}.$$

b can be calculated by assuming that molecules are hard spheres of diameter σ; the volume excluded per sphere is then

$$b = \frac{1}{2} \times \frac{4\pi}{3}\sigma^3 = 4v,$$

where v is the volume of a sphere. A prefactor $1/2$ is needed because, for each pair of spheres, only one excluded volume has to be considered (otherwise we would be counting this excluded volume twice). Then $1 - b\rho = 1 - 4\eta$, and the a constant can be defined as $a \equiv 4\lambda v$, wherefrom Eqn. (2.33) follows.

2.4.1   The distribution functions

The most useful distribution function is the *radial distribution function*, $g(r)$. It measures the amount of local order in a fluid, and can be easily defined with words: from the point of view of some particular particle (which is therefore taken as the origin), it gives the average number of particles a distance r from that particle, relative to the number that would be found if there were no interactions (i.e. relative to the ideal gas). The radial distribution function is (indirectly) accessible to experiment since it is the Fourier transform of the structure factor, which can be measured in neutron-scattering experiments.

The radial distribution function is one of a complete hierarchy of distribution functions, which can be defined rigorously, and characterise the equilibrium structure of a fluid. Let us see how this is done, using the canonical ensemble.

We define a system of N particles occupying a volume V at a temperature T, and focus on the function $p_N(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$ (where $\{\mathbf{r}_i\}$ is the set of coordinates of the particles), defined such that

$$p_N(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N \tag{2.35}$$

is the probability of finding particle 1 in a volume element $d\mathbf{r}_1$ centred at $\mathbf{r}_1$, particle 2 in a volume element $d\mathbf{r}_2$ centred at $\mathbf{r}_2$, ..., and particle N in a volume element $d\mathbf{r}_N$ centred at $\mathbf{r}_N$, all at the same time. Obviously p_N can be found, in the canonical ensemble, by suitably summing, over all microstates compatible with the above restrictions, the normalised Boltzmann factor. On performing such a sum, which extends over all momenta, it is easy to arrive at

$$p_N(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \frac{e^{-\beta U(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)}}{Z_N(V, T)}. \tag{2.36}$$

For a classical fluid, for which positions and momenta are uncoupled, this function contains all the relevant information about the fluid since momenta are integrated out. Since such an amount of information is often superfluous, one defines partial probability functions. For example:

$$p_N^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \int d\mathbf{r}_{n+1} \cdots \int d\mathbf{r}_N \, p_N(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) \tag{2.37}$$

is the probability of finding particle 1 at $\mathbf{r}_1$, particle 2 at $\mathbf{r}_2$, ..., and particle n at $\mathbf{r}_n$, irrespective of the positions occupied by particles $n+1$, $n+2$, ..., N. It is more convenient to define the *distribution functions*, $\rho_N^{(n)}$, as a measure of the probability of finding a particle at $d\mathbf{r}_1$ centred at $\mathbf{r}_1$, another particle in a volume element $d\mathbf{r}_2$ centred at $\mathbf{r}_2$, ..., and another particle n in a volume element $d\mathbf{r}_n$ centred at $\mathbf{r}_n$, irrespective of the positions occupied of the remaining $N-n$ particles. Since the identity of the particles is not specified here, and there are $N!/(N-n)!$ ways of arranging n particles in n given locations out of N possible particles, the connection between $p_N^{(n)}$ and $\rho_N^{(n)}$ is

$$\rho_N^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n) = \frac{N!}{(N-n)!} p_N^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n). \tag{2.38}$$

Note that the distribution functions $\rho_N^{(n)}$ are not probabilities, as their normalisation is

$$\int d\mathbf{r}_1 \cdots \int d\mathbf{r}_n \rho_N^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n) = \frac{N!}{(N-n)!}. \tag{2.39}$$

Their precise meaning is obtained by examining each of the members of the hierarchy. We have:

- $\rho_N^{(1)}$: from the normalisation equation,

$$\int d\mathbf{r} \rho_N^{(1)}(\mathbf{r}) = \frac{N!}{(N-1)!} = N. \tag{2.40}$$

Therefore, $\rho_N^{(1)}(\mathbf{r}) \equiv \rho(\mathbf{r})$ is the local number density. If the fluid is homogeneous, $\rho_N^{(1)} = \rho$ is constant, equal to the mean density $\rho = N/V$.

- $\rho_N^{(2)}$: for a homogeneous fluid $\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ can only depend on the relative distance $r_{12} \equiv |\mathbf{r}_2 - \mathbf{r}_1|$, since there cannot be any privileged point that can serve as origin and there is no privileged direction in space either. One can then write $\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \equiv \rho^2 g(r_{12})$, which defines the function $g(r_{12})$. This is in fact the radial distribution function introduced above. To see this, we invoke the normalisation condition:

$$\int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 V \int d\mathbf{r} g(r) = N(N-1), \tag{2.41}$$

which can be written

$$4\pi\rho \int_0^\infty dr r^2 g(r) = N - 1. \tag{2.42}$$

But this equation is telling us that $4\pi\rho r^2 g(r)$ is the number of particles at a distance r from a central particle (which does not count, hence the factor $N1$), in agreement with our previous definition.

The radial distribution function (and in general, for an inhomogeneous fluid, the two-point distribution function $\rho_N^{(2)}$) is very important. On the one hand, as already mentioned, it can be linked to an experimentally measurable quantity, the structure factor, $S(q)$ (more will be said about the structure factor later). On the other, knowledge of $g(r)$ allows to compute various thermodynamic functions; this is important, as $g(r)$ must be directly related to the interaction potential $\phi(r)$ [of course this is an abstract relation; any theory of the liquid state must provide a means for actually computing $g(r)$ from $\phi(r)$, which is a highly non-trivial task]. For example, we have the following relations:

- The *energy equation*:

$$E = \frac{3}{2} NkT + 2\pi\rho N \int_0^\infty dr r^2 g(r)\phi(r). \tag{2.43}$$

- The *virial equation* for the pressure:

$$p = \rho kT - \frac{2\pi}{3}\rho^2 \int_0^\infty dr r^3 g(r)\phi'(r). \tag{2.44}$$

Note that U and p are mechanical quantities. Thermal quantities, such as entropies or free energies, can also be written in terms of $g(r)$, but only via a coupling integral that includes radial distribution functions of families of systems with different interaction potentials. As an example, let us obtain Eqn. (2.43). We start from the relation:

$$E = -T^2 \left(\frac{\partial F/T}{\partial T} \right)_{N,V} = kT^2 \left(\frac{\partial \log Q}{\partial T} \right)_{N,V} = \frac{kT^2}{Q} \left(\frac{\partial Q}{\partial T} \right)_{N,V}. \tag{2.45}$$

Then:

$$
\begin{aligned}
E &= \frac{kT^2}{Q} \frac{\partial}{\partial T} \left\{ \frac{1}{N! h^{3N}} \int d\mathbf{p}_1 \cdots \int d\mathbf{p}_N \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N e^{-\beta \sum_i p_i^2/2m - \beta U} \right\} \\
&= \frac{kT^2}{QN!} \frac{\partial}{\partial T} \left\{ \frac{1}{\Lambda^{3N}} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N e^{-\beta U} \right\}. \tag{2.46}
\end{aligned}
$$

Now since

$$\frac{\partial}{\partial T} \left(\frac{1}{\Lambda^{3N}} \right) = -3N\Lambda^{-3N-1} \frac{\partial \Lambda}{\partial T} = \frac{3N}{2T\Lambda^{3N}}, \tag{2.47}$$

we have

$$
\begin{aligned}
E &= \frac{kT^2}{\left(\frac{Z_N}{N!\Lambda^{3N}} \right) N!} \\
&\times \left\{ \frac{3NZ_N}{2T\Lambda^{3N}} + \frac{1}{\Lambda^{3N}} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N \left(\frac{U}{kT^2} \right) e^{-\beta U} \right\} = \frac{3}{2} NkT + \langle U \rangle, \tag{2.48}
\end{aligned}
$$

as expected. But now:

$$
\begin{aligned}
\langle U \rangle &= \frac{1}{Z_N} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N \left(\sum_i \sum_{j>i} \phi_{ij} \right) e^{-\beta U} \\
&= \sum_i \sum_{j>i} \int d\mathbf{r}_i \int d\mathbf{r}_j \phi_{ij} \left[\frac{1}{Z_N} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_{i-1} \int d\mathbf{r}_{i+1} \cdots \int d\mathbf{r}_{j-1} \int d\mathbf{r}_{j+1} \cdots \int d\mathbf{r}_N e^{-\beta U} \right] \\
&= \sum_i \sum_{j>i} \int d\mathbf{r}_i \int d\mathbf{r}_j \phi(|\mathbf{r}_i - \mathbf{r}_j|) \left[\frac{(N-2)!}{N!} \rho_N^{(2)}(\mathbf{r}_i, \mathbf{r}_j) \right] \\
&= \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \phi(|\mathbf{r} - \mathbf{r}'|) \rho_N^{(2)}(\mathbf{r}, \mathbf{r}'). \tag{2.49}
\end{aligned}
$$

For a homogeneous fluid:

$$E = \frac{3}{2} NkT + \frac{\rho^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \phi(|\mathbf{r} - \mathbf{r}'|) g(|\mathbf{r} - \mathbf{r}'|) = \frac{3}{2} NkT + \frac{\rho^2 V}{2} \int d\mathbf{r} \phi(r) g(r), \tag{2.50}$$

from which Eqn. (2.43) follows.

An alternative way to introduce the reduced distribution functions is via the density operator $\hat{\rho}(\mathbf{r})$:

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r}_i - \mathbf{r}). \tag{2.51}$$

The one- and two-body distribution functions are:

$$\rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle = \sum_{i=1}^{N} \langle \delta(\mathbf{r}_i - \mathbf{r}) \rangle,$$

$$\rho_N^{(2)}(\mathbf{r},\mathbf{r}') = \langle \hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}') \rangle = \sum_i \sum_{j \neq i} \langle \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_j - \mathbf{r}') \rangle. \qquad (2.52)$$

By means of this definition it is sometimes simpler to obtain some relations. For example:

$$
\begin{aligned}
\langle U \rangle &= \left\langle \sum_i \sum_{j>i} \phi(|\mathbf{r}_i - \mathbf{r}_j|) \right\rangle = \left\langle \frac{1}{2} \sum_i \sum_{j \neq i} \int d\mathbf{r} \int d\mathbf{r}' \phi(|\mathbf{r} - \mathbf{r}'|)\delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j) \right\rangle \\
&= \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \phi(|\mathbf{r} - \mathbf{r}'|) \sum_i \sum_{j \neq i} \langle \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j) \rangle \\
&= \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \phi(|\mathbf{r} - \mathbf{r}'|)\rho_N^{(2)}(\mathbf{r},\mathbf{r}'). \qquad (2.53)
\end{aligned}
$$

Fig. 2.2 shows the appearance of the radial distribution function corresponding to a dense fluid (in this particular case it comes from a computer simulation of a Lennard-Jones fluid). It tends to unity at large distances. But the most salient feature is the oscillatory structure at short distances. The 'hole within the first σ comes from exclusion (particles cannot penetrate within distances much less than σ, otherwise the pair energy would become arbitrarily large). The first peak comes from the minimum of the Lennard-Jones potential: neighbouring particles take advantage of the potential well. Then, for increasing radial distances, there comes a second minimum, which results from the exclusion region around the particles in the first peak, a second peak, and so on. In the case of a crystal, $\rho_N^{(2)}$ contains a complicated network of peaks, reflecting all the distances and orientations of the relative location of pairs of particles (the radial distribution function cannot be strictly defined for a crystal).

Up to now we have defined the distribution functions in the canonical ensemble. It is also fruitful to define them in the grand canonical ensemble. We follow the same steps as before. The probability $p(N)$ that the system has N particles is

$$p(N) = \frac{1}{N!h^{3N}} \int d\mathbf{r}_1 ... \int d\mathbf{r}_N \int d\mathbf{p}_1 ... \int d\mathbf{p}_N \left[\frac{e^{-\beta(\mathcal{H}_N - \mu N)}}{\Xi(\mu,V,T)} \right] = \frac{Q_N(N,V,T)e^{\beta\mu N}}{\Xi(\mu,V,T)}. \quad (2.54)$$

The n-particle distribution functions are then

$$\rho^{(n)}(\mathbf{r}_1 \cdots \mathbf{r}_n) = \sum_{N \geq n} \rho_N^{(n)}(\mathbf{r}_1 \cdots \mathbf{r}_n)p(N) = \left\langle \rho_N^{(n)}(\mathbf{r}_1 \cdots \mathbf{r}_n) \right\rangle_N, \qquad (2.55)$$

where we have defined the average over particles

$$\langle A \rangle = \sum_{N=0}^{\infty} A(N)p(N) \qquad (2.56)$$

for an arbitrary function $A(N)$ (note that we must have $\rho_N^{(n)} = 0$ for $n > N$). Now $\rho^{(n)}$ is a measure of the probability of finding a particle at $\mathbf{r}_1$, another particle at $\mathbf{r}_2$,
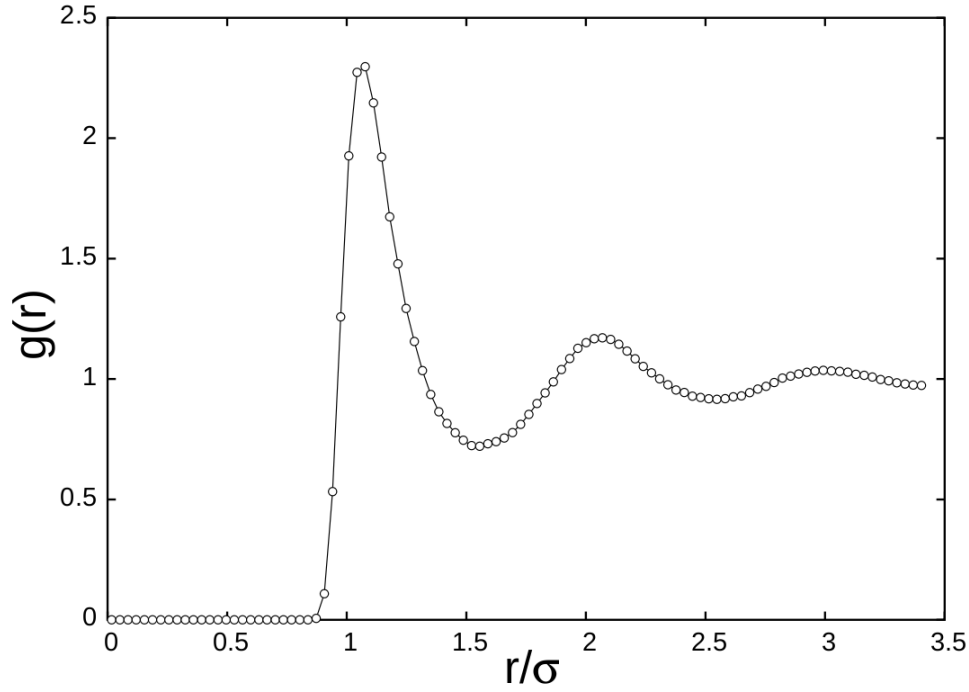
Figure 2.2: Radial distribution function of a Lennard-Jones fluid at high density.

etc., irrespective of the number of particles N and of the position of the remaining Nn particles. The normalisation of $\rho^{(n)}$ is:

$$
\int d\mathbf{r}_1 \cdots \int d\mathbf{r}_n \rho^{(n)}(\mathbf{r}_1, \cdots, \mathbf{r}_n) = \sum_{N \geq n} p(N) \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_n \rho_N^{(n)}(\mathbf{r}_1, \cdots, \mathbf{r}_n)
$$

$$
= \sum_{N \geq n} p(N) \frac{N!}{(N-n)!} = \left\langle \frac{N!}{(N-n)!} \right\rangle. \tag{2.57}
$$

For example, for $n = 1$ and $n = 2$:

$$
\int d\mathbf{r}\rho^{(1)}(\mathbf{r}) = \left\langle \frac{N!}{(N-1)!} \right\rangle = \langle N \rangle,
$$

$$
\int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho^{(1)}(\mathbf{r}_1, \mathbf{r}_2) = \left\langle \frac{N!}{(N-2)!} \right\rangle = \left\langle N^2 - N \right\rangle. \tag{2.58}
$$

Combining these two expressions:

$$
\int d\mathbf{r}_1 \int d\mathbf{r}_2 \left[\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2) \right] = \left\langle N^2 \right\rangle - \langle N \rangle - \langle N \rangle^2. \tag{2.59}
$$

For a homogeneous fluid $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g(|\mathbf{r}_1 - \mathbf{r}_2|)$; moreover, using $\rho = N/V$, we have

$$
\rho^2 V \int d\mathbf{r}_{12} \left[g(r_{12}) - 1 \right] = \left\langle N^2 \right\rangle - \langle N \rangle - \langle N \rangle^2,
$$

$$
1 + \rho \int d\mathbf{r}_{12} \left[g(r_{12}) - 1 \right] = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \rho k T \kappa_T = \frac{\kappa_T}{\kappa_T^0}. \tag{2.60}
$$

Here $\kappa_T^0 = 1/\rho k T$ is the compressibility of the ideal gas. This is the so-called *compressibility equation*. Unlike the energy and virial equations, which assume a pair-wise potential, this is a general and exact result. Also, unlike the energy and virial equations, which can be derived using either the canonical or macrocanonical ensembles, the compressibility equation can only be obtained in the macrocanonical equation since it involves the fluctuation in the number of particles.

Either of the three equations (energy, virial or compressibility) provide a route to obtain the thermodynamics (given E, p or κ_T we may obtain the free energy F -up to a constant or a term proportional to density- by integration). Use of the exact $g(r)$ will give the same F. But of course liquid-state theories only provide an approximate $g(r)$; in practice, then, the three routes are not equivalent unless forced to be so. This is a strong test on any theory of liquids.

Consider the Fourier transform of the density operator:

$$\rho_{\mathbf{q}} = \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} \hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_i}. \tag{2.61}$$

Since it involves all the atomic coordinates, $\rho_{\mathbf{q}}$ is called a *collective coordinate*. In a homogeneous liquid the average $\langle \rho_{\mathbf{q}} \rangle$ is trivial:

$$\langle \rho_{\mathbf{q}} \rangle = \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} \langle \hat{\rho}(\mathbf{r}) \rangle = \rho \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} = (2\pi)^3 \rho \delta_{\mathbf{q0}}. \tag{2.62}$$

But, even in a homogeneous liquid, the correlation of $\rho_{\mathbf{q}}$ is not trivial. The <u>structure factor</u> is defined as this correlation:

$$S(\mathbf{q}) = \frac{1}{N} \left\langle |\rho_{\mathbf{q}}|^2 \right\rangle = \frac{1}{N} \left\langle \rho_{\mathbf{q}} \rho_{\mathbf{q}}^* \right\rangle = \frac{1}{N} \left\langle \rho_{\mathbf{q}} \rho_{-\mathbf{q}} \right\rangle \tag{2.63}$$

(note that $\rho_{\mathbf{q}}^* = \rho_{-\mathbf{q}}$). Obviously, even though the averaged density is constant in a homogeneous fluid, the local density operator fluctuates from configuration to configuration, and in fact the $S(\mathbf{q})$ so defined is a measure of the fluctuations in density. We have:

$$
\begin{aligned}
S(\mathbf{q}) &= \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_i} e^{-i\mathbf{q}\cdot\mathbf{r}_j} \right\rangle = 1 + \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j\neq i}^{N} \int d\mathbf{r} \int d\mathbf{r}' e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j) \right\rangle \\
&= 1 + \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} < \sum_{i=1}^{N} \sum_{j\neq i}^{N} \langle \delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j) \rangle \\
&= 1 + \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \rho_N^{(2)}(\mathbf{r}, \mathbf{r}'). \tag{2.64}
\end{aligned}
$$

Therefore $S(\mathbf{q})$ is essentially the Fourier transform of $\rho_N^{(2)}(\mathbf{r}, \mathbf{r}') = \langle \hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}') \rangle$, and therefore it measures density fluctuations. For a homogeneous fluid:

$$S(\mathbf{q}) = 1 + \frac{V}{N} \rho^2 \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} g(r) = 1 + \rho \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} g(r), \tag{2.65}$$

so that the structure factor is essentially the Fourier transform of the radial distribution function. Note that we can write

$$S(\mathbf{q}) = 1 + \rho \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} [g(r) - 1] + \rho \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} = 1 + \rho \hat{h}(\mathbf{q}) + (2\pi)^3 \rho \delta(\mathbf{q}), \tag{2.66}$$

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where $h(r) = g(r)1$ is the *total correlation function* [the 1 subtracts the trivial ideal contribution to $g(r)$]. The $\delta(\mathbf{q})$ term accounts for the contribution of the constant tail of $g(r)$; later we will see that this corresponds to *forward scattering* in a scattering experiment (radiation that is incident on any one atom but not scattered) and therefore it is a trivial term (in the sense that it contains no structural information). Our convention here is to eliminate that term and define the structure factor as the Fourier transform of $g(r)1$:

$$S(q) = 1 + \rho \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}}[g(r) - 1]. \tag{2.67}$$

Note that $S(\mathbf{q}) = S(q)$ since $g(r)$ is isotropically invariant (i.e. it depends only on r and not on $\mathbf{r}$). Expression (2.67) is valid for a homogeneous fluid; for a crystal, $g(r)$ consists of a sequence of peaks and the structure factor is defined directly by Eqn. (2.63). In fact, one may define the function

$$\chi^{(2)}(\mathbf{r}, \mathbf{r}') = \langle (\hat{\rho}(\mathbf{r}) - \rho)(\hat{\rho}(\mathbf{r}') - \rho) \rangle, \tag{2.68}$$

which actually measures the density fluctuations about the mean density [not over zero density, as in (2.63) or (2.65).

For a homogeneous fluid, since $g(r)$ only depends on distance r:

$$S(q) = 1 + \rho \int_0^\infty dr r^2 [g(r) - 1] \int d\hat{\mathbf{r}} e^{i\mathbf{q}\cdot\mathbf{r}} = 1 + 4\pi\rho \int_0^\infty dr r^2 \frac{\sin qr}{qr}[g(r) - 1]. \tag{2.69}$$

Note that $S(q) \to 1$ as $q \to \infty$. Also, note that the left-hand side of Eqn. (2.60) is the structure factor at zero wavelength, so that $S(0) = \rho k T \kappa_T$.

The structure factor can be obtained by scattering experiments using X rays or thermal neutrons. If one lets a beam of photons or neutrons, each described by a plane wave $\psi_\mathbf{k}(\mathbf{r}) \sim e^{i\mathbf{k}\cdot\mathbf{r}}$ with wavevector $\mathbf{k}$, illuminate a liquid sample, the beam will be scattered (or diffracted), and the scattered beam will have wavevector $\mathbf{k}'$, with particles represented, very far from the scattering centre, by another plane wave $\psi_{\mathbf{k}'}(\mathbf{r}) \sim e^{i\mathbf{k}'\cdot\mathbf{r}}$ (which should in principle be a spherical wave). Assuming the scattering to be elastic (this is a good approximation, since energies of the incoming particles are $\sim 10^4$ eV, much larger than kT at normal temperatures, which is ~ 26 meV), so that $\mathbf{k}' = \mathbf{k} + \mathbf{q}$, with $\mathbf{q}$ the wavevector transferred and $|\mathbf{k}| = |\mathbf{k}'|$, the differential cross section of scattering off a fixed amount of atoms is

$$\frac{d\sigma}{d\Omega} \propto \left| \int d\mathbf{r} \psi_\mathbf{k}^*(\mathbf{r}) \Phi(\mathbf{r}) \psi_{\mathbf{k}'}(\mathbf{r}) \right|^2 = \left| \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \Phi(\mathbf{r}) e^{i\mathbf{k}'\cdot\mathbf{r}} \right|^2 = \left| \int d\mathbf{r} \Phi(\mathbf{r}) e^{i\mathbf{q}'\cdot\mathbf{r}} \right|^2, \tag{2.70}$$

where $\Phi(\mathbf{r})$ is the interaction potential felt by the incoming particle in the sample (the above expression is given by Fermis golden rule). The factor or proportionality contains a factor that depends on the scattering angle between incident and scattered wave, θ; when $\theta = 0$ the wave is not scattered and this is called forward scattering, which therefore contains no structural information. Now the potential $\Phi(\mathbf{r})$ is expressed as the sum

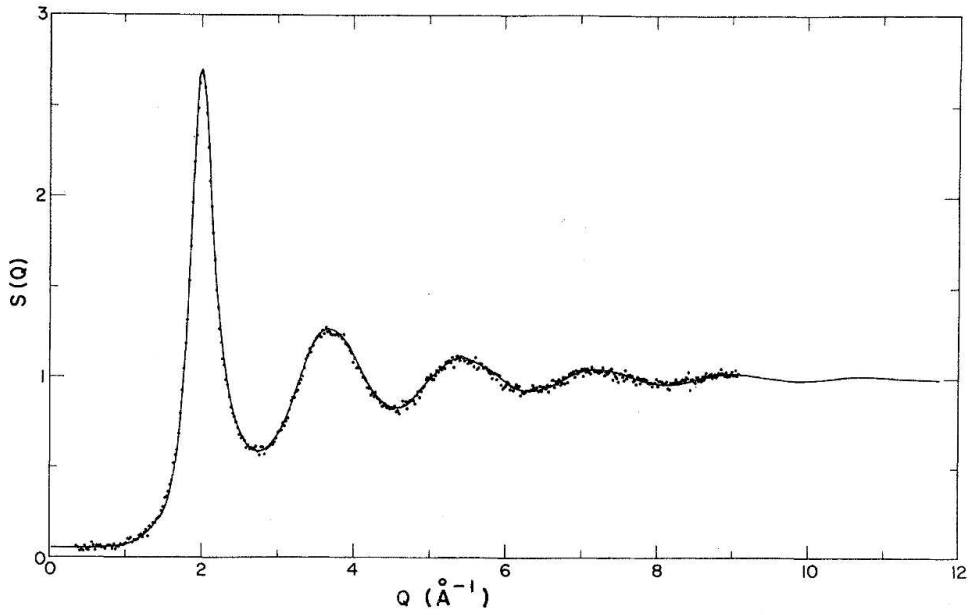$$\Phi(\mathbf{r}) = \sum_{i=1}^N \phi(\mathbf{r} - \mathbf{r}_i) \tag{2.71}$$

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Figure 2.3: Structure factor for liquid argon at 85 K, as measured by neutron scattering experiments (dots), and that obtained from computer simulation (molecular dynamics) on model argon at about the same temperature (continuous line). For more details see Yarnell et al., Phys. Rev. A**7**, 2130 (1973).

(all scattering centres are assumed to be identical) so that

$$\frac{d\sigma}{d\Omega} \propto \left| \sum_{i=1}^{N} \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} \phi(\mathbf{r} - \mathbf{r}_i) \right|^2 = \left| \sum_{i=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_i} \int d\mathbf{r} e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}_i)} \phi(\mathbf{r} - \mathbf{r}_i) \right|^2 =$$

$$= \left| \sum_{i=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_i} \right|^2 \left| \hat{\phi}(q) \right|^2 = \left| \hat{\phi}(q) \right|^2 \sum_{i=1}^{N} \sum_{j=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_i} e^{-i\mathbf{q}\cdot\mathbf{r}_j} = \left| \hat{\phi}(q) \right|^2 \rho_{\mathbf{q}}\rho_{-\mathbf{q}}. \qquad (2.72)$$

The observed or experimental scattering intensity will be given by a thermal average over atomic positions:

$$\left. \frac{d\sigma}{d\Omega} \right|_{\exp} \left| \hat{\phi}(q) \right|^2 \langle \rho_{\mathbf{q}}\rho_{-\mathbf{q}} \rangle = N \left| \hat{\phi}(q) \right|^2 S(\mathbf{q}), \qquad (2.73)$$

so that it is proportional to the structure factor. In the case of neutrons $\hat{\phi}(q)$ is essentially independent of $\mathbf{q}$ (since the scattering centres are point-like), but for electrons, which are spread over an electronic atomic shell, this is substituted by the so-called *atomic form factor* which contains the total electron density and depends on $\mathbf{q}$ (but is largely independent on the uid density). The atomic form factor has to be obtained by quantum-mechanical calculations. Note that at low density, where $S(\mathbf{q}) = 1$, the cross section is given by contributions from the N individual atoms; it is correlations between atoms that account for the observed diffraction intensity (this is not surprising considering that in crystals, where scattering produces a pattern of diffraction spots or Bragg peaks, it is the intrinsic periodicity of the lattice and the collective behaviour of the atoms that gives rise to peaks
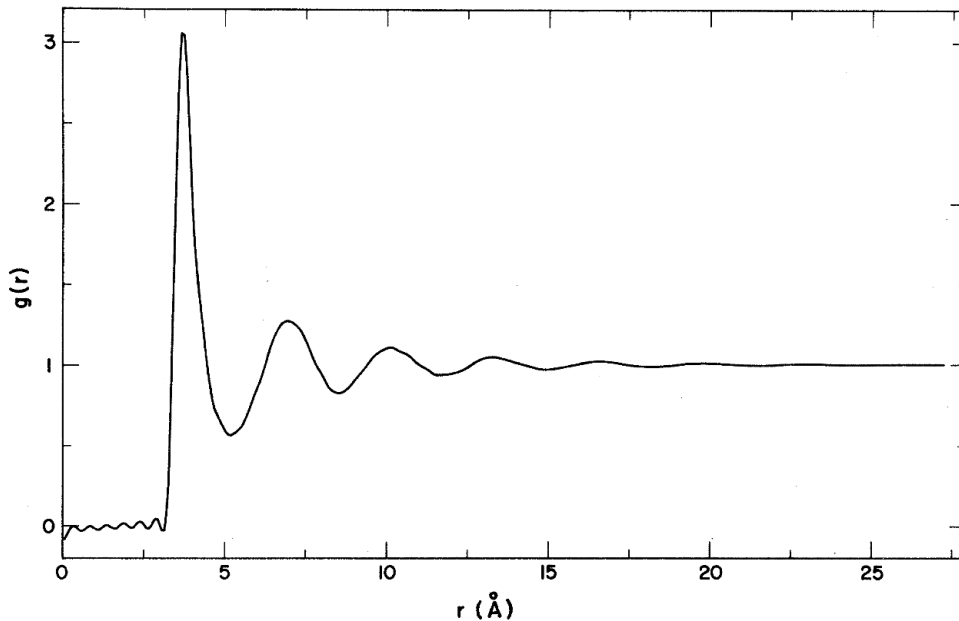
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Figure 2.4: Radial distribution function for liquid argon at 85 K, obtained by inverse Fourier transform of the experimental data in Fig. 2.3. For more details see Yarnell et al., Phys. Rev. A**7**, 2130 (1973).

of finite width; in liquids, lack of periodicity gives a smoother pattern with no angular dependence on the vector $\mathbf{q}$ but still with a pronounced structure with respect to the modulus q).

In Fig. 2.3 a comparison is made of the experimentally measured $S(q)$ for liquid argon at 85 K, using neutron scattering, and the same function obtained with computer simulation of a Lennard-Jones fluid (choosing the σ and ϵ parameters as those corresponding to argon, $\sigma = 3.405$ Åand $\epsilon/k = 119.8$ K at roughly the same temperature. As can be seen the agreement is remarkable. In Fig. 2.4 the radial distribution function is obtained by Fourier transforming the experimentally obtained $S(q)$. The agreement with the $g(r)$ as derived from simulation is also very good. Full details can be found in the original paper [Yarnell et al., Phys. Rev. A**7**, 2130 (1973), available from the web page of the course].

Another interesting result is that the structure factor of the HS model, especially when supplemented by some attractive potential, is capable of reproducing quite well the experimental structure factor of alkali metals, in particular the first peak. More details can be found in Khanna and MacLaughlin, J. Phys.: Condens. Matter **1**, 4155 (1989).

The direct correlation function

In the previous paragraphs we have introduced a hierarchy of distribution functions. It is very useful to introduce a different hierarchy of related functions, the so-called correlation functions, of which we will focus on the two-body or direct correlation function (similar to the two-body distribution function or, equivalently, the radial distribution function),

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$c(r)$. This is done through the *Orstein-Zernike* (OZ) equation,

$$h(r) = c(r) + \rho \int d\mathbf{r}' c(|\mathbf{r}' - \mathbf{r}|)h(r'), \qquad h(r) \equiv g(r) - 1, \tag{2.74}$$

which is in fact a definition of $c(r)$. Remember that $h(r)$ measures the correlation between two particles separated at a distance r, i.e. the effect of one particle on the other due to the interactions [$h(r) = 0$ for the ideal gas, since then $g(r) = 1$]. The meaning of $c(r)$ can be grasped from the previous equation: the total correlation $h(r)$ is the sum of the direct correlation, given by $c(r)$, and all indirect interactions mediated by a third particle at position $\mathbf{r}'$; a sum is taken over $\mathbf{r}'$ since all possible locations of the third particle contribute. We can see this more precisely by iterating the OZ equation: taking first $h(r) = c(r)$ (i.e. assuming as a first approximation that only direct correlations are important), substituting in the integral, then doing it again and so on, we get a kind of density expansion:

$$h(r) = c(r) + \rho \int d\mathbf{r}' c(|\mathbf{r}' - \mathbf{r}|)c(r') + \rho^2 \int d\mathbf{r}' \int d\mathbf{r}'' c(|\mathbf{r}' - \mathbf{r}|)c(|\mathbf{r}' - \mathbf{r}''|)c(r'') + ... \tag{2.75}$$

(this is not a real density expansion as $c(r)$ depends implicitely on density). We see that the total correlation $h(r)$ between two particles is given by the bare or direct correlation $c(r)$, plus correlations mediated by a third, fourth, etc. particle.

The interest of the direct correlation function, in the theory of liquids, as an alternative to $h(r)$ or $g(r)$, is that it is much less oscillatory and of shorter range; in fact, in the low-density and high-temperature limits, it has the range of the interaction potential, since it can be shown that

$$c(r) \quad \rightarrow \quad -\beta\phi(r) \quad \text{as} \quad r \rightarrow \infty, \quad \rho \rightarrow \infty. \tag{2.76}$$

This follows from the virial expansion of $c(r)$, which can be shown to be

$$c(r) = f(r) + \rho \int d\mathbf{r}' f(r)f(|\mathbf{r}' - \mathbf{r}|) + \cdots = e^{-\beta\phi(r)} - 1 + \cdots = -\beta\phi(r) + \cdots \tag{2.77}$$

This behaviour is also true for other thermodynamic conditions when $r \rightarrow \infty$, except in the neighbourhood of the critical point. Also, from the OZ equation it follows that, to lowest order in density,

$$h(r) = f(r) + \cdots \quad \rightarrow \quad g(r) = e^{-\beta\phi(r)} + \cdots \tag{2.78}$$

Note that $g(r)$ is just the Boltzmann factor associated with a pair of particles at low densities.

Since $c(r)$ is a simpler function than $g(r)$, it should in principle be much easier to obtain reasonable approximations for $c(r)$ than for $g(r)$, an idea that is exploited by a family of liquid theories. First, we note that, Fourier-transforming the OZ equation:

$$\hat{h}(q) = \hat{c}(q) + \rho\hat{h}(q)\hat{c}(q) \quad \rightarrow \quad \hat{h}(q) = \frac{\hat{c}(q)}{1 - \rho\hat{c}(q)} \tag{2.79}$$

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or, since $S(q) = 1 + \rho\hat{h}(q)$,

$$S(q) = \frac{1}{1 - \rho\hat{c}(q)}, \quad \rho\hat{c}(q) = 1 - \frac{1}{S(q)}. \tag{2.80}$$

These results are exact. In particular, $\rho\hat{c}(0) = 1 - \kappa_T^0/\kappa_T$ (a very large and negative quantity in view of the small value of κ_T in dense liquids).

Some liquidstate theories propose closure relations between $h(r)$ and $c(r)$ which are used to recast the OZ equation in terms of $h(r)$ or $c(r)$ only. Some of the best known theories are:

- *Random Phase Approximation* (RPA). This is the simplest of such theories; it is based on the closure relation

$$c(r) = -\beta\phi(r) \quad \forall r, \tag{2.81}$$

  which extends the asymptotic result (2.76) to all distances and densities. To see the implications of this approximation, let us use Eqn. (2.80) and the RPA, i.e. $\hat{c}(q) = -\beta\hat{\phi}(q)$:

$$S_{\text{RPA}}(q) = \frac{1}{1 + \beta\rho\hat{\phi}(q)}, \tag{2.82}$$

  with the Fourier transform of the potential being

$$\hat{\phi}(q) = \int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}}\phi(r) = 4\pi \int_0^\infty dr\, r^2 \phi(r)\frac{\sin qr}{qr}. \tag{2.83}$$

  This theory makes sense (a different thing is whether it gives good results!) provided $\hat{\phi}(q)$ exists; in order for this to happen $\phi(r)$ must decay sufficiently fast for large r (i.e. faster than r^{-2}) and diverge sufficiently slowly for small r (i.e. slower than r^{-2}). These conditions are not met by, for example, the Lennard-Jones potential!

- *Mean-spherical approximation* (MSA). This is applied for pair potentials that exhibit a hard-sphere core, i.e. potentials with $\phi(r) = \infty$ for $r < \sigma$. The approximation consists of writing

$$\begin{cases} g(r) = 0, & r < \sigma, \\[2mm] c(r) = -\beta\phi(r), & r > \sigma. \end{cases} \tag{2.84}$$

  The condition on $g(r)$ is obvious due to the hard-sphere core. The first condition extends the asymptotic behaviour of $c(r)$ to all distances. This approximation can be solved analytically for some particular potentials, such as Coulomb, screened Coulomb, hard-sphere, and other potentials. For the hard-sphere potential this approximation is seen to be equivalent to the Percus-Yevick (PY) approximation (see later), and leads to the well-known PY solution [M. S. Wertheim, Phys. Rev. Lett. **10**, 321 (1963); E. J. Thiele, J. Chem. Phys. **38**, 1959 (1963)]:

$$c(r) = \begin{cases} -\lambda_1 - 6\eta\lambda_2\left(\dfrac{r}{\sigma}\right) - \dfrac{\lambda_1\eta}{2}\left(\dfrac{r}{\sigma}\right)^3, & r < \sigma, \\[4mm] 0, & r > \sigma, \end{cases} \tag{2.85}$$

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with

$$\lambda_1 = \frac{(1+2\eta)^2}{(1-\eta)^4}, \quad \lambda_2 = -\frac{\left(1+\dfrac{\eta}{2}\right)^2}{(1-\eta)^4}. \tag{2.86}$$

In Fig. 2.5 the $c(r)$ obtained from the PY approximation is shown and compared with (essentially) the exact function (see Henderson and Grundke's paper on the web page of the course). We can see how smooth the direct correlation function is. The PY approximation is overall quite accurate. The exact function leads to small corrections in the 'core' (i.e. $r < \sigma$) with respect to PY's result and a small-amplitude oscillatory 'tail' for $r > \sigma$. The $g(r)$ obtained from the PY direct correlation function is reasonable accurate.

- *General Percus-Yevick approximation.* This theory assumes the closure relation

$$c(r) = g(r)y(r), \quad y(r) \equiv g(r)e^{\beta\phi(r)}, \tag{2.87}$$

which is valid for any pair potential $\phi(r)$ [not just hard spheres].

- *Hypernetted-chain approximation* (HNC). The closure relation is now

$$c(r) = h(r) - \log g(r) - \beta\phi(r). \tag{2.88}$$

- There are many other closure relations that we do not mention here.

In all the approximations either $c(r)$ or $h(r)$ is obtained. Then, use of the OZ equation allows calculation of the other function. But we can see that, if the 'simple' function $c(r)$ is known, use of the OZ equation will give an oscillatory (i.e. 'complicated') function $h(r)$; for example, the discontinuity of $c(r)$ (as given, e.g. by the PY approximation) will produce, in Fourier space, a highly oscillatory function $\hat{\phi}(q)$, which will give an oscillatory structure factor $S(q)$ via Eqn. (2.80) and then, on Fourier-transforming back to real space, an oscillatory function $h(r)$.

Critical opalescence

Density fluctuations in liquids at normal conditions of density and temperature occur at length scales of the order of a few Ångström. Scattering experiments have to be performed with probes of corresponding wavelengths, i.e. X rays or fast neutrons. There is a phenomenon that occurs at visible wavelenghts, i.e. ~ 5000 Å, called critical opalescence, discovered in 1869 by Andrews, whereby the liquid becomes very turbid due to strong scattering of visible light when close to the critical point (ρ_c, T_c). This is because density fluctuations occur at wavevectors $k \sim 2\pi/5000 \sim 10^{-3}$ Å^{-1} in these conditions.

Much more will be said about the critical point later. For the moment, we describe a theory that was put forward in 1914 by Orstein and Zernike to account for density flutuations near the critical point. First the phenomenology of the structure factor. Scattering experiments show that the behaviour of $S(q)$ close to the critical point is very unusual: it begins to exhibit a high peak at very small q, with the rest of the function
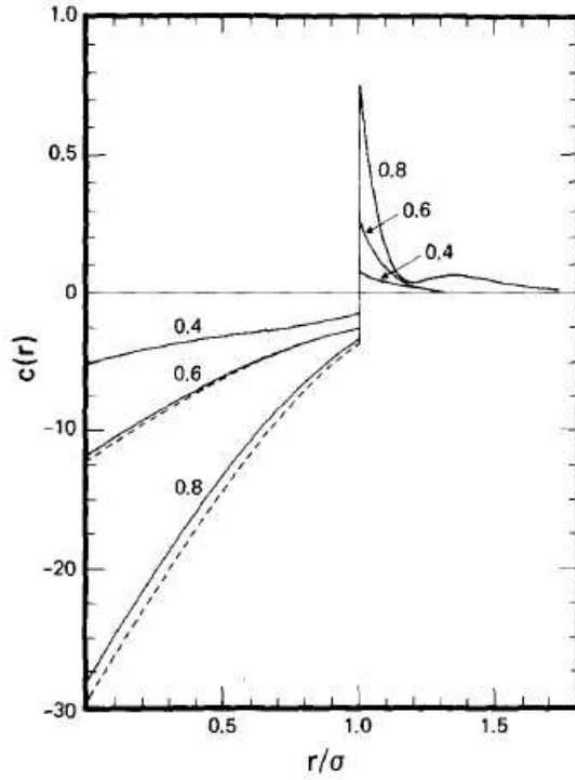
Figure 2.5: Direct correlation function for hard spheres. Densities in units of the hard-sphere diameter are shown as labels. Continuous lines: exact results. Dashed lines: PY result. Note the different negative and positive scales.

being more or less unchanged. To understand its origin, we examine the low-q behaviour of the correlation functions. First, since $S(0) = \kappa_T / \kappa_T^0$ and $\kappa_T \to \infty$ at the critical point, we have $S(0) \to \infty$. Now, from $S(q) = 1 + \rho h(q)$, we get $\hat{h}(0) \to \infty$ also. And from (2.80), $\rho\hat{c}(0) \to 1$. So that $c(q)$ is the only correlation function that does not diverge at $q = 0$ as the critical point is approached, and this is another of its advantages (and in fact the reason why it was introduced by Orstein and Zernike in the first place). This property of $\hat{c}(q)$ allows us to write a power series:

$$\hat{c}(q) = \hat{c}(0) + c_1 q^2 + \cdots \tag{2.89}$$

Only even powers in q are allowed. This can be seen explicitly:

$$\hat{c}(q) = 4\pi \int_0^\infty dr\, r^2 \frac{\sin qr}{qr} c(r) = 4\pi \int_0^\infty dr\, r^2 \left(1 - \frac{(qr)^2}{3!} + \cdots\right) c(r), \tag{2.90}$$

so that odd powers in q are absent (this is a consequence of the isotropy of the fluid). We also have

$$c_1 = -\frac{2\pi}{3} \int_0^\infty dr\, r^4 c(r), \tag{2.91}$$

which is expected to be negative since the tail of $c(r)$ is positive for attractive interactions (remember that $c(r) \to -\beta\phi(r)$ for large r and it is this region which contributes most to

the integral). Then

$$S(q) = \frac{1}{1 - \rho\hat{c}(q)} = \frac{1}{1 - \rho\hat{c}(0) - c_1\rho q^2} = \frac{S(0)}{1 + \xi^2 q^2}, \quad \xi^2 = -\rho c_1 S(0) \sim \kappa_T. \quad (2.92)$$

ξ is the *correlation length*. The Fourier transform of the correlation function is a Lorentzian of width ξ. The correlation length is a measure of the range of the correlation in the system, and it is tied to the structure factor at $q = 0$ and hence to the compressibility, $\xi \sim \kappa_T^{1/2}$. The above expression for $S(q)$, valid for small q, explains the experimental behaviour of $S(q)$ close to q, but also when $T \to T_c$: since then κ_T and ξ grows without limit, $S(q) \sim q^{-2}$ as $q \to 0$.

Close to the critical point $\xi \to \infty$, which means that correlations appear everywhere in the system and fluctuations occur at all length scales. From (2.92) it is possible to obtain the general large-r behaviour of $h(r) = g(r)1$ by Fourier transforming back to real space:

$$h(r) = \frac{S(0)}{\rho(2\pi)^3} \int d\mathbf{q} \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{1 + \xi^2 q^2} \sim \frac{e^{-r/\xi}}{r}. \quad (2.93)$$

Therefore, very close to the critical point, $h(r) \sim 1/r$, so that $h(r)$ becomes long-ranged (and the integral in the compressibility equation diverges, as it should be). One recent verification of critical fluctuations with both direct visualisation by atomic-force microscopy (AFM) and structure-factor measurements was made by Nielsen et al., Nature **404**, 352 (2000), on monolayers of phospholipids adsorbed on mica surfaces. These molecules undergo a two-dimensional phase transition involving collective excitation of chain defects; islands of the two phases (with ordered and disordered chains) form close to the critical point and fluctuations of these can be seen by AFM. The structure factor is seen to increase as $\sim q^{-2}$ for low q. See the paper for more details.

Perturbation theory

Pertubation theory is a helpful tool in many branches of theoretical physics, and also in the statistical mechanics of classical liquids. Assume our potential energy function can be split in two terms, U_0 and U_1:

$$U(\{\mathbf{r}_i\}; \lambda) = U_0(\{\mathbf{r}_i\}) + \lambda U_1(\{\mathbf{r}_i\}). \quad (2.94)$$

U_0 is a potential energy function whose statistical mechanics we can solve (or have good approximations for). U_1 is a perturbation. λ is a coupling parameter such that when $\lambda = 1$ then U is the potential we would like to investigate. The partition function is

$$Q(\lambda) = \frac{Z_N(\lambda)}{N!\Lambda^{3N}} = \frac{1}{N!\Lambda^{3N}} \text{Tr}_c \left\{ e^{-\beta U(\lambda)} \right\}, \quad \text{Tr}_c \equiv \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N. \quad (2.95)$$

Tr_c is the configurational trace. Now we differentiate $F = -kT \log Q$ with respect to λ:

$$\frac{\partial F}{\partial \lambda} = -\frac{kT}{Q}\frac{\partial Q}{\partial \lambda} = \frac{\text{Tr}_c \left\{ \dfrac{\partial U(\lambda)}{\partial \lambda} e^{-\beta U(\lambda)} \right\}}{\text{Tr}_c \left\{ e^{-\beta U(\lambda)} \right\}} = \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_\lambda = \langle U_1 \rangle_\lambda. \quad (2.96)$$

We now integrate in λ from 0, corresponding to the reference system (with known free energy F_0) to 1 (corresponding to the target system, with free energy F):

$$\int_0^1 d\lambda \frac{\partial F}{\partial \lambda} = \int_0^1 d\lambda \langle U_1 \rangle_\lambda \quad \rightarrow \quad F = F_0 + \int_0^1 d\lambda \langle U_1 \rangle_\lambda . \tag{2.97}$$

But $\langle U_1 \rangle_\lambda$ can be written in terms of the two-particle distribution function $\rho_N^{(2)}(\lambda)$ of a system with potential energy $U(\lambda)$:

$$\langle U_1 \rangle_\lambda = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \phi_1(|\mathbf{r} - \mathbf{r}'|) \rho_N^{(2)}(\mathbf{r}, \mathbf{r}'; \lambda), \tag{2.98}$$

so that the free energy can be written as

$$F = F_0 + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \phi_1(|\mathbf{r} - \mathbf{r}'|) \tilde{\rho}_N^{(2)}(\mathbf{r}, \mathbf{r}'), \quad \tilde{\rho}_N^{(2)}(\mathbf{r}, \mathbf{r}') \equiv \int_0^1 d\lambda \rho_N^{(2)}(\mathbf{r}, \mathbf{r}'; \lambda). \tag{2.99}$$

This equation says that the free energy of the full system has to be augmented by a term that contains the perturbation pair potential ϕ_1 weighted by the correlations of systems with the whole continuum of potentials between U_0 and U_1; here the implicit assumption is made that U_1 can be written using a pair potential:

$$U_1(\{\mathbf{r}_k\}) = \sum_i \sum_{j>i} \phi_1(|\mathbf{r}_i - \mathbf{r}_j|). \tag{2.100}$$

Up to now this is exact. But, since the whole family of functions $\rho_N^{(2)}(\lambda)$ is not known, some approximation is required. But we are supposed to know F_0 and $\rho_N^{(2)}(\lambda = 0)$ (i.e. the thermodynamics and structure) of the reference system. The simplest approximation then is to take

$$\tilde{\rho}_N^{(2)}(\mathbf{r}, \mathbf{r}') \simeq \rho_N^{(2)}(\mathbf{r}, \mathbf{r}'; \lambda = 0) \tag{2.101}$$

which, for a homogeneous fluid, gives

$$F = F_0 + \frac{\rho N}{2} \int d\mathbf{r} \phi_1(r) g_0(r). \tag{2.102}$$

This is the so-called *first-order perturbation theory*.

As a typical application of first-order perturbation theory, we consider the square-well potential. We need F_0, the free-energy of the hardsphere system, and $g_0(r)$, the radial distribution function of the hard-sphere system. These in turn can be obtained from many different approximations. One typical choice is to take one of the PY expressions for the thermodynamics (e.g. the one coming from the compressibility route) and the PY result for the radial distribution function. A more sophisticated expression for the thermodynamics is the Carnahan-Starling approximation, which is a quasi-exact but phenomenological (i.e. not having a completely theoretical foundation) expression[2]

$$\frac{\beta F_{\text{exc}}}{N} = \frac{(4 - 3\eta)\eta}{(1 - \eta)^2}. \tag{2.103}$$

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[2]The Carnahan-Staling expression for the pressure is obtained by assuming a simple law for the virial coefficients of the virial expansion in η:

$$\frac{\beta p}{\rho} = 1 + 4\eta + 10\eta^2 + 18.365\eta^3 + 28.24\eta^4 + 39.5\eta^5 + 56.5\eta^6 + \cdots$$

For $g_0(r)$ it is quite usual, when only a rough estimate of the system's behaviour is needed, to approximate $g_0(r) \simeq \Theta(\sigma - r)$, where $\Theta(x)$ is the step function (i.e. $\Theta(x) = 1$ for $x > 0$ and $\Theta(x) = 0$ for $x < 0$). This approximation is in fact equivalent to taking the low-density limit of $g_0(r)$:

$$g_0(r) = e^{-\beta\phi_{\mathrm{HS}}(r)} - 1 = \Theta(\sigma - r). \tag{2.104}$$

We then have

$$\begin{aligned}
\frac{\beta F}{N} &= \log\left(\rho\Lambda^3\right) - 1 + \frac{(4 - 3\eta)\eta}{(1 - \eta)^2} + 2\pi\beta\rho \int_0^\infty dr\, r^2 \phi_1(r) g_0(r) \\
&= \log\left(\rho\Lambda^3\right) - 1 + \frac{(4 - 3\eta)\eta}{(1 - \eta)^2} - 2\pi\rho\beta\epsilon \int_\sigma^{\sigma+\delta} dr\, r^2. \tag{2.105}
\end{aligned}$$

Integrating:

$$\frac{\beta F}{N} = \log\left(\rho\Lambda^3\right) - 1 + \frac{(4 - 3\eta)\eta}{(1 - \eta)^2} - \frac{2\pi}{3}\rho\sigma^3\beta\epsilon\lambda, \tag{2.106}$$

where λ was defined in Eqn. (2.32). The pressure is obtained as

$$p = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = -\left(\frac{\partial (fV)}{\partial V}\right)_{N,T} = -V\left(\frac{\partial f}{\partial V}\right)_{N,T} - f = \rho\left(\frac{\partial f}{\partial \rho}\right)_T - f, \tag{2.107}$$

with $f = F/V$ the free-energy density. We have:

$$\frac{\beta p}{\rho} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \frac{4\pi}{3}\rho\sigma^3\beta\epsilon\lambda. \tag{2.108}$$

Incidentally, this has the same form as the van der Waals equation of state, obtained using the second-virial approximation in Eqn. (2.33), except for the hard-sphere term where Clausius' approximation is replaced by the more sophisticated Carnahan-Starling expression. Thus, perturbation theory also leads to a simple explanation of the liquid-vapour phase transition, providing at the same time a different route to the van der Waals equation of state.

2.5   Computer simulation of fluids

In this method one uses the computer to generate configurations of the system that have a significant statistical weight (in the sense that the Boltzmann factor is large). Two methods are available, each of which corresponds to a way to perform averages in statistical physics.

The law is $B_{n+1} = n^2 + 3n$, which gives the virial coefficients $B_2 = 4$, $B_3 = 10$, $B_4 = 18$, $B_5 = 28$, $B_6 = 40$, $B_7 = 54$, ... The first two are exact, while the rest are quite close to the actual values. The resulting expansion can be summed to give

$$\frac{\beta p}{\rho} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad \rightarrow \quad \frac{\beta F_{\mathrm{exc}}}{N} = \frac{(4 - 3\eta)\eta}{(1 - \eta)^2},$$

where F_{exc} is the excess (over the ideal) free energy.

- **Molecular Dynamics** (MD): here one solves Newton's equations of motion for all the particles in the fluid. Knowledge of the forces is required, and a discrete difference method is used to extrapolate in time the microstate of the system (positions and momenta of all particles). Since the dynamics of many-body systems in chaotic, trajectories in phase space cannot be obtained accurately, so that simple numerical schemes that respect basic properties of the dynamics (e.g. time-reversibility, simplecticity or conservation of phase-space volume) are used, typically a second order Euler scheme (which is called *Verlet algorithm* in this field). Thermodynamic and other quantities are obtained by time averaging of the corresponding quantity along the trajectory. This method is in the spirit of Boltzmann's view of statistical mechanics. Only limited evolution times are accessible (due to the difficulties associated with calculation of forces and implementation of the algorithm) so one is limited to equilibrium properties with sufficiently fast relaxation times or to dynamical properties that occur in time scales within the simulation time.

- **Monte Carlo** (MC): here one generates configurations of the system by random sampling. Averages are taken over the configurations (which are necessarily finite in number), each weighted by the corresponding normalised Boltzmann factor. Uniform sampling of the configurations is impractical, since the Boltzmann factor is negligible but for a few typical configurations of the system (this is a basic fact of statistical physics!), so the so-called *importance sampling* is used, where configurations are sampled according to the value of the Boltzmann factor; in this way only 'important' configurations are generated and contribute to the average. A number of methods exist to implement importance sampling, but the most popular is the *Metropolis algorithm*, which is asymptotic but enjoys the advantageous feature that knowledge of the normalisation of the Boltzmann factor (the partition function) is not needed.

In general computer simulation methods are very useful both to interpret experimental results and to check theoretical approximations. They lie at one of the vertices of an imaginary triangle representing available tools to study fluids and matter in general. That is why computer simulation is so widely used in all fields of condensed-matter physics.

The Monte Carlo method was devised in a seminal paper by Metropolis et al., working in collaboration with the Rosenbluth and the Teller (in fact the creator of the method was Marshall Rosenbluth, but the algorithm was later named 'Metropolis algorithm' because it was Nicholas Metropolis who named it). They were all working at the Los Alamos laboratory when, after the war, Metropolis was introducing computers in scientific applications. The method was initially applied to hard discs and spheres, using very few particles due to the technical limitations of the computers. The growth in computer power that followed allowed for the successful application of computer simulation methods to condensed matter physics and to other areas in science.

We will discuss an implementation of the Monte Carlo method when we have a look at the Ising model in two dimensions. Otherwise the techniques of computer simulation in statistical physics are too specialised to be reviewed in this course.