

CHAPTER 1

STATIC STRUCTURE AND THERMODYNAMICS

The most basic characteristic of a liquid is that it possesses short-range order, as opposed to the long-range periodicity of a crystalline solid. Since the structure of a crystal is determined experimentally by observing the Bragg reflections of X-rays, it is natural to seek a quantitative description of the liquid structure via the intensity I of X-rays scattered through an angle 2θ say, from the liquid. If we introduce the usual variable $k = 4\pi \sin \theta / \lambda$, λ being the X-ray wavelength, then the liquid structure factor $S(k)$ is defined by

$$S(k) = I/Nf^2 \quad (1.1)$$

where N is the total number of atoms in the liquid, assumed monatomic. In eqn (1.1), $f(k)$ is the atomic scattering factor, i.e. the Fourier transform of the electron density in the atom. $f(k)$ falls from a value Z , the atomic number, at $k=0$ to zero at large k , the asymptotic behaviour being proportional to k^{-4} .

1.1 Definition of radial distribution function $g(r)$ and structure factor $S(k)$

To gain insight into the relation between the liquid structure factor $S(k)$ in (1.1) and the atomic arrangement, one now uses the Debye theory of the diffraction of X-rays by a liquid (see for example Gingrich, 1943 or March, 1968 for a detailed discussion), which yields

$$I = Nf^2 \left[1 + \sum'_n \frac{\sin kR_{nm}}{kR_{nm}} \right] \quad (1.2)$$

Here the R_{nm} denote the interatomic distances in the fluid, while the prime denotes the exclusion of the term $R_{nm}=0$ from the summation. Clearly, eqn (1.2) is revealing an interference pattern between scattered X-rays from pairs of atoms. Therefore, it is helpful to introduce the pair distribution function $g(r)$, which, following Zernike and Prins (1927), is defined by setting $\rho g(r)4\pi r^2 dr$ equal to the total number of atoms in a spherical shell of radius r and thickness dr centred on a chosen atom at the origin of coordinates. Here, $\rho = N/V$ is the average number density of N atoms in volume V .

Replacing the summation in eqn (1.2) by an integration, and omitting the

X-ray scattering from a uniform density of electrons (merely a delta function at $k=0$ in the limit of an infinite liquid sample), we find from eqns (1.1) and (1.2) that

$$S(k) = 1 + \rho \int_0^\infty 4\pi r^2 [g(r) - 1] \frac{\sin kr}{kr} dr \quad (1.3)$$

Hence, the liquid structure factor is related by Fourier transform to the atomic arrangement around a given atom at the origin. By noting that $\sin kr/kr$ is the s wave ($l=0$ term) in the expansion of the plane wave $\exp(ik \cdot r)$ in spherical waves, $S(k)$ in (1.3) can be rewritten as

$$S(k) = 1 + \rho \int [g(r) - 1] \exp(ik \cdot r) dr \quad (1.4)$$

In a crystalline solid, $g(r)$ in (1.4) would not be isotropic but would be a sum of delta functions (neglecting atomic vibrations) centred on the crystal lattice sites. Evidently, eqn (1.4) would lead then to non-zero $S(k)$ only when k was a reciprocal lattice vector. These Bragg reflections can be thought of, roughly, as blurred out and spherically averaged in the liquid, leading to a continuous function $S(k)$ reflecting directly the short-range order via $g(r)$.

We could view eqns (1.3) or (1.4) as the forms from which X-ray intensity could be predicted from a calculated pair distribution function $g(r)$. But a more fruitful approach to date has been to invert the Fourier transform and hence to derive $g(r)$ from the measured $S(k)$ via

$$\begin{aligned} g(r) &= 1 + \frac{1}{8\pi^3 \rho} \int [S(k) - 1] \exp(-ik \cdot r) dk \\ &= 1 + \frac{1}{2\pi^2 \rho r} \int_0^\infty [S(k) - 1] k \sin kr dk \end{aligned} \quad (1.5)$$

Of course, the determination of $g(r)$ from the measured $S(k)$ is subject to some problems and the kind of errors which can arise have been discussed by Paalman and Pings (1963).

The static structure factor $S(k)$ for liquid thallium near its freezing point, as determined by neutron scattering (see Enderby and March, 1966), is recorded in figure 1.1, while figure 2.10 (page 33) shows the radial distribution function $g(r)$ in a Lennard-Jones fluid simulating liquid argon, as determined by computer simulation† by Verlet (1968).

It is important to stress here that a great deal of the theory of liquids is centred round the pair distribution function $g(r)$, and its dynamic generalisation given in chapter 3. Therefore, we turn immediately to discuss how some important thermodynamic properties are related to $g(r)$.

†For a short discussion, see chapter 2.

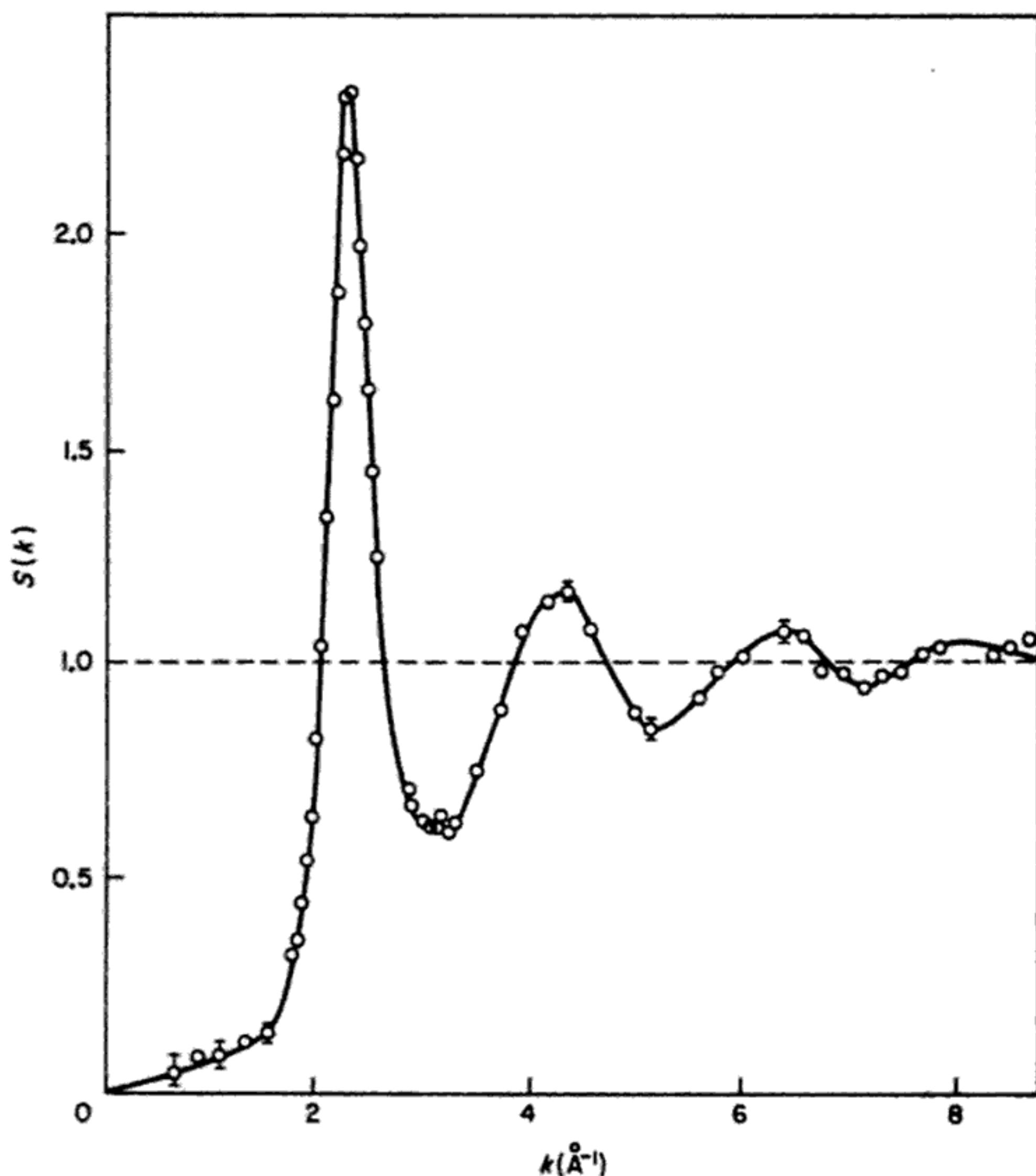


Figure 1.1 Static structure factor $S(k)$ for liquid thallium at 600 K, as determined by neutron scattering (see Enderby and March, 1966)

1.2 Internal energy and equation of state with pair forces

In this section expressions will be derived for the internal energy E and the equation of state. The assumption will be made that the intermolecular potential energy Φ can be decomposed into a sum of pair potentials

$$\Phi(R_1 \dots R_N) = \sum_{i < j} \phi(R_{ij}) \quad (1.6)$$

The objectives will be to obtain E and the pressure p in terms of the pair distribution function $g(r)$ and the potential $\phi(r)$.

In a classical monatomic liquid at temperature T , the kinetic energy per degree of freedom is $\frac{1}{2}k_B T$ and hence

$$E = \frac{3}{2}Nk_B T + \langle \Phi \rangle \quad (1.7)$$

The mean potential energy $\langle \Phi \rangle$ is simply

$$\langle \Phi \rangle = Z^{-1} \int \cdots \int \exp(-\Phi/k_B T) \Phi dR_1 \cdots dR_N \quad (1.8)$$

where Z is the partition function. From the assumption (1.6) of pair forces, the sum consists of $N(N-1)/2$ terms, all of which make equal contributions to $\langle \Phi \rangle$. Hence we find

$$\langle \Phi \rangle = \frac{N(N-1)}{2} \iint \phi(R_{12}) \left[\frac{\int \cdots \int \exp(-\Phi/k_B T) dR_3 \cdots dR_N}{Z} \right] dR_1 dR_2 \quad (1.9)$$

But from the definition of the distribution functions (see also equation (2.3) of section 2.1) we can introduce the radial distribution function and write

$$\begin{aligned} \langle \Phi \rangle &= \frac{N(N-1)}{2} \iint \phi(R_{12}) \frac{(N-2)!}{N!} \rho^2 g(R_{12}) dR_1 dR_2 \\ &= \frac{1}{2} \rho^2 V \int_0^\infty \phi(r) g(r) 4\pi r^2 dr \end{aligned} \quad (1.10)$$

one of the integrations yielding immediately the volume V of the fluid. Hence we have finally (cf. H. S. Green, 1952)

$$E = \frac{3}{2} N k_B T + \frac{N \rho}{2} \int_0^\infty \phi(r) g(r) 4\pi r^2 dr \quad (1.11)$$

The potential energy term exhibited in this equation for the internal energy could have been written down directly on physical grounds, since the number of molecules on average within a distance between r and $r+dr$ of a given molecule is $\rho g(r) 4\pi r^2 dr$ and the factor $\frac{1}{2}$ avoids counting interactions twice over.

Similarly, the equation of state can be obtained. To do so, we make use of the classical virial theorem, which relates the average of the kinetic energy, \bar{K} say, to the virial of the forces. The virial of the pressure p is $3pV$, yielding, for a perfect gas

$$2\bar{K} = 3pV \quad (1.12)$$

When there is a force F_i acting on the i th molecule at R_i , the average of $-\sum R_i \cdot F_i$ has to be calculated, the summation extending over all the molecules. For central pair forces, this becomes again the average of $N(N-1)/2$ terms, one term being

$$\int R_{12} \frac{\partial \phi(R_{12})}{\partial R_{12}} \left[\int \frac{\exp(-\Phi/k_B T)}{Z} dR_3 \cdots dR_N \right] dR_1 dR_2 \quad (1.13)$$

Expressing this once more in terms of the radial distribution function yields, since $\bar{K} = \frac{3}{2} N k_B T$, as used in the calculation of E ,

$$3pV = 3Nk_B T - \frac{N(N-1)}{2} \int R_{12} \frac{\partial \phi(R_{12})}{\partial R_{12}} \frac{(N-2)!}{N!} \rho^2 g(R_{12}) dR_1 dR_2 \quad (1.14)$$

or

$$p = \rho k_B T - \frac{\rho^2}{6} \int r \frac{\partial \phi}{\partial r} g(r) dr \quad (1.15)$$

In principle then, from an assumed law of force and knowledge of the corresponding radial distribution function, the internal energy E and the fluid pressure p can be estimated from eqns (1.11) and (1.15).

It is important to note at this point that while equation (1.15) requires knowledge of both $g(r)$ and $\phi(r)$, there is another route to the equation of state of a fluid, which is more fundamental in that it does not require the assumption (1.6) of pair potentials. However, to derive this further relation we must go from the canonical ensemble used above to the grand canonical ensemble.

1.3 Relation of liquid structure factor at $k=0$ to compressibility

Let us consider an open region, i.e. one in which particles can come and go freely, drawn in a system of infinite extent. We shall now show that the fluctuation in the number of particles in this region is given by the volume integral of $g(r)-1$, which is specifically the isothermal compressibility of the liquid. Another interesting example of such a relation between fluctuations and thermodynamic quantities yields the specific heat c_v , which is discussed in appendix 2.1.

One reason for the interest in the above relation between the volume integral of the radial distribution function, or equivalently, from eqn (1.3), the long wavelength limit of $S(k)$, and the compressibility (first derived by Ornstein and Zernike, 1914), is because of the difficulty of extending the diffraction experiments, referred to in section 1.1, to small scattering angles.

Consider a member of the grand canonical ensemble in which the open region, of volume V , contains exactly N particles. For a specified configuration of the particles, R , say, the singlet density $\rho(\mathbf{r}_1)$ at point \mathbf{r}_1 in this region, and the density $\rho^{(2)}(\mathbf{r}_1 \mathbf{r}_2)$ of pairs of particles at points \mathbf{r}_1 and \mathbf{r}_2 are respectively given by

$$\rho(\mathbf{r}_1) = \sum_{i=1}^N \delta(\mathbf{R}_i - \mathbf{r}_1) \quad (1.16)$$

and

$$\rho^{(2)}(\mathbf{r}_1 \mathbf{r}_2) = \sum_{i \neq j=1}^N \delta(\mathbf{R}_i - \mathbf{r}_1) \delta(\mathbf{R}_j - \mathbf{r}_2) \quad (1.17)$$

It follows immediately from these definitions that

$$\int_V d\mathbf{r}_1 \rho(\mathbf{r}_1) = N \quad (1.18)$$

$$\int_V \int_V d\mathbf{r}_1 d\mathbf{r}_2 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = N^2 - N \quad (1.19)$$

The distribution functions for single particles and for pairs of particles are obtained by averaging the respective densities over phase space and over all numbers N of particles with the probability distribution of the grand canonical ensemble,

$$w_{GC} = \exp [(\Omega + N\mu - H_N)/k_B T] \quad (1.20)$$

where $\Omega = -pV$, μ is the chemical potential, and H_N is the Hamiltonian of the set of N particles. In a fluid the averaged densities have the form $\langle \rho(\mathbf{r}_1) \rangle = \langle N \rangle / V = \rho$ and $\langle \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle = \rho^2 g(r_{12})$, where ρ is the bulk number density of the fluid and $g(r_{12})$ is the radial distribution function, dependent only on the scalar distance r_{12} . By taking the average of eqn (1.19) it therefore follows that

$$\lim_{k \rightarrow 0} S(k) \equiv 1 + \rho \int dV [g(r_{12}) - 1] = \frac{\langle N^2 \rangle - \langle \langle N \rangle \rangle^2}{\langle N \rangle} \quad (1.21)$$

which is the desired relation between the structure factor at long wavelengths and the particle number fluctuations.

Next, we recall from fluctuation theory that the particle number fluctuations are related to thermodynamic properties of the system. The grand partition function is

$$\exp(-\Omega/k_B T) = \sum_{N=0}^{\infty} \exp[N\mu - F(N, T, V)]/k_B T \quad (1.22)$$

where $F(N, T, V)$ is the Helmholtz free energy of a member of the grand ensemble containing N particles. By differentiating Ω and the average number of particles,

$$\langle N \rangle = \sum_{N=0}^{\infty} N \exp[\Omega + N\mu - F(N, T, V)]/k_B T \quad (1.23)$$

with respect to the chemical potential we find

$$\left(\frac{\partial \Omega}{\partial \mu} \right)_{T, V} = -\langle N \rangle \quad (1.24)$$

and

$$\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = \frac{1}{k_B T} \left[\langle N \rangle \left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} + \langle N^2 \rangle \right] \quad (1.25)$$

whence it follows that

$$\langle N^2 \rangle - (\langle N \rangle)^2 = k_B T \left(\frac{\partial N}{\partial \mu}\right)_{T,V} \quad (1.26)$$

Finally, by using the thermodynamic identity

$$\left(\frac{\partial \mu}{\partial N}\right)_{T,V} = -\frac{1}{\rho^2} \left(\frac{\partial p}{\partial V}\right)_{T,N} \equiv \frac{1}{\rho^2 V K_T}$$

where K_T is the isothermal compressibility, we arrive at the Ornstein-Zernike relation,

$$\lim_{k \rightarrow 0} S(k) = \rho k_B T K_T \quad (1.27)$$

As we shall see in section 4.3.2, the above relation admits a dynamic interpretation, in that it is a consequence of the fact that the long wavelength excitations of the fluid are sound waves. In this connection we should then stress that, in the case of a fluid of charged particles, the fluctuations in the particle number must be such as to preserve the electrical neutrality of the open region. Charge separation involves the excitation of the plasmon mode, which contributes to the k^2 term in the expansion of $S(k)$ at small k (see section 7.1.2).

In summary, the tools for describing the short-range order in a monatomic liquid, $S(k)$ and $g(r)$ have been introduced. These, plus the pair potential $\phi(r)$, have been shown to be closely related to the thermodynamic properties of the liquids and, in particular, formulae have been derived for the internal energy, pressure and compressibility. Of course, a first principles approach to the theory of the liquid state should ideally allow all physical properties to be calculated from an assumed force law. The next chapter is concerned with this problem.

CHAPTER 2

CALCULATION OF LIQUID STRUCTURE FROM A LAW OF FORCE

The radial distribution function $g(r)$, by itself, gives a valuable but nevertheless limited picture of liquid structure, even for a monatomic fluid. Finer details of the structure of such a one-component fluid are contained in higher order correlation functions. These describe the relative distribution in space of groups of three or more atoms.

Though such a description would work in principle for a molecular fluid such as N_2 or Br_2 , it is often useful in such a case to include the molecular unit, from the outset, in the structural distribution functions. Thus, in such cases the structure could be expressed not only by giving the relative distributions of the centres of mass for groups of two or more molecules, but also distribution functions describing the relative orientations of the molecules in space. However, such a description would get into some difficulty if we could heat the fluid sufficiently for an appreciable fraction of the molecules to be dissociated, whereas the original (though more cumbersome) description of the monatomic fluid by multi-particle correlation functions will always work for liquids with only one type of atom.

As we shall see in detail later, the structure of a liquid mixture has to be expressed in terms of partial distribution functions for the various types of atomic or molecular constituents.

In this chapter the multi-particle correlation functions for a monatomic classical liquid will be introduced and their relation to its radial distribution function discussed. Two essential points then emerge. First, a theoretical determination of the radial distribution function itself from an assumed pair force law requires detailed knowledge of the three-particle, or triplet, correlation function $g^{(3)}$. Indeed, as discussed below, the various theories of liquid structure can be classified according to the approximations they make to relate $g^{(3)}$ and g . Secondly, measurements of the structure factor, when the fluid is subject to an external perturbation, such as high pressure, allow experimental information to be obtained on some properties of the triplet function.

Before defining three-particle and higher order correlation functions, which will permit a first principles calculation of the liquid structure from a force law,

we want to emphasise that there is an experimental route by which the structure can be obtained from the forces. This is the method of 'computer simulation', which has had a major impact on our understanding of the liquid state. Since it is not the object in this book to discuss details of experiments, we shall confine ourselves to the role of computer simulation in throwing light on the validity of the approximate theories of liquid structure discussed below. We stress that the merit of the experimental data supplied by computer simulation for the structure, is that we are given precisely that structure which comes from a pair force law. In real liquids, of course, additional questions as to the role of many-body forces arise and prevent a completely clear-cut comparison with structural theories. In the more powerful of the two methods available for computer simulation, that of molecular dynamics, one simply tells the computer to solve Newton's equation of motion for a system of particles in a box, interacting via a given pair force law. To avoid surface effects and give equal weight to all particles, it is customary to impose periodic boundary conditions. As a starting point of the calculation one can, for example, place the particles on a face-centred cubic lattice and give them random displacements (for details see Croxton, 1974 or Schofield, 1973). While this method is essential for dynamical properties (e.g. calculating the diffusion constant), Monte Carlo methods suffice for a determination of the liquid structure from a force law. We shall confront, below, the assumptions underlying the approximate theories of structure with the predictions of such computer experiments.

2.1 Multi-particle correlation functions

The procedure followed in section 1.3 in defining the singlet and the pair distribution function in the grand canonical ensemble may be generalised without difficulty to distribution functions for sets of s particles. We consider again a member of the grand ensemble in which an open region of volume V contains N particles, and write the density $\rho^{(s)}(\mathbf{r}_1, \dots, \mathbf{r}_s)$ of groups of s particles at points $\mathbf{r}_1, \dots, \mathbf{r}_s$, for a given configuration $\mathbf{R}_1, \dots, \mathbf{R}_N$ of the N particles, as

$$\rho^{(s)}(\mathbf{r}_1, \dots, \mathbf{r}_s) = \sum'_{i_1, \dots, i_s=1}^N \delta(\mathbf{R}_{i_1} - \mathbf{r}_1) \cdots \delta(\mathbf{R}_{i_s} - \mathbf{r}_s) \quad (2.1)$$

where the primed sum is restricted to the case where the indices i_1, \dots, i_s are all different. The corresponding distribution function is obtained by averaging the density (2.1) with the probability distribution of the grand canonical ensemble, given in eqn (1.20).

Let us carry out the average explicitly for the pair function, in order to see the structure of the general result. For a classical liquid we can carry out the integration over momentum space independently of the integration over the coordinates, when we have

$$\begin{aligned}
 \langle \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle &\equiv \rho^2 g(r_{12}) \\
 &= \sum_{N=2}^{\infty} \frac{\exp [(\Omega + N\mu)/k_B T]}{(2\pi\hbar)^{3N} N!} \int \cdots \int d\mathbf{p}_1 \dots d\mathbf{p}_N d\mathbf{R}_1 \cdots d\mathbf{R}_N \\
 &\quad \times \exp (-H_N/k_B T) \sum_{i \neq j=1}^N \delta(\mathbf{R}_i - \mathbf{r}_1) \delta(\mathbf{R}_j - \mathbf{r}_2) \\
 &= \sum_{N=2}^{\infty} \frac{\exp [(\Omega + N\mu)/k_B T]}{N!} \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3N/2} \int \cdots \int d\mathbf{R}_1 \cdots d\mathbf{R}_N \\
 &\quad \times \exp (-\Phi_N/k_B T) \sum_{i \neq j=1}^N \delta(\mathbf{R}_i - \mathbf{r}_1) \delta(\mathbf{R}_j - \mathbf{r}_2) \tag{2.2}
 \end{aligned}$$

Since the particles are identical we can choose two particular values for the indices i and j ($i=1$ and $j=2$, say) and multiply the result by the number of ordered pairs, which is $N(N-1)$. We can therefore write

$$\rho^2 g(r_{12}) = \frac{1}{\Xi} \sum_{N=2}^{\infty} \frac{z^N}{(N-2)!} \int \cdots \int d\mathbf{R}_3 \cdots d\mathbf{R}_N \exp [-\Phi_N(\mathbf{r}_1, \dots, \mathbf{R}_N)/k_B T] \tag{2.3}$$

In these expressions, Φ_N is the potential energy for a set of N particles, Ξ is the grand partition function,

$$\Xi \equiv \exp (-\Omega/k_B T) = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int \cdots \int d\mathbf{R}_1 \cdots d\mathbf{R}_N \exp [-\Phi_N(\mathbf{R}_1, \dots, \mathbf{R}_N)/k_B T] \tag{2.4}$$

and z is a thermodynamic property of the system,

$$z = \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \exp (\mu/k_B T) \tag{2.5}$$

known as its fugacity. This is to be determined as a function of temperature and density from the requirement that $\langle N \rangle/V$ in the thermodynamic limit ($V \rightarrow \infty$) coincides with the observed density of the fluid under the prevailing conditions of temperature and pressure.

The obvious extension of eqn (2.3) to the s -particle distribution function is

$$\begin{aligned}
 \langle \rho^{(s)}(\mathbf{r}_1, \dots, \mathbf{r}_s) \rangle &\equiv \rho^s g^{(s)}(\mathbf{r}_1, \dots, \mathbf{r}_s) \\
 &= \frac{1}{\Xi} \sum_{N=s}^{\infty} \frac{z^N}{(N-s)!} \int \cdots \int d\mathbf{R}_{s+1} \cdots d\mathbf{R}_N \\
 &\quad \exp [-\Phi_N(\mathbf{r}_1, \dots, \mathbf{R}_N)/k_B T] \tag{2.6}
 \end{aligned}$$

Of course, the properties of translational and rotational invariance of the fluid imply that $g^{(s)}$ depends explicitly on fewer variables than the s vectors $\mathbf{r}_1, \dots, \mathbf{r}_s$.

(for example, $g^{(3)}$ depends only on the lengths of two vectors and the angle between them).

Obviously we expect that if one of the s particles is taken to an infinite distance from the others, the s -particle function should reduce to the $(s-1)$ -particle function. It is useful to isolate the s -particle correlations by subtracting from $g^{(s)}$ such asymptotic behaviours, which are already contained in the distribution functions of lower order. In particular, for a pair of particles it is useful to introduce the total correlation (or 'hole') function $h(r)$ as

$$h(r) = g(r) - 1 \quad (2.7)$$

Similarly, the total correlation function for triplets is defined as

$$t(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - g(r_{12}) - g(r_{23}) - g(r_{31}) + 2 \quad (2.8)$$

Such functions describe intrinsic s -body correlations in that they vanish if any one particle of the set is taken to infinity.

2.2 Force equation and theories of structure

A relation between the radial distribution function and higher order correlations is obtained by taking the gradient of $g(r_{12})$ with respect to the position of one particle. We assume that the particles interact via a two-body, central potential, $\phi(|\mathbf{R}_1 - \mathbf{R}_2|)$, and we write the potential energy Φ_N explicitly in the form

$$\Phi_N(\mathbf{R}_1, \dots, \mathbf{R}_N) = \phi(R_{12}) + \sum_{i=3}^N \phi(R_{1i}) + (\text{terms independent of } R_1) \quad (2.9)$$

We then find from eqn (2.3)

$$\rho^2 \nabla_{\mathbf{r}_1} g(r_{12}) = -\frac{1}{k_B T \Xi} \sum_{N=2}^{\infty} \frac{z^N}{(N-2)!} \int \cdots \int d\mathbf{R}_3 \cdots d\mathbf{R}_N \exp(-\Phi_N/k_B T) \left[\nabla_{\mathbf{r}_1} \phi(r_{12}) + \sum_{i=3}^N \nabla_{\mathbf{r}_1} \phi(|\mathbf{r}_1 - \mathbf{R}_i|) \right] \quad (2.10)$$

The sum in the square bracket contributes $(N-2)$ equal terms, whose value can be determined by taking $i=3$, say. By the use of eqn (2.6) for $s=3$ we then have

$$\nabla_{\mathbf{r}_1} g(r_{12}) = -\frac{g(r_{12})}{k_B T} \nabla_{\mathbf{r}_1} \phi(r_{12}) - \frac{\rho}{k_B T} \int d\mathbf{r}_3 g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \nabla_{\mathbf{r}_1} \phi(r_{13}) \quad (2.11)$$

It is worth while to rewrite this equation by expressing $g(r_{12})$ in the form

$$g(r_{12}) = \exp[-U(r_{12})/k_B T] \quad (2.12)$$

where $U(r_{12})$ is playing the role of a 'potential of mean force' and is, of course, defined by equation (2.12). Then, eqn (2.11) immediately takes the form

$$-\nabla_{r_1} U(r_{12}) = -\nabla_{r_1} \phi(r_{12}) - \rho \int d\mathbf{r}_3 \frac{g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{g(r_{12})} \nabla_{r_1} \phi(r_{13}) \quad (2.13)$$

In this form, the physical interpretation is quite clear. The left-hand side represents the total force on particle 1 when another atom is distant r_{12} from it and on the right-hand side this is split into two parts (see also Cole, 1967):

- (1) From the direct interaction between particles 1 and 2.
- (2) From the interaction between atom 1 and a third atom at \mathbf{r}_3 , the force $\nabla_{r_1} \phi(r_{13})$ being simply weighted with the factor $g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)/g(r_{12})$ giving the probability of finding particle 3 at \mathbf{r}_3 , given that there are certainly particles at \mathbf{r}_1 and \mathbf{r}_2 .

Because of this physical interpretation we shall refer to eqn (2.13) as the 'force equation'. It provides us with a starting point for a theory of liquid structure, by which we mean a theory which allows the calculation of $g(r)$ from a given pair potential $\phi(r)$.

The presence of $g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, the three-atom correlation function, means that approximations have to be made. However, it is worth examining $g^{(3)}$ a little further in order to isolate which part is actually involved in the relation between ϕ and g . To do this, it is useful to take the scalar product of $(\mathbf{r}_2 - \mathbf{r}_1)$ with eqn (2.11). Then we find

$$\begin{aligned} -r_{12} \frac{\partial g(r_{12})}{\partial r_{12}} - \frac{r_{12}}{k_B T} g(r_{12}) \frac{\partial \phi(r_{12})}{\partial r_{12}} \\ = \frac{\rho}{k_B T} \int d\mathbf{r}_3 g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) r_{12} \cos \theta \frac{\partial \phi(r_{13})}{\partial r_{13}} \end{aligned} \quad (2.14)$$

where θ is the angle between $(\mathbf{r}_3 - \mathbf{r}_1)$ and $(\mathbf{r}_2 - \mathbf{r}_1)$. It will be convenient to simplify the notation by introducing $r_{12} = s$, $r_{13} = t$. Furthermore, $g^{(3)}$ will only depend on s , t and $\cos \theta$, for, in a homogeneous, isotropic fluid, it cannot depend on the choice of origin nor on the orientation of the triplet configuration in space. Exploiting this fact, we may write

$$\begin{aligned} g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= g^{(3)}(s, t, \cos \theta) \\ &= \sum_{l=0}^{\infty} Q_l(s, t) P_l(\cos \theta) \end{aligned} \quad (2.15)$$

where the quantities $Q_l(s, t)$, as indicated, are now independent of $\cos \theta$, after the expansion in Legendre polynomials $P_l(\cos \theta)$. If we now insert (2.15) in (2.14), then because of the presence of $\cos \theta$ ($\equiv P_1(\cos \theta)$), only the $l=1$ term in (2.15) contributes (see for example Hutchinson, 1967). This shows that much less than complete knowledge of the three-body function is required in relating structure and forces. In particular, we could add any terms with $l=0$ to $g^{(3)}$ in

(2.14) and not affect the final equation. We shall use this fact below, in discussing approximate theories. Before doing so, it is of interest in view of the presence of $g^{(3)}$ in the force equation (2.13) to discuss how far the three-particle function is accessible to experimental determination.

2.3 Pressure dependence of structure factor $S(k)$ and three-atom correlation function

We have derived the force equation in section 2.2 by differentiating $g(r)$ with respect to r at constant density and temperature. Other relations between the pair distribution function and higher order correlation functions can be found by differentiating $g(r)$ with respect to density or temperature (Schofield, 1966). These relations imply the possibility of determining experimentally some properties of higher order correlations by diffraction experiments under different thermodynamic conditions, a possibility which has been exploited for liquid argon and liquid rubidium by Egelstaff, Page and Heard (1969 and 1971) using data from diffraction experiments under pressure.

Let us then consider, in particular, the density dependence of the pair function. In the grand ensemble the dependence of $g(r)$ on density at constant temperature is only in the fugacity z , and we can write

$$\left(\frac{\partial[\rho^2 g(r)]}{\partial \rho} \right)_T = V \left(\frac{\partial[\rho^2 g(r)]}{\partial \langle N \rangle} \right)_T = V \left(\frac{\partial[\rho^2 g(r)]}{\partial z} \right)_T / \left(\frac{\partial \langle N \rangle}{\partial z} \right)_T \quad (2.16)$$

From eqn (2.3) we find

$$z \left(\frac{\partial[\rho^2 g(r)]}{\partial z} \right)_T = \Xi^{-1} \sum_{N=2}^{\infty} (N - \langle N \rangle) \frac{z^N}{(N-2)!} \int \cdots \int dR_3 \cdots dR_N \exp[-\Phi_N(r_1, \dots, R_N)/k_B T] = \langle N \rho^{(2)}(r_1, r_2) \rangle - \langle N \rangle \langle \rho^{(2)}(r_1, r_2) \rangle \quad (2.17)$$

which evidently represents the fluctuation in the product of N with the pair density. After some manipulation the expression above is easily rewritten in terms of the three-atom function defined in eqn (2.6),

$$z \left(\frac{\partial[\rho^2 g(r)]}{\partial z} \right)_T = 2\rho^2 g(r) + \rho^3 \int dR_3 [g^{(3)}(r_1, r_2, r_3) - g(r)] \quad (2.18)$$

From eqn (2.5) we also have

$$\frac{z}{V} \left(\frac{\partial \langle N \rangle}{\partial z} \right)_T = \frac{z}{V} \left(\frac{\partial N}{\partial \mu} \right)_T \left(\frac{\partial \mu}{\partial z} \right)_T = \frac{k_B T}{V} \left(\frac{\partial N}{\partial \mu} \right)_T = \rho k_B T \left(\frac{\partial \rho}{\partial p} \right)_T \quad (2.19)$$

and we arrive then at the result

$$\begin{aligned} \left(\frac{\partial[\rho^2 g(r)]}{\partial p} \right)_T &= \left(\frac{\partial[\rho^2 g(r)]}{\partial \rho} \right)_T / \left(\frac{\partial p}{\partial \rho} \right)_T \\ &= (k_B T)^{-1} \{ 2\rho g(r) + \rho^2 \int d\mathbf{r}_3 [g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - g(r)] \} \end{aligned} \quad (2.20)$$

Finally, the use of eqn (1.27) allows us to rewrite the expression above in its most transparent form,

$$k_B T \left(\frac{\partial g(r)}{\partial p} \right)_T = \int d\mathbf{r}_3 [g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - g(r)g(r_{23}) - g(r)g(r_{31}) + g(r)] \quad (2.21)$$

Thus we see that the experimental study of the pressure dependence of the pair function gives information on the three-body correlations, integrated over all values of the coordinates of the third particle. The appearance of the various pair functions in the square bracket in eqn (2.21) implies that only the behaviour of the triplet function over the configurations in which the third particle is close to the other two particles is relevant.

A brief discussion of the temperature dependence of correlation functions and of the hierarchy of relations between s -particle and $(s+1)$ -particle correlation functions is given in appendix 2.1.

2.4 Tests of primitive approximations to triplet correlation function

2.4.1 Superposition approximation

To make any further progress with the theory it is essential to relate the triplet function $g^{(3)}$ to the pair function $g(r)$. This can be done, by now, at various levels of sophistication.

Still, one of the useful approaches is to build from the so-called superposition approximation of Kirkwood (1935). By assuming, say, the measured form of $g(r)$, pair correlations can be treated exactly but $g^{(3)}$ is then built up as a product of pair terms†, namely

$$g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = g(r_{12})g(r_{23})g(r_{31}) \quad (2.22)$$

This is the basis of the Born-Green (1946) theory of structure which will be discussed in more detail later.

2.4.2 Experimental test

Our purpose at present is to confront the experiments referred to above on the pressure dependence of $S(k)$ with the predictions resulting from the superposi-

†The term superposition arises from a generalisation of the potential of mean force $U(r)$, in eqn (2.12), to describe $g^{(3)}$. The additivity of U_3 obviously leads to products of g 's.

tion approximation. Inserting (2.22) in (2.21), leads to the relation

$$k_B T \left(\frac{\partial g(r)}{\partial p} \right)_T = g(r) \int d\mathbf{r}_3 [g(r_{23}) - 1][g(r_{31}) - 1] \quad (2.23)$$

This has been tested by Egelstaff, Page and Heard (1971) using their own data on liquid rubidium near the triple point and the data of Mikolaj and Pings (1967) for liquid argon near the critical point (see figure 2.1).

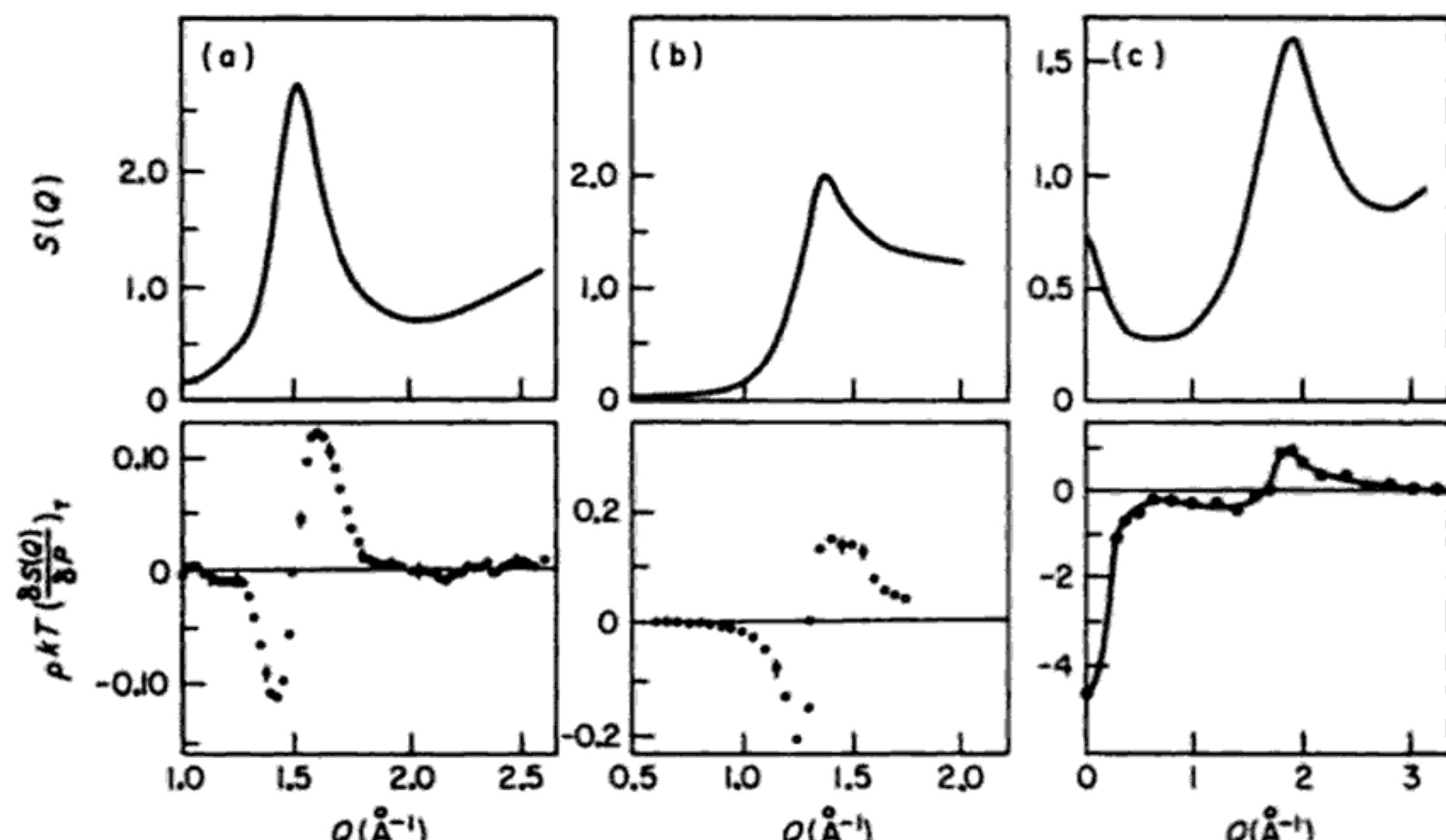


Figure 2.1 Experimental structure factors and isothermal pressure derivatives for: (a) rubidium at 333 K and 420 atm; (b) carbon tetrachloride at 296 K and 420 atm; (c) argon at 143 K and 52.5 atm (from Egelstaff, Page and Heard, 1971)

Our main interest until chapter 9 is with liquids near the triple point. Therefore, we simply comment here that for the critical point data on liquid argon (see figure 2.2) the superposition approximation is in reasonable agreement with the data except at small wave vectors where the experimental data for $(\partial S(k)/\partial p)_T$ show a large negative dip.[†] This can be interpreted as indicating that the triplet function is intrinsically longer ranged than the pair function, at the critical point.

But more important for our present purposes is the fact that the superposition approximation differs very significantly from the experimental data on liquid rubidium near the triple point (see figure 2.3). On the other hand, a modification of the Born-Green theory given in section 2.5.2, and known as the hypernetted-chain (HNC) approximation, gives very reasonable results, even though it fails to account for the shift in the main peak of the structure factor with the applica-

[†]This statement also applies to two other approximate theories, the Percus-Yevick and hypernetted-chain theories (see sections 2.5.2 and 2.6.3 below).

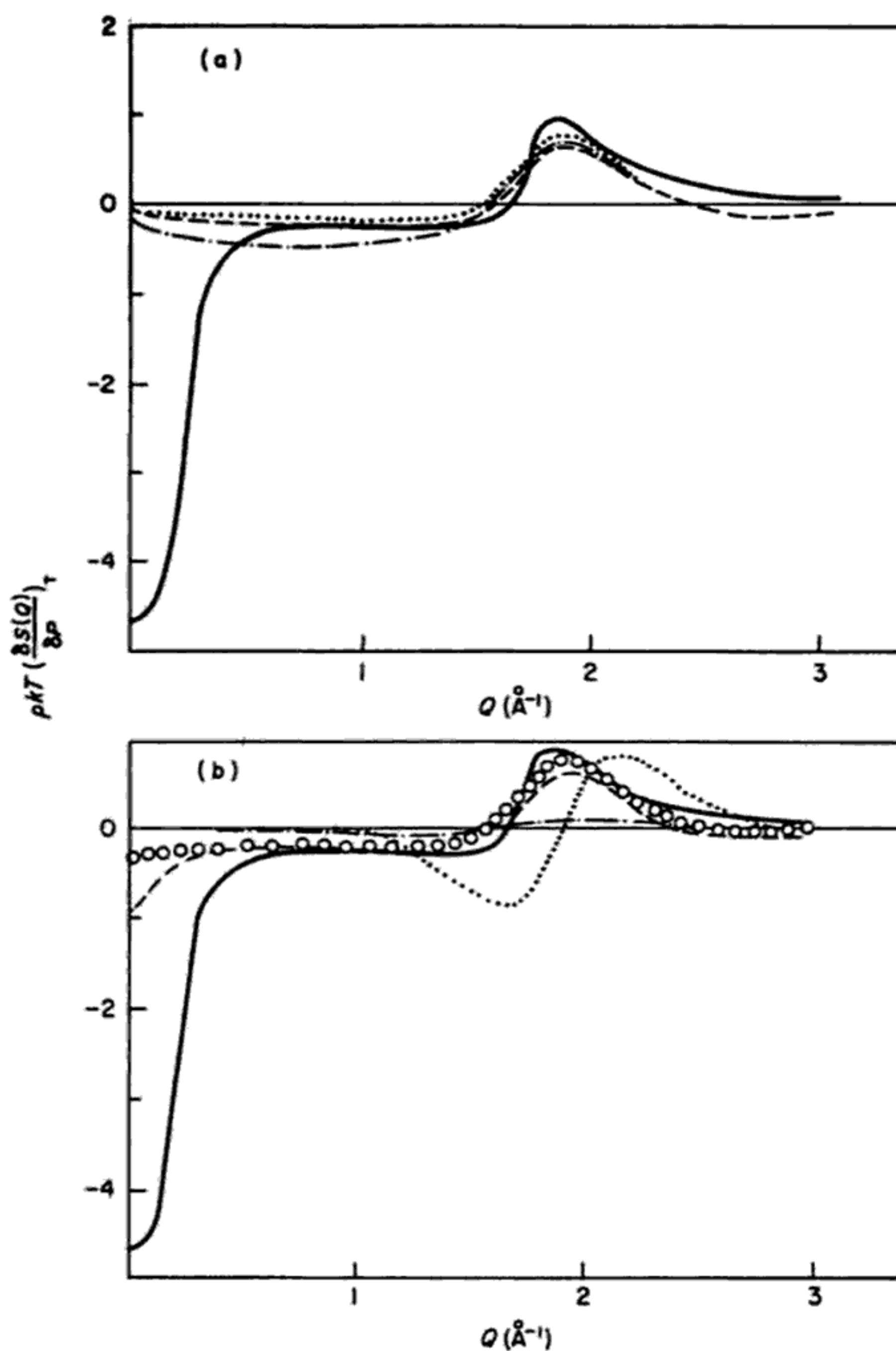


Figure 2.2 Comparison between experiment (full curves) and theories for the pressure dependence of the structure factor in liquid argon near the critical point (from Egelstaff, Page and Heard, 1971). The superposition, Abe and Percus-Yevick approximations are represented, respectively, by the broken curve in part (a), by the circles in part (b), and by the broken curve in part (b)

tion of pressure (see part (b) of figure 2.3). This shift arises through the rearrangement of the near-neighbour atoms and is most simply accounted for by the uniform compression of the liquid under application of pressure.

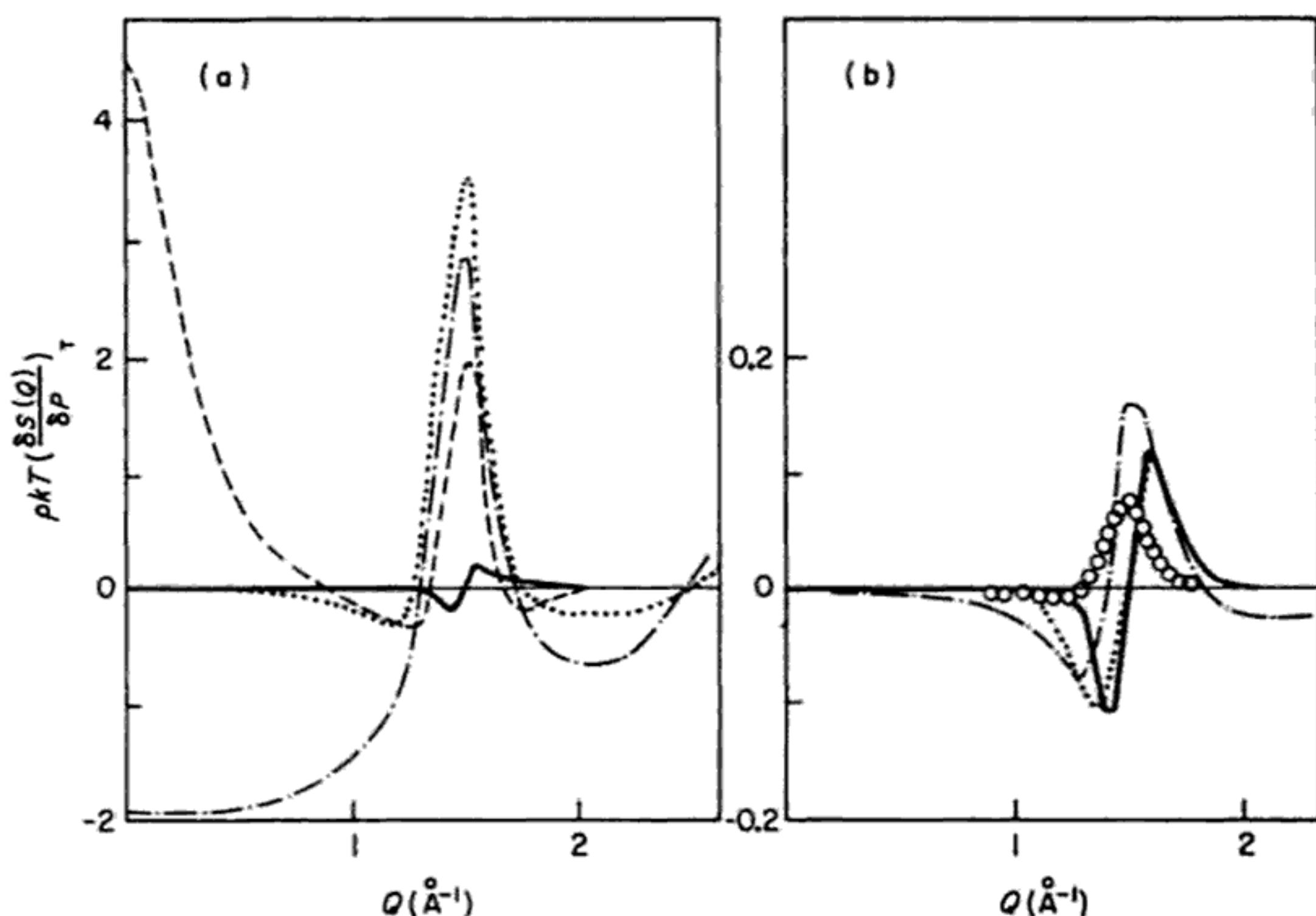


Figure 2.3 Comparison between experiment (full curves) and theories for the pressure dependence of the structure factor in liquid rubidium near the triple point (from Egelstaff, Page and Heard, 1971). The superposition approximation and the hypernetted-chain approximation are represented by the broken curve in part (a) and by the circles in part (b) respectively

2.4.3 Computer simulation test

To supplement the above discussion we record here briefly some results obtained by computer simulation on hard spheres and on liquid argon.

Alder (1964) has thereby shown that for configurations of three atoms in a fluid of hard spheres which are equilateral triangles, $g^{(3)} = [g(r)]^3$ to high accuracy.

This result has been confirmed for liquid argon at various temperatures by Krumhansl and Wang (1972), who demonstrate that the deviations are well within 10% over a limited range of r . For less symmetrical triplet configurations, they report up to 20% deviations from superposition at the lowest temperatures, such deviations correlating with the structure in $g(r)$ itself.

Two comments need making on the relation between these findings and those of Egelstaff, Page and Heard (1971):

- (1) Though superposition is often numerically a good approximation to $g^{(3)}$, great care is obviously needed in deciding in what physical situations to use it.
- (2) The pressure dependence of $g(r)$ is easily seen to depend only on the s term in the Legendre polynomial expansion (2.15), whereas the force equation depends on the p ($l=1$) term. Thus, no direct deduction about the validity of the

Born-Green theory of structure follows from the pressure experiments, although obviously caution is indicated in the application to metals.

Nevertheless, the three simple theories of structure—Born-Green, Percus-Yevick and HNC—are still of sufficient interest to justify a fuller discussion, to which we now turn.

2.5 Approximate theories of structure

2.5.1 Born-Green theory

In utilising the superposition approximation (2.22) in the force equation (2.14), it should be noted that only the term $g(r_{23})$ depends on $\cos \theta$, and because of the argument given at the end of section 2.2 we can subtract a spherical part and therefore substitute $g(r_{12})g(r_{31})[g(r_{23})-1]$ in place of $g^{(3)}$ in (2.14), without changing the result. This latter substitution will be convenient, because the total correlation function, $h(r)=g(r)-1$, is a well-behaved function, tending to zero at infinity. Thus we find, after a simple calculation from (2.14),

$$\frac{d}{ds} \left[\ln g(s) + \frac{\phi(s)}{k_B T} \right] = -\frac{\rho}{k_B T} \int d\mathbf{r}_3 h(r_{23}) g(t) \frac{t_z}{t} \phi'(t) \quad (2.24)$$

where t_z is the resolved part of t on s . Integration over s yields

$$\ln g(s) + \frac{\phi(s)}{k_B T} = \frac{\rho}{k_B T} \int_s^\infty dx \int d\mathbf{r}_3 h(r_{23}) g(t) \frac{t_z}{t} \phi'(t) \quad (2.25)$$

By adopting now, as integration variables, the vector $\mathbf{r}_{32} \equiv \mathbf{r}$ and the length t , and noticing that a change dx in the length x at constant \mathbf{r} is equivalent to a change $t dt/t_z$ in the length t , we can write this equation in the form (see, for instance Rushbrooke, 1960)

$$\ln g(s) + \frac{\phi(s)}{k_B T} = \rho \int E(|\mathbf{r}-s|) h(\mathbf{r}) d\mathbf{r} \quad (2.26)$$

where

$$E(t) = \frac{1}{k_B T} \int_t^\infty g(x) \phi'(x) dx \quad (2.27)$$

This is the Born-Green (1946) equation, which gives us an explicit integral equation connecting the structure $g(r)$ and the pair potential $\phi(r)$.

We shall consider some properties of the solution of this equation below, but for the moment let us comment on two properties of $E(t)$ which will be useful later:

- (1) At sufficiently large t , we can evidently replace $g(x)$ by unity in (2.27) when

we immediately obtain

$$E(t) \sim -\frac{\phi(t)}{k_B T} \quad (2.28)$$

(2) We can calculate the integral of $E(t)$ over the volume of the fluid, in terms of the fluid pressure p . Defining the Fourier transform $\tilde{E}(k)$ of $E(t)$ by

$$\tilde{E}(k) = \rho \int dt \exp(-ik \cdot t) E(t) \quad (2.29)$$

then evidently

$$\tilde{E}(0) = \rho \int dt E(t) \quad (2.30)$$

and substituting from (2.27) we may write

$$\tilde{E}(0) = \rho \int dr \int_0^\infty dt H(r, t) g(t) \frac{\phi'(t)}{k_B T} \quad (2.31)$$

where

$$H(r, t) = \begin{cases} 1, & t > r \\ 0, & t < r \end{cases} \quad (2.32)$$

We can now interchange the order of integration and we find

$$\int H(r, t) dr = \int_0^r 4\pi r^2 dr = \frac{4\pi r^3}{3} \quad (2.33)$$

and hence

$$\tilde{E}(0) = \frac{4\pi\rho}{3k_B T} \int_0^\infty g(t) \phi'(t) t^3 dt \quad (2.34)$$

But we saw in section 1.2, eqn (1.15), that the fluid pressure involved this integral and we find (Gaskell, 1965; see also p. 25 and p. 31)

$$\tilde{E}(0) = 2 \left[1 - \frac{p}{\rho k_B T} \right] \quad (2.35)$$

For a perfect gas, with $p = \rho k_B T$, we see that $\tilde{E}(0)$ vanishes, which is evidently correct from (2.31) when $\phi' = 0$.

Before discussing the use of these results in an explicit asymptotic solution of the Born-Green equation for van der Waals interactions, we shall discuss a further approximate equation of liquid state theory, given by Abe (1958) and many other workers.

2.5.2 Abe's approximate form of the Born-Green theory (hypernetted-chain theory)

To see how Abe's method results from the Born-Green equation we rewrite $E(r)$ from (2.27) in the form

$$E(r) = \frac{1}{k_B T} \int_r^\infty ds g(s) \frac{d}{ds} [\phi(s) - U(s)] + \frac{1}{k_B T} \int_r^\infty ds g(s) \frac{dU}{ds} \quad (2.36)$$

where $U(s) = -k_B T \ln g(s)$. Then, the last term can be integrated explicitly and is simply the total correlation function $h(r)$. Thus we find

$$E(r) = \frac{1}{k_B T} \int_r^\infty ds g(s) \frac{d}{ds} [\phi(s) - U(s)] + h(r) \quad (2.37)$$

Abe's approximation is now obtained (see Gaskell, 1966) by putting $g(s)$ in the integral term in (2.37) as unity, that is, replacing it by its asymptotic value. Such a procedure would seem to lead to a less accurate theory than the Born-Green theory, although the possibility exists that this second approximation could counteract the superposition assumption of the Born-Green theory. We shall see that, in at least one respect, this latter circumstance seems to exist! Then, we replace the function $E(r)$ of (2.27) by $c(r)$, say, defined by

$$c(r) = \frac{1}{k_B T} [U(r) - \phi(r)] + h(r) \quad (2.38)$$

This leads to the second approximate equation of structure theory, namely,

$$\ln g(s) + \frac{\phi(s)}{k_B T} = \rho \int d\mathbf{r} c(|\mathbf{r} - \mathbf{s}|) h(r) \quad (2.39)$$

This equation and the Born-Green theory are so similar in structure that we can apply essentially the same method of solution, usually numerical, to both. Before discussing these equations further, it will be convenient to deal with the physical significance of the quantity $c(r)$ above and to introduce the Percus-Yevick equation

2.6 Ornstein-Zernike direct correlation function and Percus-Yevick theory

Let us substitute for $U - \phi$ from (2.38) into the left-hand side of (2.39) when we find

$$h(r) = c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|) h(\mathbf{r}') d\mathbf{r}' \quad (2.40)$$

We see that this equation relates $c(r)$ to $h(r)$ for a given density and we take it as the fundamental definition of $c(r)$, independently of approximate theories.

Clearly, if we measure $S(k)$ by X-ray or neutron scattering and hence get $h(r)$, we can obtain $c(r)$ directly from experiment. The function $c(r)$, as defined by (2.40), was first introduced by Ornstein and Zernike in connection with critical fluctuations. We shall see in chapter 9 that it does indeed play a central role in any discussion of critical phenomena. Most usually, $c(r)$ is referred to nowadays as the *direct* correlation function, for reasons we shall briefly discuss at this point.

From (2.26) we see that the ‘potential of mean force’ U is split into a direct part ϕ and a convolution of E and h . Asymptotically, as we have seen, $E \sim \phi$ and $h \sim U$, and if we make these replacements we see that (2.40) and the Born–Green equation (2.26) have then the same form. We are then, in defining c , splitting the total correlation function h into a direct part c and an indirect part. Strictly by analogy with the force equation, some three-body correlation function should be involved and we can expect $c(r)$ to have a simple physical significance, at most, asymptotically.

From the Abe theory, we then find

$$h - c = -\frac{U - \phi}{k_B T} \quad (2.41)$$

and hence, for large r ,

$$c(r) \sim -\frac{\phi(r)}{k_B T} \quad (2.42)$$

provided $h^2 < |c|$. This is true well away from the critical point. Since $c(r)$ is, in fact, defined in terms of $h(r)$, we can calculate it from the measured structure factor. Taking the Fourier transform of (2.40) we find

$$\tilde{h}(k) = \tilde{c}(k) + \tilde{h}(k)\tilde{c}(k) \quad (2.43)$$

or

$$\tilde{c}(k) = \frac{\tilde{h}(k)}{1 + \tilde{h}(k)} = \frac{S(k) - 1}{S(k)} \quad (2.44)$$

Thus the direct correlation function in k space is simply $1 - 1/S(k)$ but since $S(0)$ is typically 0.01–0.03 in liquid metals, the form of $c(k)$ is very different from $S(k)$, as can be seen by comparing figure 1.1 for $S(k)$ with the form of $\tilde{c}(k)$ shown in figure 2.4 for liquid thallium just above its melting point, as measured by neutron experiments.

Having discussed the Born-Green and the Abe (often called hypernetted-chain because of its connection with diagrammatic analysis) theories, and noting that they are most conveniently discussed in r space, we turn now to two further treatments which are more basically formulated in k space, although they will turn out to have a close relation to the Abe theory.

2.6.1 Density fluctuations and correlation functions

In order to reformulate the force equation (2.14) in k space, we introduce the

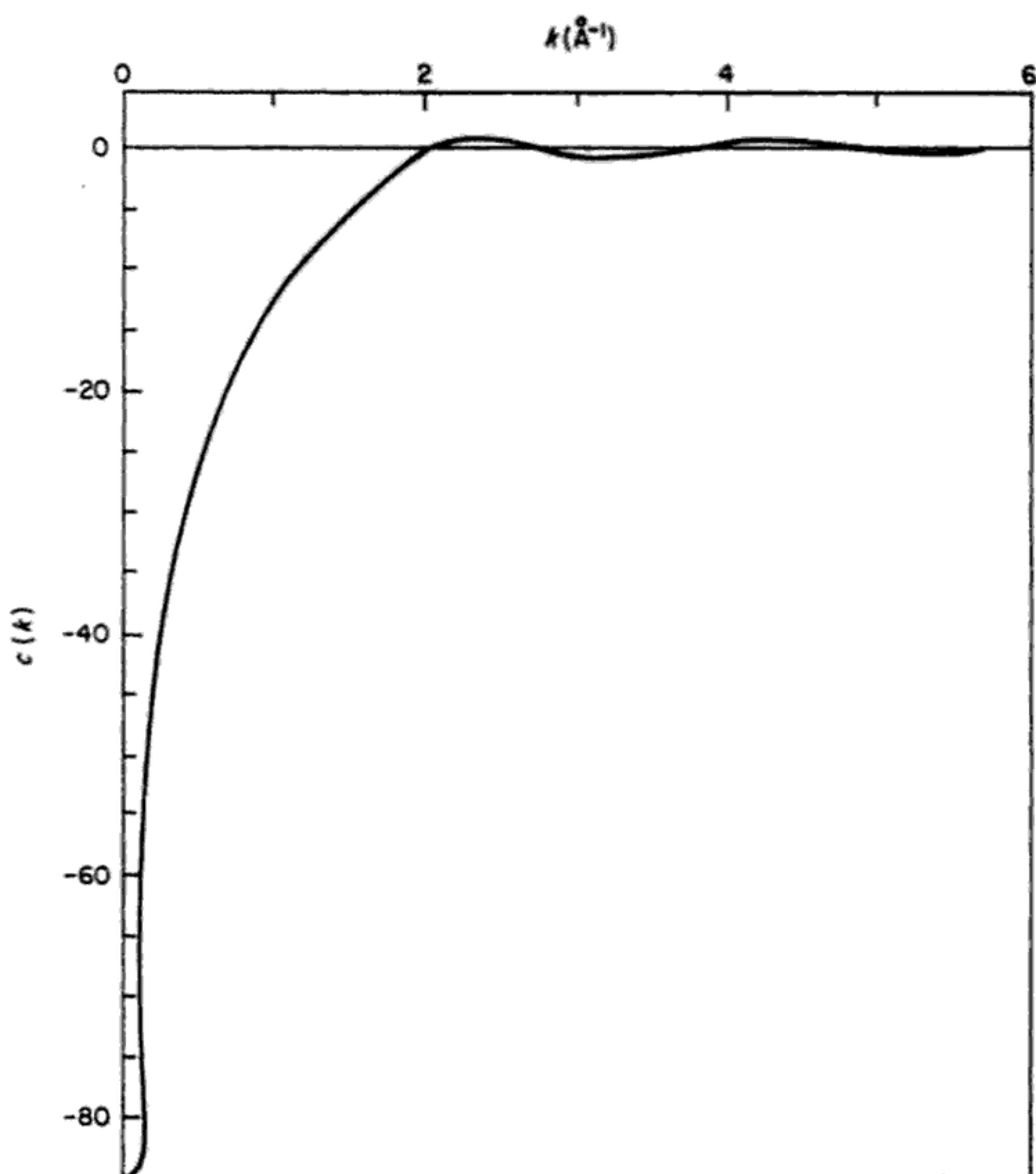


Figure 2.4 Direct correlation function $c(k)$ for liquid thallium at 600 K, as determined from the neutron-scattering data reported in figure 1.1 (see Enderby and March, 1966)

Fourier components $\rho_{\mathbf{k}}$ of the density $\rho(\mathbf{r})$ defined in (1.16), which are

$$\rho_{\mathbf{k}} = \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{R}_i) \quad (2.45)$$

The variables $\rho_{\mathbf{k}}$ describe density fluctuations of given wave vector, and, since they involve the positions of all the atoms, they may be viewed as collective coordinates.

Let us now briefly consider how the two-particle distribution function $\rho^{(2)}(r) = \rho^2 g(r)$ may be expressed in terms of the density fluctuations. From (1.17) we can write, by use of the translational invariance of the fluid,

$$\rho g(r) = \frac{1}{N} \left\langle \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{R}_i + \mathbf{R}_j) \right\rangle \quad (2.46)$$

We now show that the Fourier transform of this, the structure factor $S(k)$, is simply related to correlations between density fluctuations of given wave vector. To do this, we form

$$\rho_k \rho_{-k} = \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{R}_i) \sum_{j=1}^N \exp(-i\mathbf{k} \cdot \mathbf{R}_j) \quad (2.47)$$

or

$$\rho_k \rho_{-k} - N = \sum_{i \neq j} \exp[i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)] \quad (2.48)$$

Thus, by Fourier transform of (2.46), we obtain the result

$$S(k) = \frac{1}{N} \langle \rho_k \rho_{-k} \rangle \quad (2.49)$$

Likewise, we can obtain the higher order distribution functions in terms of the ρ_k . We now return to the exact force equation (2.14) and converting it into k space we find

$$S(k) = 1 + \frac{1}{Nk^2} \sum_n \frac{\tilde{\phi}(n)}{k_B T} \langle \rho_{k+n} \rho_k \rho_n \rangle \mathbf{k} \cdot \mathbf{n} \quad (2.50)$$

where we have assumed, for the moment, that the pair potential $\phi(r)$ has a Fourier transform, given by

$$\tilde{\phi}(k) = \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) \phi(r) \quad (2.51)$$

This equation is exact for a potential that can be Fourier transformed. $\langle \rho_{k+n} \rho_k \rho_n \rangle$ involving three ρ_k 's, comes from the three-body correlation function.

2.6.2 Random-phase approximation

As in the earlier theories based on the force equation, we must now approximate. Since we want to relate $S(k)$ and $\tilde{\phi}(k)$, we must somehow reduce $\langle \rho_{k+n} \rho_k \rho_n \rangle$ to $S(k)$ and, if we pick out from the sum the term $n = -k$, this is evidently related to $S(k)$. This is, in fact, the random-phase approximation which will be discussed more fully in chapter 7. The qualitative argument is that unless \mathbf{k} and \mathbf{n} bear this simple relation, destructive interference between the various oscillatory components will tend to annul the other terms. Actually, such an argument turns out to be a long wavelength approximation. We then find, collecting the terms in $S(k)$,

$$S(k) = \left[1 + \frac{\rho \tilde{\phi}(k)}{k_B T} \right]^{-1} \quad (2.52)$$

Comparing this with the result (2.44), rewritten as

$$S(k) = [1 - \tilde{c}(k)]^{-1} \quad (2.53)$$

we see that the direct correlation function is assumed in the random-phase approximation to have its asymptotic form

$$\tilde{c}(k) = -\rho \tilde{\phi}(k)/k_B T \quad (2.54)$$

or in r space

$$c(r) = -\phi(r)/k_B T \quad (2.55)$$

This is the same result as the Abe approximation yields for large r .

Actually, without going through the \mathbf{k} space analysis, this same form arises from replacing $g^{(3)}$ inside the integration over \mathbf{r}_3 in the force equation by $h(\mathbf{r}_{23})$. However, its basic theoretical justification for small \mathbf{k} comes from the random-phase approximation.

2.6.3 Effective interatomic potential and the Percus-Yevick theory

The crippling limitation of the above approximation is that it assumes an interaction with a Fourier transform. For liquids, in general, the interaction has almost a hard core, and we cannot Fourier transform it. The Percus-Yevick (1958) method is an attempt to produce an effective potential which will replace the Fourier components $\phi(k)$ above.

The idea behind it is to use the $\rho_{\mathbf{k}}$ as collective coordinates. For them to afford an accurate approximation we must be able to express the Hamiltonian in terms of them and the corresponding momenta, and then to treat them as if they were 'almost' independent. There are $3N$ coordinates, $\mathbf{R}_1 \dots \mathbf{R}_N$, in the original Hamiltonian and while, in a finite system with, say, periodic boundary conditions imposed over a large cube of side L , \mathbf{k} has discrete though dense values, all such discrete \mathbf{k} are allowed in enumerating the $\rho_{\mathbf{k}}$. Actually, we would transform naturally to centre of mass coordinates,

$$X = \frac{1}{N} \sum_{i=1}^N \mathbf{R}_i \quad (2.56)$$

and $(3N-3)$ $\rho_{\mathbf{k}} \dagger$.

Suppose we consider the potential energy. Then, in (1.10), we found it in terms of $\phi(r)$ and $g(r)$ and by Fourier transform we get

$$\text{Potential energy} = \frac{1}{2} \sum_{all \mathbf{k}} \tilde{\phi}(k) \langle [\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - N] \rangle \quad (2.57)$$

We can, at this stage, ask whether we can choose $\tilde{\phi}_{eff}(k)$ to get the 'best' possible approximation. There is ambiguity in this statement, but we might determine the

[†]Some difficulties arise from redundant variables as in, for example, collective coordinates theories of an electron gas (see Bohm and Pines, 1953). We need not elaborate this further for our present purposes.

effective potential

$$\phi_{\text{eff}}(\mathbf{r}) = \sum_{(3N-3)\mathbf{k}'s} \tilde{\phi}_{\text{eff}}(\mathbf{k}) \exp(-i\mathbf{k} \cdot \mathbf{r}) \quad (2.58)$$

by requiring that the mean square difference

$$\left\langle \left\{ \phi(\mathbf{R}_i - \mathbf{R}_j) - \sum_{(3N-3)\mathbf{k}'s} \tilde{\phi}_{\text{eff}}(\mathbf{k}) \exp[-i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)] \right\}^2 \right\rangle \quad (2.59)$$

be a minimum. A first-order approximation to this indicates that the choice is

$$\tilde{\phi}_{\text{eff}}(\mathbf{k}) = FT[\phi(r)g(r)] \quad (2.60)$$

where, by the right-hand side, we mean the Fourier transform of the product of $\phi(r)$ and $g(r)$. We see already that we have avoided the very strong repulsive potential inside the core by weighting the interaction with the probability of the occurrence of the pair of atoms i, j at separation $\mathbf{r} = \mathbf{R}_i - \mathbf{R}_j$.

Actually, since we wish to calculate structure, it is better to minimise averages of $\rho_k \rho_{-k}$ with respect to the exact distribution function (involving ϕ) and the approximation to it (involving ϕ_{eff}). We then find, after numerous approximations,

$$\tilde{\phi}_{\text{eff}}(\mathbf{k}) = k_B T FT[g(r)\{\exp[\phi(r)/k_B T] - 1\}] \quad (2.61)$$

which clearly reduces to the earlier choice (2.60) if we take $\phi(r)/k_B T$ to be small. This is the choice of the $\tilde{\phi}_{\text{eff}}(\mathbf{k})$'s generally referred to as *the Percus-Yevick approximation*. Thus we have, from (2.54),

$$c(k) = -\rho FT[g(r)\{\exp[\phi(r)/k_B T] - 1\}] \quad (2.62)$$

and if we assume (doubtfully, because of the use of the random-phase approximation) that this is true for all k , then we may write finally,

$$c(r) = g(r)[1 - \exp[\phi(r)/k_B T]] \quad (2.63)$$

Clearly again†

$$c(r) \sim -\phi(r)/k_B T \quad (2.64)$$

for large r , and there is a direct equivalence with the Abe approximation if U and ϕ are small.

If we examine the asymptotic form of the Born-Green equation for the specific case of van der Waals interaction, then (2.64) is regained, but with a different multiplying constant (Gaskell, 1965). This is obviously a serious defect of the

†Sufficiently far from the critical point, the available evidence points to the fact that this is the *exact* asymptotic form. However, the authors know of rigorous proofs only in very special cases (e.g. Lebowitz and Percus, 1963 and other references given there).

Born-Green equation. Using the result (2.64) with $\phi(r) = -Ar^{-6}$, it is readily shown that the structure factor $S(k)$ has the small k form for van der Waals fluids (Enderby, Gaskell and March, 1965):

$$S(k) = S(0) + a_2 k^2 + a_3 k^3 + \dots; \quad a_3 = \frac{\pi^2 \rho A [S(0)]^2}{12 k_B T} \quad (2.65)$$

2.6.4 Direct correlation function for fluid argon

We are now in a position to construct an approximate $c(r)$ for fluid argon. To do so simply, we shall divide the pair potential $\phi(r)$ into two parts, which we shall call ϕ_{sr} and ϕ_{lr} . The short-range part we shall define as the part inside the atomic diameter σ , as shown in figure 2.5. If we take a Lennard-Jones (6-12) potential, to be quite specific, that is

$$\phi(r) = \frac{D}{r^{12}} - \frac{A}{r^6} \quad (2.66)$$

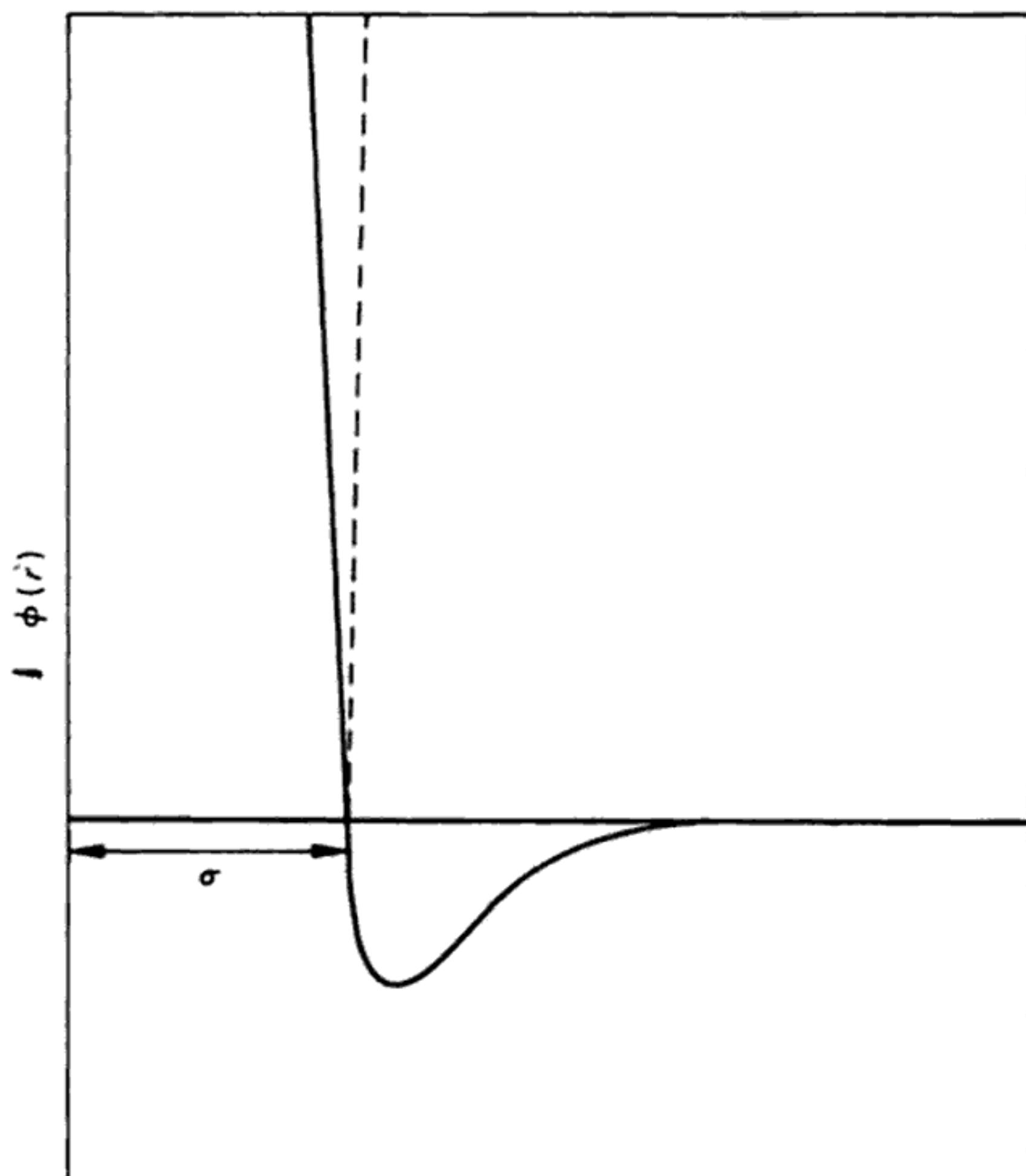


Figure 2.5 Schematic form of pair potential for liquid argon. Broken curve shows the steep repulsive part as represented in hard core approximation with hard core parameter σ (from Woodhead-Galloway et al., 1968)

then we define σ by $\phi(\sigma)=0$, and then $D=A\sigma^6$. However, for $r < \sigma$ we assume a rigid hard core, as shown by the dotted line in the figure. This is *not* essential, but we can now get an *exact* solution of the Percus-Yevick equation for hard spheres (Wertheim, 1963; Thiele, 1963). While this is an important result, we shall not derive it here, but refer to the account in Frisch and Lebowitz (1964) and to our subsequent discussion in section 6.5.1.

It is, in fact, immediately clear from (2.63) that

$$c_{hs}(r)=0 \quad \text{for } r > \sigma \quad (2.67)$$

It turns out that $c_{hs}(r)$ is a polynomial inside σ and if we use σ as the unit of length and write $x=r/\sigma$ then

$$\begin{aligned} c_{hs}(x) &= A_0 + A_1 x + A_3 x^3, & x < 1 \\ &= 0 & x > 1 \end{aligned} \quad (2.68)$$

where A_0 , A_1 and A_3 are functions of the packing fraction η given by

$$\eta = \frac{1}{6}\pi\rho\sigma^3 \quad (2.69)$$

Substituting in the Percus-Yevick equation, it can be shown that A_0 , A_1 and A_3 are defined by

$$\begin{aligned} A_0 &= -(1+2\eta)^2(1-\eta)^{-4} \\ A_1 &= 6\eta(1+\frac{1}{2}\eta)^2(1-\eta)^{-4} \\ A_3 &= -\frac{1}{2}\eta(1+2\eta)^2(1-\eta)^{-4} \end{aligned} \quad (2.70)$$

$c(r)$ has then the form shown schematically in figure 2.6 while, if we calculate the structure factor $S(k)$, we find, for a chosen value of η , the upper curve in figure 2.7. Actually, it seems likely that both the Born-Green and the Abe approximation would give similar results, but so far the corresponding equations have not been solved exactly. However, the lower part of figure 2.7 shows density expansions of these theories and, except at small k , the results are quite similar. The other theories do not give $c(r)=0$ for $r > \sigma$ and, in fact, it may be shown that the exact $c(r)$ for hard spheres does not vanish. But we expect it to be small and we now turn to discuss the modified form the above theories suggest for $c(r)$ in fluid argon.

The form of $\bar{c}_{hs}(k)/\bar{c}_{hs}(0)$ is shown in figure 2.8, along with experimental results for fluid argon at 84 K. The model obviously has the general features of the experimental data.

2.6.5 Equation of state of fluid argon

We have seen in the Percus-Yevick theory that c_{hs} is zero outside σ . On the other hand, if we use the result (2.64) for the long-range part, we have immediately the form shown in figure 2.6, the tail directly reflecting the Lennard-Jones potential. This general form of $c(r)$ has been confirmed from scattering data by a

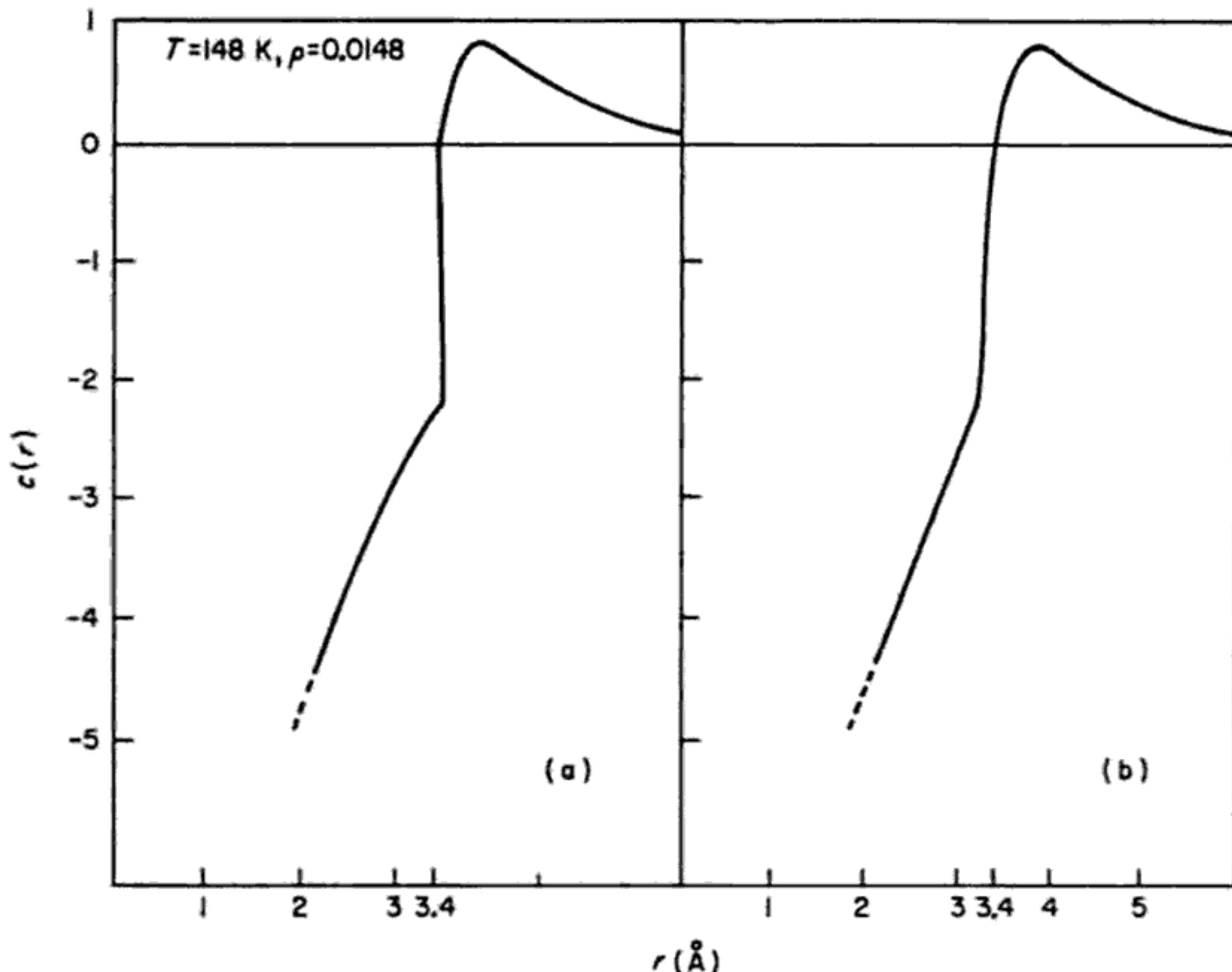


Figure 2.6 Direct correlation function $c(r)$ for a hard sphere fluid modified by an attractive potential tail (a) and after smoothing the singularities arising from the infinitely steep repulsive potential (from Woodhead-Galloway, Gaskell and March, 1968)

number of workers. We do not expect the step at σ , of course, in a real liquid, though we expect a rather steep rise which will lead to oscillations in $\tilde{c}(k)$ at large k .

One rather striking confirmation that this approach is quite appropriate to fluid argon comes from studying its equation of state at high density (i.e. near the triple point). Thus, Longuet-Higgins and Widom (1964) have shown that in this regime the equation of state is well represented by a modified van der Waals theory. In the van der Waals equation of state we have

$$p = \frac{\rho k_B T}{1 - b\rho} - a\rho^2 \quad (2.71)$$

where a and b are constants, independent of ρ and T . The first term is designed to take account of the ‘finite size’ of the molecules, i.e. it is the analogue of a hard sphere term, while the second term takes account of the attractive forces. In present terms, we want therefore to write

$$p = p_{hs}(\rho, T) - a\rho^2 \quad (2.72)$$

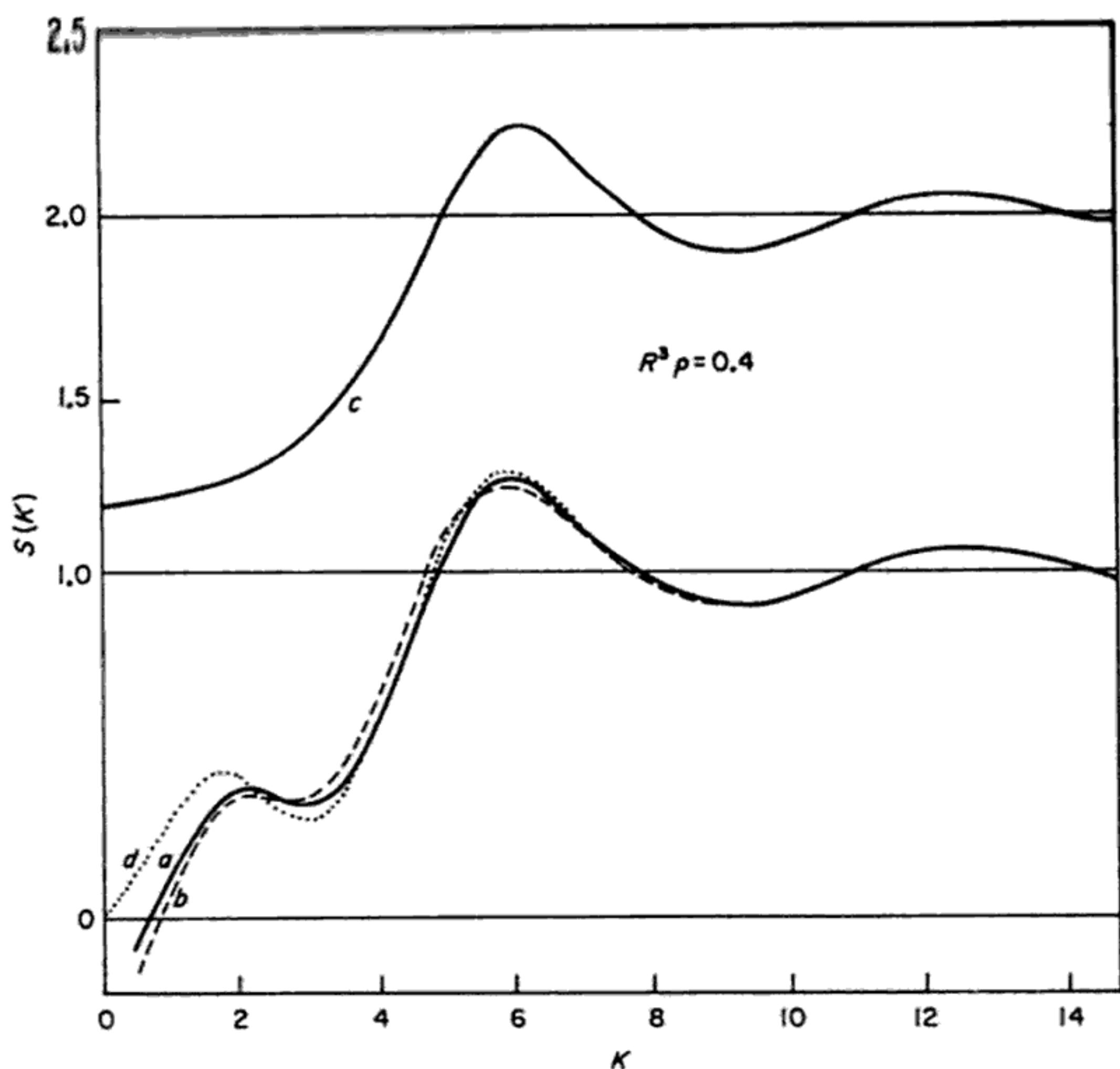


Figure 2.7 Static structure factor $S(k)$ for hard spheres with $\rho\sigma^3=0.4$ (from Ashcroft and March, 1967). Upper curve—Percus-Yevick results: lower curves: results obtained by density expansion in (a) exact theory, (b) Born-Green theory, and (d) Abe theory

Longuet-Higgins and Widom show that this equation of state gives a quantitative account of the properties of fluid argon near the triple point. To show this, we reproduce in table 2.1 some results they obtained at the triple point, together with the corresponding experimental results.

Table 2.1 Properties of argon at triple point

	V_L/V_s	p	$\Delta S/Nk_B$	Cohesive energy
Theory	1.19	-5.9	1.64	-8.6
Experiment	1.11	-5.88	1.69	-8.53

The dimensionless quantities shown in table 2.1 are: first the ratio of the liquid and solid volumes at the triple point; second the pressure; third the entropy of fusion ΔS , in units of Nk_B ; and fourth the cohesive energy of the liquid. Certain

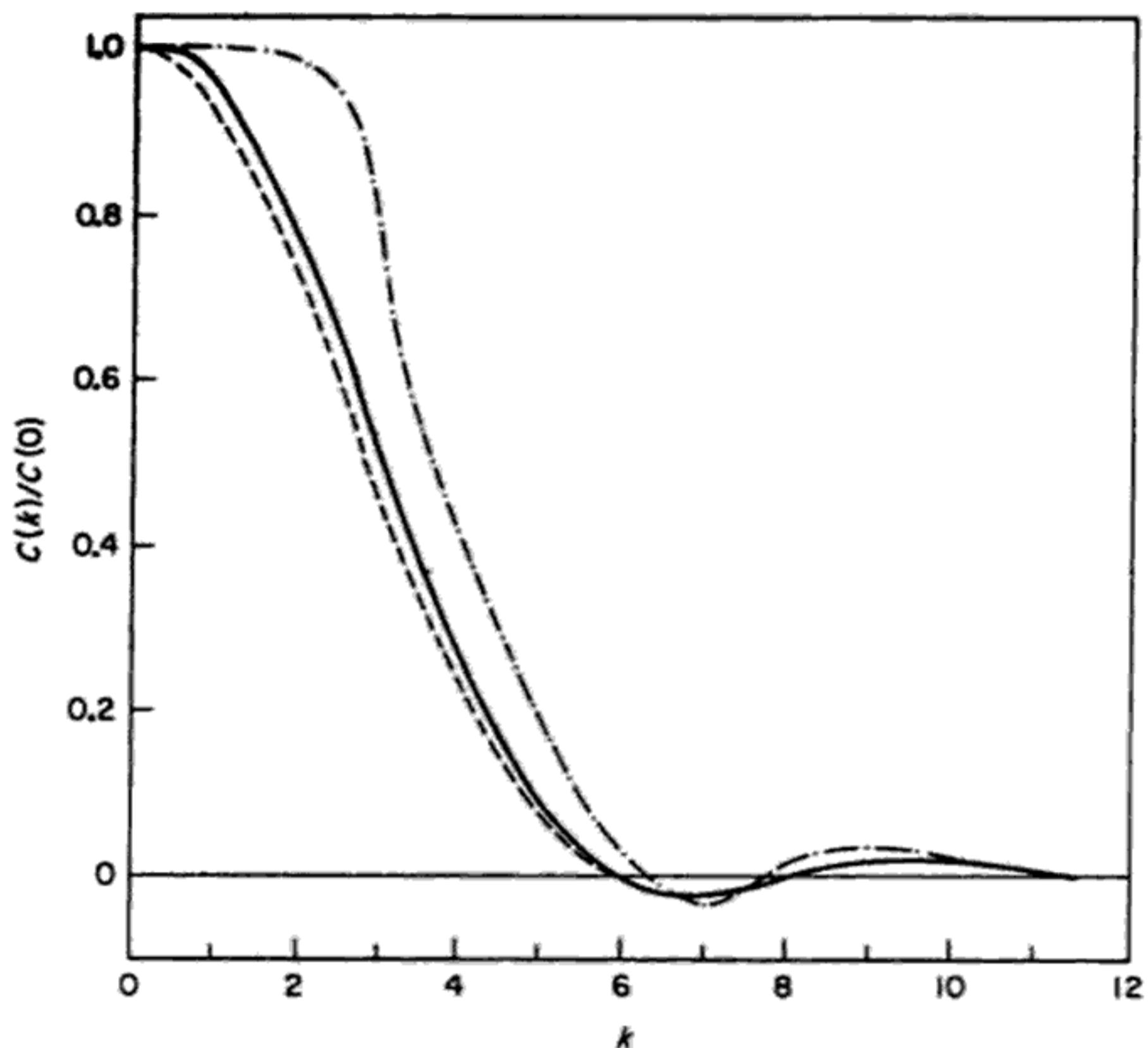


Figure 2.8 Direct correlation function in k space for fluid argon at 84 K. Dash-dot curve: experiment; other curves are slightly different ways of calculating hard sphere result (from Ashcroft and March, 1967)

second derivatives of the free energy are given less satisfactorily and, in particular, the configurational specific heat is zero. But the numbers above are given to illustrate that this is really a good equation of state for the high density fluid.

The link with our calculation of $c(r)$ may now be made by the fluctuation formula for $S(0)$, which relates $S(0)$ to the isothermal compressibility, eqn (1.27). From (2.55) we then have

$$\left(\frac{\partial p}{\partial \rho}\right)_T = \frac{k_B T}{S(0)} = k_B T [1 - \bar{c}(0)] \quad (2.73)$$

Now we return to our results for $c(r)$, namely

$$c(r) \approx c_{hs}(r) + c_{lr}(r) \quad (2.74)$$

and

$$\bar{c}(0) = \bar{c}_{hs}(0) + \bar{c}_{lr}(0) \quad (2.75)$$

Hence it follows that

$$\left(\frac{\partial p}{\partial \rho}\right)_T = \left(\frac{\partial p_{hs}}{\partial \rho}\right)_T - k_B T \bar{c}_{lr}(0) = \left(\frac{\partial p_{hs}}{\partial \rho}\right)_T + \rho \dot{\phi}_{lr}(0) \quad (2.76)$$

from (2.64). Differentiating (2.72) with respect to ρ at constant temperature we see immediately that these two expressions agree, provided

$$a = -\frac{1}{2}\tilde{\phi}_{lr}(0) \quad (2.77)$$

But this quantity, from the definition (2.64), is simply given by

$$a = -\frac{1}{2} \int_{\sigma}^{\infty} 4\pi r^2 \left(\frac{A\sigma^6}{r^{12}} - \frac{A}{r^6} \right) dr = \frac{4\pi}{9} A/\sigma^3 \quad (2.78)$$

This is in excellent agreement (within about 10%) of the empirical value of a . If we had used the Born-Green asymptotic form, we would have been quite wrong. Thus we conclude that this confirms the result (2.64) for argon and enables the equation of state to be calculated directly from the parameters in the force law (Woodhead-Galloway, Gaskell and March, 1968).

Actually Longuet-Higgins and Widom used the results of machine calculations for $p_{hs}(\rho, T)$. If we are content with slightly less accuracy, we could use the Percus-Yevick result. From (2.73) we find for the equation of state, using (2.68) and (2.70),

$$\frac{p}{\rho k_B T} = (1 - \eta)^{-3} (1 + \eta + \eta^2) \quad (2.79)$$

This result is not unique, but if we use the virial expression for the pressure we get a rather similar result and thermodynamic inconsistencies are not too serious in this case.

If we use this argument in a metal, $\tilde{c}_{hs}(0)$ is made *more* negative by adding $\tilde{c}_{lr}(0)$, whereas in fluid argon it is made *less* negative. A crude calculation in a metal shows that c is derivable from the pseudo-potential which, as Ziman (1961) has discussed, tends to $\frac{2}{3}E_f$ as $k \rightarrow 0$. But $E_f \propto \rho^{2/3}$ from electron theory, and integrating this we get a term in the equation of state $\propto \rho^{5/3}$. This replaces the ρ^2 term in argon, the difference coming from the density dependence of the pair potential. Unfortunately, in a metal, σ defined by $\phi(\sigma) = 0$ for present purposes, is significantly density dependent. This means a more complex situation in a liquid metal than in fluid argon (see, for example, Watabe and Young, 1974). It would take us too far from our main theme to pursue matters specific to liquid metals further, at this point.

2.6.6 Softness corrections to hard-core potential

Considerable detailed refinements have been developed in recent work, taking full advantage of the computer simulation techniques. In particular, much effort has been devoted to the question of how best to correct the thermodynamic properties and the pair correlation function of a hard-core fluid for the finite steepness of the repulsive potential in real fluids. The most successful scheme, by comparison with Monte Carlo simulations (Hoover et al., 1970; Hansen, 1970),

has been proposed by Andersen, Weeks and Chandler (1971). Defining the function

$$y(r) = g(r) \exp [\phi(r)/k_B T] \quad (2.80)$$

where $\phi(r)$ is, as usual, the pair potential, taken to be purely repulsive, and similarly introducing the function $y_d(r)$ for a hard-core fluid of core diameter d , these authors show that the relation

$$y(r) = y_d(r) \quad (2.81)$$

is exact to first order in the range of the deviation between the two potentials provided that the hard-core diameter is chosen so as to satisfy the relation

$$\int d\mathbf{r} y_d(r) [\exp [-\beta\phi(r)] - \exp [-\beta\phi_d(r)]] = 0 \quad (2.82)$$

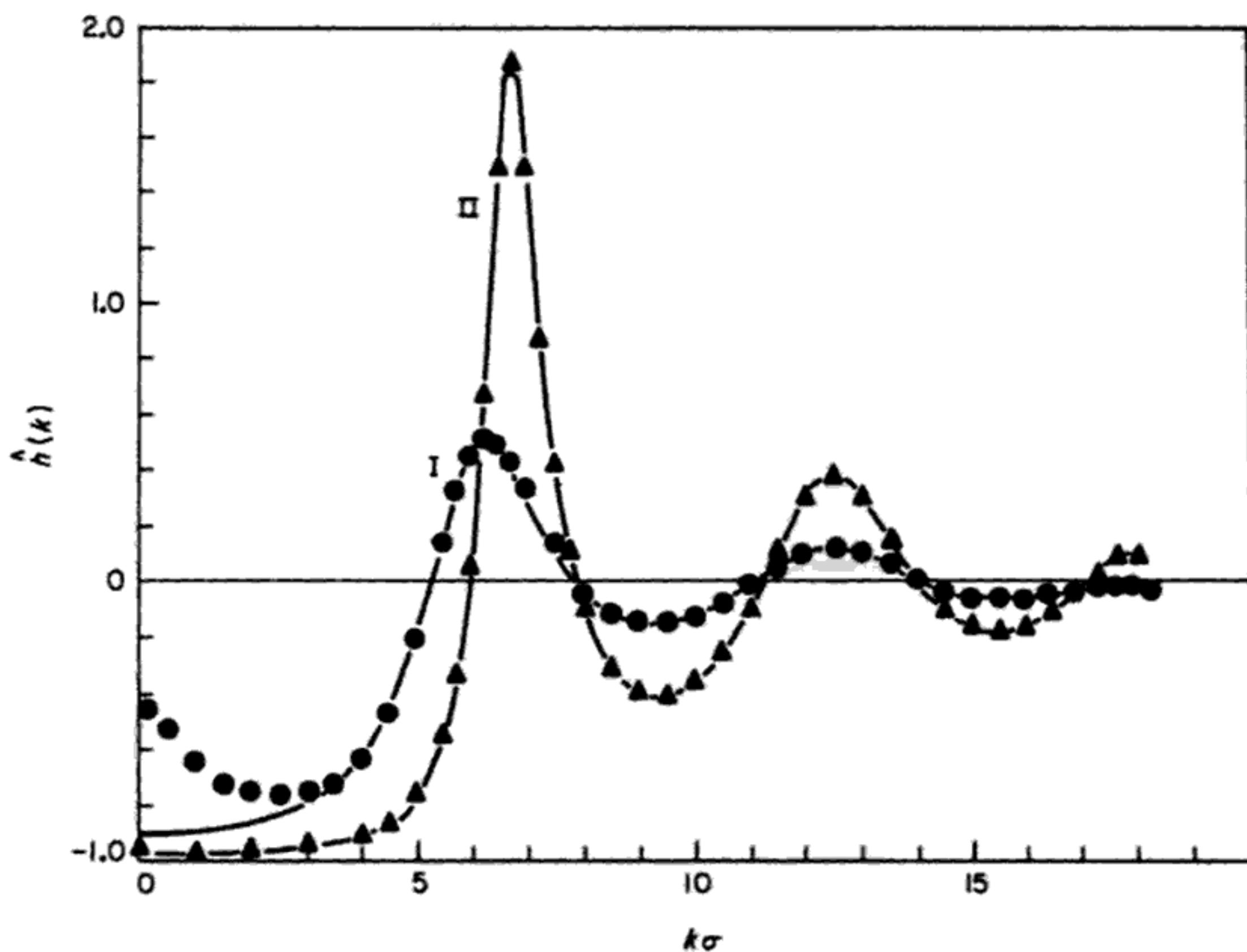


Figure 2.9 Fourier transform of the total correlation function, $S(k) - 1$, for a fluid having the same repulsive forces as those of the Lennard-Jones potential, as calculated by the relations (2.81) and (2.82) from the Percus-Yevick hard-core fluid (from Chandler and Weeks, 1970). The two states refer to $\rho\sigma^3 = 0.5426$ and $(\beta\epsilon)^{-1} = 1.326$ (state I) and to $\rho\sigma^3 = 0.844$ and $(\beta\epsilon)^{-1} = 0.723$ (state II), σ and ϵ being the usual parameters of the Lennard-Jones potential. The circles and the triangles are molecular dynamics results by Verlet (1968) for the full Lennard-Jones potential, including an attractive tail.

This simple approximation yields excellent agreement with the Monte Carlo data on the equation of state, at the expense of having a hard-core diameter which is dependent on temperature and density.

The results for $S(k) - 1$ obtained by this approximation are compared with the molecular dynamics results of Verlet (1968) for a Lennard-Jones fluid in figure 2.9 (from Chandler and Weeks, 1970). The agreement is especially remarkable because the theory has omitted the attractive part of the potential, but evidently the latter becomes noticeable only at relatively small wave vectors ($k\sigma \lesssim \pi$, where σ is the radial parameter in the Lennard-Jones potential) and that only if the density is not too high. The parallel results for $g(r)$ at high density are reported in figure 2.10, where they are also compared with the numerical solution of the Percus-Yevick theory for the full Lennard-Jones potential given by Mandel, Bearman and Bearman (1970). As noted by Chandler and Weeks, their results for $g(r)$ are much poorer at lower densities, where the errors in $S(k)$ at small k affect the form of $g(r)$ at all r .

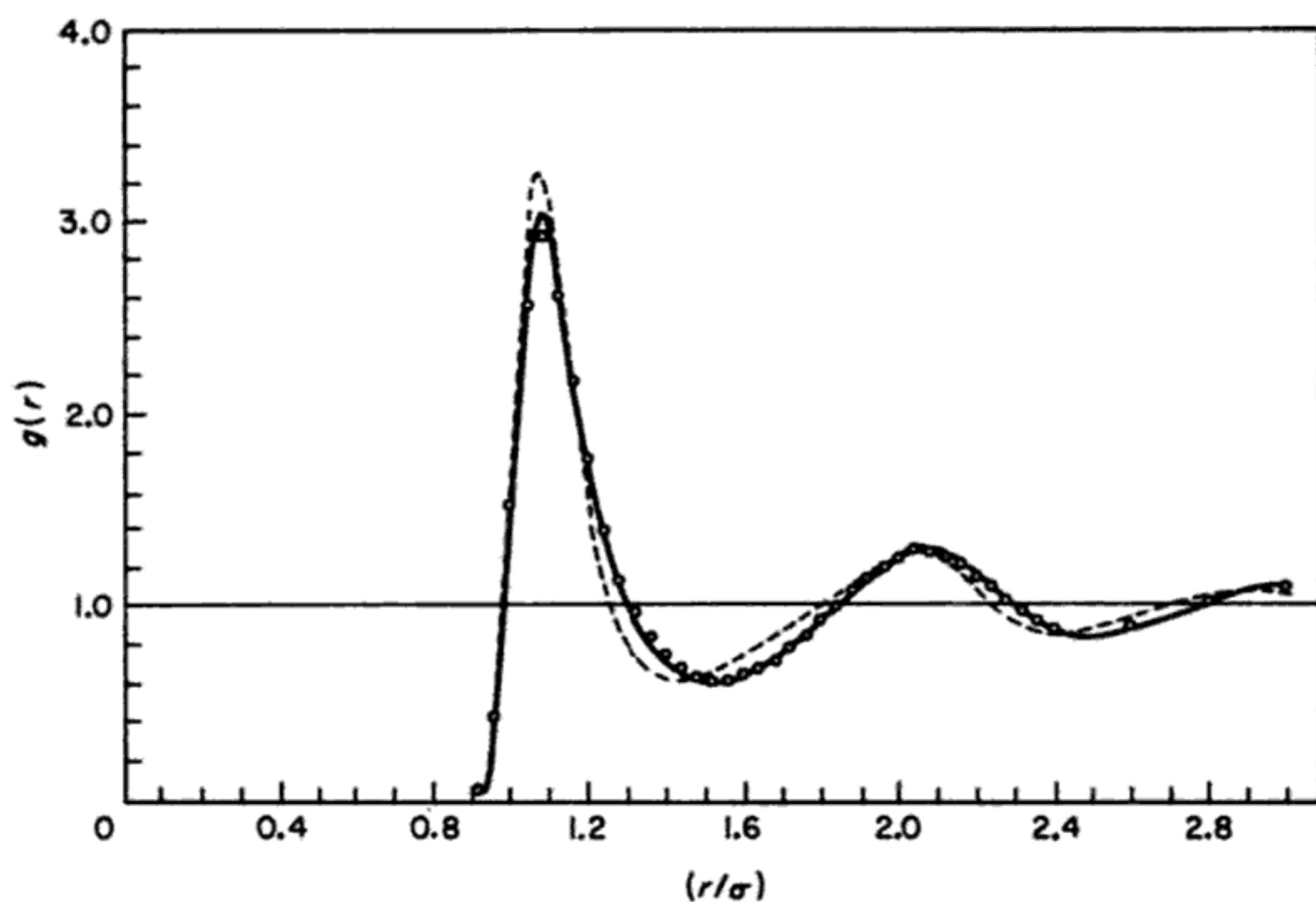


Figure 2.10 Pair correlation function $g(r)$ for a fluid having the same repulsive forces as those of the Lennard-Jones potential, as calculated by Chandler and Weeks (1970) for $\rho\sigma^3 = 0.85$ and $(\beta\varepsilon)^{-1} = 0.88$. The results are compared with molecular dynamics results of Verlet (circles) and with the numerical Percus-Yevick solution (broken line) for the full Lennard-Jones potential

2.7 Summary and comments on approximate theories of structure

The following paragraphs summarise a few conclusions about the relative merits of the approximate theories:

- (1) For short range forces, the Percus-Yevick method seems best. In partic-

ular, the equation of state for hard spheres which it predicts is in reasonable agreement with machine calculations.

(2) The random-phase approximation, while of value as we have seen for argon, is not directly applicable to fluids until the hard core is subtracted and treated separately. It is, on the other hand, a very useful approximation for fluids with strictly long-range forces, such as plasmas (see chapter 7).

(3) It appears that the correct asymptotic result for $c(r)$ is $c(r) \sim -\phi(r)/k_B T$ provided $h^2 < |c|$, the inequality defining the range of validity readily following from the Abe approximation. The condition is satisfied well away from the critical point.

One final comment seems called for. We began by asking how $g^{(3)}$ could be related to the two-body correlations. In retrospect, it seems that we should first have asked about the range of the forces! It seems clear that a relation between $g^{(3)}$ and g , which will be useful for long-range forces, is not likely to be valid for short-range interactions. This probably means that it is going to be hard to find a single equation for relating structure and forces which will successfully describe both liquid argon and liquid lead.

CHAPTER 3

LIQUID DYNAMICS AND TIME-DEPENDENT CORRELATION FUNCTIONS

3.1 Time-dependent density correlations

We shall introduce the van Hove correlation function in an intuitive way, and will later point out its intimate connection with neutron scattering (van Hove 1954a). We argue purely classically at first. Suppose that we define $G(\mathbf{r}, t)$ as the average density of atoms at the point \mathbf{r} at time t , if an atom was at the origin $\mathbf{r}=0$ at time $t=0$. Thus, $G(\mathbf{r}, t)$ gives us the correlation in the positions of two atoms, which may or may not be different, at different times. This function can be expressed in the form

$$G(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i,j=1}^N \delta[\mathbf{r} + \mathbf{R}_i(0) - \mathbf{R}_j(t)] \right\rangle \quad (3.1)$$

The average of the δ function involved in eqn (3.1) is obviously the probability that at time t the j th atom will be at \mathbf{r} with respect to the position of the i th atom at time $t=0$. We then sum this probability over j and average over i . $G(\mathbf{r}, t)$ is the space-time pair correlation function.

The quantum mechanical generalisation of eqn (3.1) is, in fact,

$$G_{\text{Quantum}}(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i,j=1}^N \int d\mathbf{r}' \delta[\mathbf{r} + \mathbf{R}_i(0) - \mathbf{r}'] \delta[\mathbf{r}' - \mathbf{R}_j(t)] \right\rangle \quad (3.2)$$

where $\mathbf{R}_i(0)$ and $\mathbf{R}_j(t)$ are now Heisenberg operators which do not commute. If this failure to commute is ignored, it proves possible to integrate over \mathbf{r}' , and then eqn (3.1) is regained.

An alternative and sometimes useful form for $G(\mathbf{r}, t)$ is obtained by introducing the density operator $\rho(\mathbf{r}, t)$ of the atoms at the point \mathbf{r} at the time t (cf. eqn (1.16)):

$$\rho(\mathbf{r}, t) = \sum_{i=1}^N \delta[\mathbf{r} - \mathbf{R}_i(t)] \quad (3.3)$$

If we employ this form in the definition (3.2) and change the origin by substituting $\mathbf{r}'' = \mathbf{r}' - \mathbf{r}$ we find

$$G(\mathbf{r}, t) = \frac{1}{N} \left\langle \int d\mathbf{r}'' \rho(\mathbf{r}'', 0) \rho(\mathbf{r}'' + \mathbf{r}, t) \right\rangle \quad (3.4)$$

Thus, we can interpret $G(\mathbf{r}, t)$ as the space-time correlation of the density ρ .

If we now take explicit account of the homogeneity of the liquid, then the integrand in (3.4) is independent of \mathbf{r}' and we find

$$G(\mathbf{r} - \mathbf{r}', t - t') = \frac{1}{\rho} \langle \rho(\mathbf{r}', t') \rho(\mathbf{r}, t) \rangle \quad (3.5)$$

At this point we follow van Hove, and take the diagonal term $i=j$ out of the sum over i and j in (3.2) when we obtain

$$G(\mathbf{r}, t) = G_s(\mathbf{r}, t) + G_d(\mathbf{r}, t) \quad (3.6)$$

where

$$G_s(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \int d\mathbf{r}' \delta[\mathbf{r} + \mathbf{R}_i(0) - \mathbf{r}'] \delta[\mathbf{r}' - \mathbf{R}_i(t)] \right\rangle \quad (3.7)$$

and

$$G_d(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i \neq j=1}^N \int d\mathbf{r}' \delta[\mathbf{r} + \mathbf{R}_i(0) - \mathbf{r}'] \delta[\mathbf{r}' - \mathbf{R}_j(t)] \right\rangle \quad (3.8)$$

By this separation, we can interpret G_s as the correlation function which tells us the probability that a particle which was at the origin at time $t=0$, will be at \mathbf{r} at time t . The part G_d obviously refers to the analogous conditional probability of finding a different atom at \mathbf{r} at time t .

Let us now investigate the correlation functions at time $t=0$. Going back to (3.2) and noting that $\mathbf{R}_i(0)$ and $\mathbf{R}_j(0)$ commute, we can integrate over \mathbf{r}' (cf. remarks after (3.2)) and we find

$$G(\mathbf{r}, 0) = \frac{1}{N} \left\langle \sum_{i,j=1}^N \delta[\mathbf{r} + \mathbf{R}_i(0) - \mathbf{R}_j(0)] \right\rangle \quad (3.9)$$

Splitting this according to (3.6), we find almost immediately

$$G_s(\mathbf{r}, 0) = \delta(\mathbf{r}) \quad (3.10)$$

$$G(\mathbf{r}, 0) = \delta(\mathbf{r}) + \rho g(r) \quad (3.11)$$

where $g(r)$ is given by

$$\rho g(r) = \frac{1}{N} \sum_{i \neq j=1}^N \langle \delta(\mathbf{r} + \mathbf{R}_i - \mathbf{R}_j) \rangle \quad (3.12)$$

the usual radial distribution function we have discussed earlier.

In the limit of long times, we can assume there is no correlation between positions of particles. Thus, in (3.2) we can replace the average of the product of the δ -functions by the product of the averages:

$$\sum_{i,j=1}^N \langle \delta[\mathbf{r} + \mathbf{R}_i(0) - \mathbf{r}'] \delta[\mathbf{r}' - \mathbf{R}_j(t)] \rangle \sim \left\langle \sum_{i=1}^N \delta[\mathbf{r} + \mathbf{R}_i(0) - \mathbf{r}'] \right\rangle \left\langle \sum_{j=1}^N \delta[\mathbf{r}' - \mathbf{R}_j(t)] \right\rangle \quad (3.13)$$

Thus, for large t (or, in the absence of long-range order, for large r) we may write

$$G(r, t) \approx \frac{1}{N} \int d\mathbf{r}' \rho(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}') \quad (3.14)$$

For systems with long-range order, $\rho(\mathbf{r})$ and $G(r, t)$ are periodic in space. For a fluid, $\rho = N/V$ where V is the volume, and therefore

$$G(r, \infty) \approx \rho \quad (3.15)$$

Similarly, for the self-correlation function we can show that for a homogeneous system

$$G_s(r, \infty) = \frac{1}{V} \quad (3.16)$$

which tends to zero as V tends to infinity. This is in marked contrast to the situation in which atoms are not free to move far from some 'lattice' sites. In this case, appropriate to solids when we neglect diffusion, $G_s(r, \infty) \neq 0$.

For short times $G_s(r, t)$ approximates to a δ -function according to (3.10), while $G_d(r, t)$ is approximately the pair correlation function $g(r)$. As $t \rightarrow \infty$, $G_s(r, t) \rightarrow 0$ and $G_d(r, t) \rightarrow \rho$, and these forms are shown schematically in figure 3.1.

3.2 Intermediate scattering function and van Hove structure factor

Having defined the time-dependent correlation function $G(r, t)$, and having examined its general properties for short and for long times, we shall proceed to discuss two equivalent forms. Whereas $G(r, t)$ is a sum of two parts G_s and G_d , the latter part being the time-dependent generalisation of the radial distribution function $g(r)$ (actually $G_d \rightarrow \rho g(r)$ as $t \rightarrow 0$), the desired generalisation of the structure factor $S(k)$ is obtained by taking a double Fourier transform of $G(r, t)$. The resulting function $S(k, \omega)$, introduced by van Hove (1954a) and known as the dynamic structure factor, is directly related to inelastic scattering of neutrons from the fluid and gives the probability that there is a momentum transfer $\hbar k$ and an energy transfer $\hbar \omega$ between the neutron and the fluid.

3.2.1 Intermediate scattering function

We begin by taking the space Fourier transform of $G(r, t)$, which defines the so-called intermediate scattering function $F(k, t)$,

$$F(k, t) = \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) G(r, t) \quad (3.17)$$

with a corresponding relation between $G_s(r, t)$ and $F_s(k, t)$. Using (3.5), and taking account of the homogeneity of the liquid, we immediately find

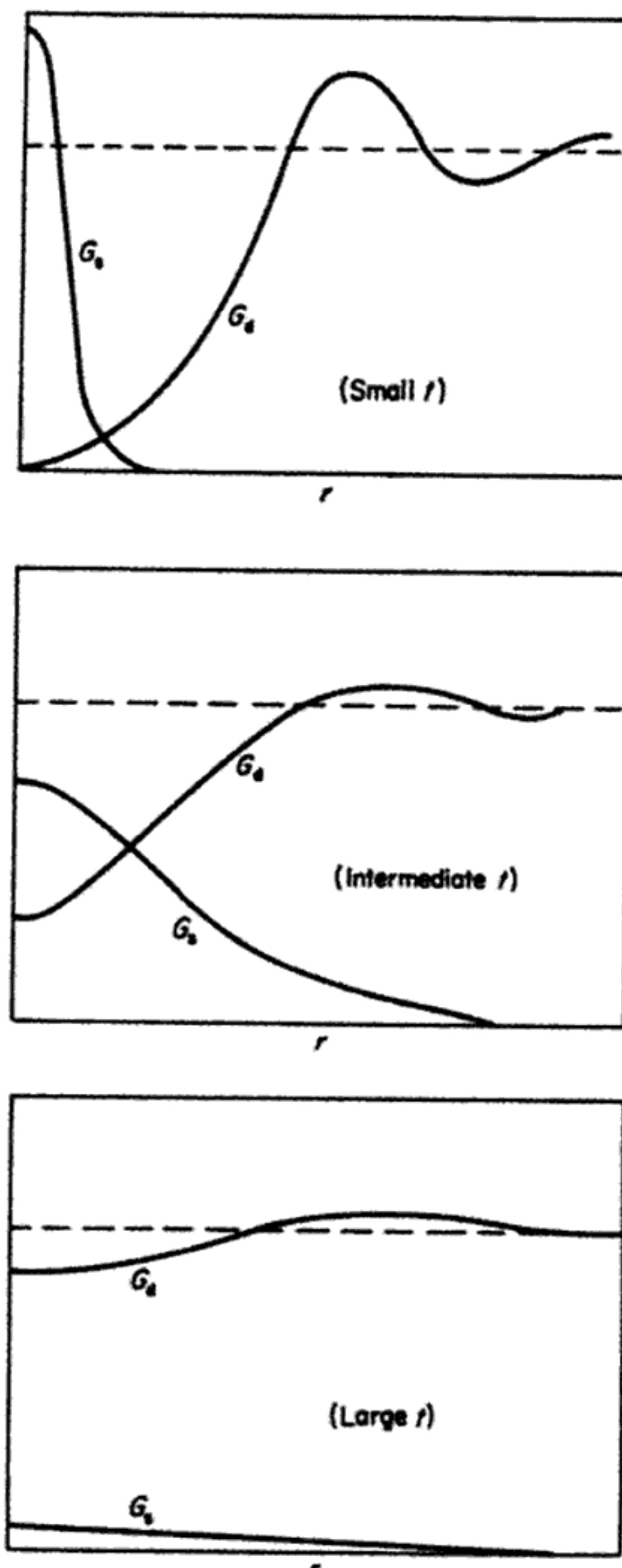


Figure 3.1 Schematic drawing of the spreading of the van Hove correlation functions with increasing time

$$\begin{aligned}
 F(k, t) &= \frac{1}{\rho} \int d(\mathbf{r} - \mathbf{r}') \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')] \langle \rho(\mathbf{r}', 0) \rho(\mathbf{r}, t) \rangle \\
 &= \frac{1}{N} \iint d\mathbf{r} d\mathbf{r}' \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')] \langle \rho(\mathbf{r}', 0) \rho(\mathbf{r}, t) \rangle = \frac{1}{N} \langle \rho_{-\mathbf{k}}(0) \rho_{\mathbf{k}}(t) \rangle \quad (3.18)
 \end{aligned}$$

where

$$\rho_{\mathbf{k}}(t) = \sum_{i=1}^N \exp[i\mathbf{k} \cdot \mathbf{R}_i(t)] \quad (3.19)$$

is the space Fourier transform of the density operator introduced in (3.3). As we see by comparison with (2.49), $F(\mathbf{k}, t)$ is the time dependent generalisation of the structure factor $S(\mathbf{k})$, and describes time correlations between density fluctuations of equal and opposite wave vector.

The physical meaning of the intermediate scattering function is clear from (3.18). According to this equation, $F(\mathbf{k}, t)$ expresses the probability amplitude that, having started with the fluid in its equilibrium state and having created a density fluctuation of wave vector \mathbf{k} at time t and a density fluctuation of wave vector $-\mathbf{k}$ at time $t=0$, we find the system again in the same equilibrium state. We clearly must expect that, if such a density fluctuation is an exact eigenmode of the fluid, then $F(\mathbf{k}, t)$ will vary with time as $\exp(-i\omega_{\mathbf{k}}t)$ where $\omega_{\mathbf{k}}$ is the frequency of the eigenmode. More generally, the decay of $F(\mathbf{k}, t)$ in time will be determined by the lifetime of approximate eigenmodes of the system with wave vector \mathbf{k} . In practice, we shall usually meet situations where the density fluctuations are overdamped oscillations, except for special ranges of wave vector.

We also find from (3.7)

$$F_s(k, t) \equiv \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) G_s(r, t) = \langle \exp[-i\mathbf{k} \cdot \mathbf{R}_1(0)] \exp[i\mathbf{k} \cdot \mathbf{R}_1(t)] \rangle \quad (3.20)$$

where $\mathbf{R}_1(t)$ denotes the position of any one particle in the fluid at time t .

3.2.2 Dynamic structure factor $S(k, \omega)$

We now define the dynamic structure factor $S(k, \omega)$ as

$$\begin{aligned} S(k, \omega) &= \int dt \exp(-i\omega t) F(k, t) \\ &= \int \int d\mathbf{r} dt \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] G(r, t) \end{aligned} \quad (3.21)$$

with an analogous definition for $S_s(k, \omega)$ in terms of $F_s(k, t)$ and $G_s(r, t)$. If we introduce the frequency components of the density fluctuations,

$$\rho_{\mathbf{k}}(\omega) = \int dt \exp(-i\omega t) \rho_{\mathbf{k}}(t) \quad (3.22)$$

and take into account the invariance of the fluid at equilibrium under time translation, we find that $S(k, \omega)$ is determined by the correlations between the frequency components of the density fluctuations according to

$$\langle \rho_{-\mathbf{k}}(\omega') \rho_{\mathbf{k}}(\omega) \rangle = 2\pi S(k, \omega) \delta(\omega + \omega') \quad (3.23)$$

Thus, $S(k, \omega)$ gives the frequency spectrum of the correlations between density fluctuations of the given wave vector.

According to the argument developed in the preceding section, we expect that an approximate eigenmode of the fluid will appear in $S(k, \omega)$ as a more or less sharp peak at the frequency of the mode. Also, we note that

$$\int \frac{d\omega}{2\pi} S(k, \omega) = F(k, 0) = S(k) \quad (3.24)$$

the usual (static) structure factor.

3.2.3 Relation to neutron scattering

The process of inelastic scattering of a beam of incident particles (typically, neutrons) from a liquid serves as a microscopic probe of the dynamics of this many-particle system. More precisely, as first shown by van Hove (1954a), a measurement of coherent inelastic scattering yields $S(k, \omega)$ (see, for example, Lomer and Low, 1965; Marshall and Lovesey, 1973). Actually, this result is a special case of the fluctuation-dissipation theorem (see section 3.2.5 below) in statistical mechanics (Callen and Welton, 1951), according to which a measurement of the dissipation of energy by an external probe weakly coupled to a many-particle system is directly related to correlations between *equilibrium* fluctuations in the system.

To discuss the process of neutron inelastic scattering, we consider the neutron as coupled to the fluid through a Hamiltonian

$$H_1 = \sum_{i=1}^N V_i(|R_i - R_n|) = \int d\mathbf{r} \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{R}_i) V_i(|\mathbf{r} - \mathbf{R}_n|) \quad (3.25)$$

where \mathbf{R}_n is the position of the neutron and $V_i(|\mathbf{r} - \mathbf{R}_n|)$ is the potential of interaction between the neutron and the nucleus of the i th atom. This interaction depends on the individual nucleus, as indicated by the suffix i , since even a pure liquid is usually a mixture of different isotopes. In practice, a Fermi δ -function potential (Fermi, 1936)

$$V_i(|\mathbf{r} - \mathbf{R}_n|) = a_i \delta(\mathbf{r} - \mathbf{R}_n) \quad (3.26)$$

provides a good representation of the neutron-nucleus interaction, whose properties are thus fully described by just one nuclear parameter, the scattering length a_i .

If we assume the interaction (3.25) to be weak, we can use the golden rule formula of perturbation theory to write the probability of a process in which the neutron transfers momentum $\hbar\mathbf{k}$ and energy $\hbar\omega$ to the fluid as

$$P(\mathbf{k}, \omega) = \frac{2\pi}{\hbar} \sum_m w_m \sum_{m'} |M_{m'm}(\mathbf{k})|^2 \delta(E_{m'} - E_m - \hbar\omega) \quad (3.27)$$

where the transition matrix element $M_{m',m}(\mathbf{k})$ is given by

$$M_{m',m}(\mathbf{k}) = \int d\mathbf{R}_n \exp(-i\mathbf{k}'_n \cdot \mathbf{R}_n) \langle \Psi_{m'} | H_1 | \Psi_m \rangle \exp(i\mathbf{k}_n \cdot \mathbf{R}_n) \quad (3.28)$$

In this equation, the initial and the final state of the neutron are plane waves of wave vectors \mathbf{k}_n and \mathbf{k}'_n , with $\mathbf{k}_n - \mathbf{k}'_n = \mathbf{k}$; Ψ_m and $\Psi_{m'}$ are the initial and the final state of the fluid, of energies E_m and $E_{m'}$; and we have supposed that the fluid is initially in its equilibrium state described by the distribution w_m . Use of (3.25) yields

$$M_{m',m}(\mathbf{k}) = \sum_{i=1}^N \mathcal{V}_i(k) \langle \Psi_{m'} | \exp(i\mathbf{k} \cdot \mathbf{R}_i) | \Psi_m \rangle \quad (3.29)$$

where $\mathcal{V}_i(k)$ is the Fourier transform of the neutron-nucleus interaction, which, of course, reduces to a_i for the Fermi potential. By using the integral representation of the δ -function,

$$\delta(E_{m'} - E_m - \hbar\omega) = \frac{\hbar}{2\pi} \int dt \exp[i\hbar(E_{m'} - E_m - \hbar\omega)/\hbar] \quad (3.30)$$

and the usual definition of an operator in the Heisenberg representation, we can now write (3.27) in the form

$$\begin{aligned} P(\mathbf{k}, \omega) &= \sum_{i,j=1}^N \mathcal{V}_i(k) \mathcal{V}_j^*(k) \int dt \exp(-i\omega t) \sum_{m,m'} w_m \langle \Psi_{m'} | \exp[-i\mathbf{k} \cdot \mathbf{R}_i(0)] | \Psi_m \rangle \\ &\times \langle \Psi_{m'} | \exp[i\mathbf{k} \cdot \mathbf{R}_j(t)] | \Psi_m \rangle = \sum_{i,j=1}^N \mathcal{V}_i(k) \mathcal{V}_j^*(k) \int dt \exp(-i\omega t) \sum_m w_m \\ &\times \langle \Psi_m | \exp[-i\mathbf{k} \cdot \mathbf{R}_i(0)] \exp[i\mathbf{k} \cdot \mathbf{R}_j(t)] | \Psi_m \rangle = \sum_{i,j=1}^N \mathcal{V}_i(k) \mathcal{V}_j^*(k) \\ &\times \int dt \exp(-i\omega t) \langle \exp[-i\mathbf{k} \cdot \mathbf{R}_i(0)] \exp[i\mathbf{k} \cdot \mathbf{R}_j(t)] \rangle \end{aligned} \quad (3.31)$$

If the fluid contains only one type of nucleus, that is $\mathcal{V}_i(k) = \mathcal{V}(k)$, then the above expression becomes

$$\begin{aligned} P_{coh}(\mathbf{k}, \omega) &= |\mathcal{V}(k)|^2 \int dt \exp(-i\omega t) \sum_{i,j=1}^N \langle \exp[-i\mathbf{k} \cdot \mathbf{R}_i(0)] \exp[i\mathbf{k} \cdot \mathbf{R}_j(t)] \rangle \\ &= N|\mathcal{V}(k)|^2 \int dt \exp(-i\omega t) F(k, t) \\ &= N|\mathcal{V}(k)|^2 S(k, \omega) \end{aligned} \quad (3.32)$$

Thus, the differential scattering cross-section, which differs from $P(\mathbf{k}, \omega)$ merely by a trivial kinetic factor, is proportional to the dynamic structure factor.

In a mixture of isotopes, instead, (3.32) gives only the coherent part of the

scattering, with $\mathcal{V}(k)$ defined by

$$\mathcal{V}(k) = \frac{1}{N} \sum_{i=1}^N \mathcal{V}_i(k) \equiv \overline{\mathcal{V}(k)} \quad (3.33)$$

The remaining part, namely the incoherent scattering

$$P_{\text{incoh}}(\mathbf{k}, \omega) = \sum_{i,j=1}^N [\mathcal{V}_i(k)\mathcal{V}_j^*(k) - |\overline{\mathcal{V}(k)}|^2] \int dt \exp(-i\omega t) \langle \exp[-i\mathbf{k} \cdot \mathbf{R}_i(0)] \\ \exp[i\mathbf{k} \cdot \mathbf{R}_j(t)] \rangle \quad (3.34)$$

may be expressed through $S_s(k, \omega)$ if we assume that the expression in the square bracket becomes negligible for $i \neq j$. We then find

$$P_{\text{incoh}}(\mathbf{k}, \omega) = \sum_{i=1}^N [|\mathcal{V}_i(k)|^2 - |\overline{\mathcal{V}(k)}|^2] \int dt \exp(-i\omega t) \langle \exp[-i\mathbf{k} \cdot \mathbf{R}_i(0)] \\ \exp[i\mathbf{k} \cdot \mathbf{R}_i(t)] \rangle \\ = N |\overline{\delta \mathcal{V}(k)}|^2 \int dt \exp(-i\omega t) F_s(k, t) \\ = N |\overline{\delta \mathcal{V}(k)}|^2 S_s(k, \omega) \quad (3.35)$$

with

$$|\overline{\delta \mathcal{V}(k)}|^2 = \frac{1}{N} \sum_{i=1}^N |\mathcal{V}_i(k)|^2 - |\overline{\mathcal{V}(k)}|^2 = \langle |\mathcal{V}(k)|^2 \rangle - |\overline{\mathcal{V}(k)}|^2 \quad (3.36)$$

The neutron inelastic scattering from an isotopic mixture is discussed more systematically in appendix 6.6.

The above results actually describe inelastic scattering of any type of particles coupled to the fluid by an interaction of the type (3.25). Cold neutrons from a nuclear reactor provide the best microscopic probe for liquids because both their momenta and energies are in the range of the characteristic wave vectors and frequencies for the dynamics of liquids ($k \sim 1 \text{ \AA}^{-1}$, $\omega \sim 10^{13} \text{ sec}^{-1}$), and it is therefore feasible to perform an energy analysis of the radiation scattered within a given solid angle.[†] In an X-ray scattering experiment, with wave vectors of the order of 1 \AA^{-1} the incoming photons have an energy which is larger than the energy transferred to atomic motions by several orders of magnitude. Thus, X-ray scattering experiments are used to measure $S(k)$, that is, the dynamic structure factor integrated over all energy transfers (see (3.24)). On the other hand, an energy analysis of inelastically scattered photons becomes feasible for photons in the infrared, but then the transferred wave vector is bound to be very small, and the experiment provides information only on long wavelength density fluctuations in the fluid. We shall briefly discuss such experiments in the next chapter, in connection with the hydrodynamic modes.

[†]For a recent review of neutron inelastic scattering from monatomic liquids, see Copley and Lovesey (1974).

3.2.4 Relation between $S(k, \omega)$ and self-function $S_s(k, \omega)$

Equation (3.18) for the intermediate scattering function can be written

$$\begin{aligned} F(k, t) &= F_s(k, t) + \frac{1}{N} \sum_{i \neq j=1}^N \langle \exp[-ik \cdot R_i(0)] \exp[ik \cdot R_j(t)] \rangle \\ &= F_s(k, t) + \frac{1}{N} \sum_{i \neq j=1}^N \langle \exp[-ik \cdot [R_i(0) - R_j(0)]] \exp[-ik \cdot R_j(0)] \\ &\quad \times \exp[ik \cdot R_j(t)] \rangle \end{aligned} \quad (3.37)$$

If we now approximate the thermal average in the above equation by the product of two thermal averages, we can write

$$\begin{aligned} F(k, t) &\simeq F_s(k, t) + [F(k, 0) - 1] F_s(k, t) \\ &= S(k) F_s(k, t) \end{aligned}$$

or equivalently

$$S(k, \omega) = S(k) S_s(k, \omega) \quad (3.38)$$

which is the so-called convolution approximation proposed by Vineyard (1958). It is clearly equivalent to expressing the difference between $G(r, t)$ and $G_s(r, t)$ as a convolution of $G_s(r, t)$ and $g(r)$,

$$G(r, t) = G_s(r, t) + \rho \int d\mathbf{r}' g(\mathbf{r}') G_s(\mathbf{r} - \mathbf{r}', t) \quad (3.39)$$

as is easily verified by Fourier transform. The approximation thus assumes that the motion of an atom which at time $t=0$ is at a distance \mathbf{r}' from the atom at the origin is not affected by the presence of the latter atom.

The convolution approximation provides a simple way of relating the coherent scattering to the incoherent scattering if the structure of the liquid is known. A number of its deficiencies have been pointed out over the years, one such deficiency being its inapplicability in the hydrodynamic regime, where it fails to predict the existence of the Brillouin doublet (see section 4.3). The approximation as originally proposed is also unsatisfactory in the finite frequency regime of interest in neutron scattering, as it violates the moment sum rules for the scattering function starting from the second moment (see section 3.3). This defect can, however, be partly remedied by simple modifications (Sköld, 1967; Rahman, 1967a) which satisfy up to the fourth moment sum rule and provide empirically useful relations between coherent and incoherent scattering functions through the static structure factor. For instance, the recipe proposed by Sköld (1967) satisfies the second moment sum rule by scaling the wave vector in $F_s(k, t)$ on the right-hand side of (3.38), which is written in the form

$$F(k, t) = S(k) F_s(k / \sqrt{S(k)}, t) \quad (3.40)$$

This relation has proved successful in the analysis of neutron scattering from liquid argon.

Actually, Vineyard's philosophy of expressing the dynamic structure factor $S(k, \omega)$ in terms of the self-function $S_s(k, \omega)$ and the static structure factor $S(k)$ has been shown by Gyorffy and March (1971) to be exact in the sense that $S(k, \omega)$ is a functional of $S_s(k, \omega)$, plus the static correlation functions. Some approximate forms of such a functional relation are available (see, for example, Hubbard and Beeby, 1969; Kerr, 1968; Singwi, Skold and Tosi, 1970) going beyond the Vineyard form corresponding to (3.38). Barker et al. (1973) discuss, from experiment, some features of such a functional relation.

3.2.5 Fluctuation-dissipation theorem

We conclude this section by giving the explicit relation between the dynamic structure factor $S(k, \omega)$ and the density response function $\chi(k, \omega)$. The latter is introduced by considering the fluid under a weak potential field $V_e(\mathbf{r}, t)$ coupled with the density fluctuations, which to linear terms produces a density change $\delta\rho(\mathbf{r}, t)$ given by

$$\delta\rho(\mathbf{r}, t) = \int \int d\mathbf{r}' dt' \chi(\mathbf{r} - \mathbf{r}', t - t') V_e(\mathbf{r}', t') \quad (3.41)$$

or, in Fourier transform,

$$\rho_{\mathbf{k}}(\omega) = \chi(\mathbf{k}, \omega) V_e(\mathbf{k}, \omega) \quad (3.42)$$

Explicit calculation by time-dependent perturbation theory yields

$$\chi(\mathbf{k}, \omega) = \frac{1}{\hbar} \sum_{m,m'} w_m |\langle \Psi_m | \rho_{\mathbf{k}}^+ | \Psi_m' \rangle|^2 \left\{ \frac{1}{\omega - \omega_{m'm} + i\eta} - \frac{1}{\omega + \omega_{m'm} + i\eta} \right\} \quad (3.43)$$

where $\omega_{m'm} = (E_{m'} - E_m)/\hbar$ and $\eta = 0^+$. If we write

$$\chi(\mathbf{k}, \omega) = \chi'(k, \omega) + i\chi''(k, \omega) \quad (3.44)$$

and use the identity

$$\frac{1}{x \pm i\eta} = P \left(\frac{1}{x} \right) \mp i\pi\delta(x) \quad (3.45)$$

comparison with eqns (3.32) and (3.27) yields

$$\begin{aligned} \chi''(k, \omega) &= -\frac{\rho}{2\hbar} [S(k, \omega) - S(-k, -\omega)] \\ &= -\frac{\rho}{2\hbar} [1 - \exp(-\hbar\beta\omega)] S(k, \omega) \\ &\xrightarrow{(\hbar \rightarrow 0)} -\frac{\rho\omega}{2k_B T} S(k, \omega) \end{aligned} \quad (3.46)$$

This is the precise statement of the fluctuation-dissipation theorem in the present case. Of course, the imaginary part of the response function describes energy dissipation in the system, while its real part describes reversible polarisation processes.

Since $\delta\rho(\mathbf{r}, t)$ cannot depend on $V_e(\mathbf{r}', t')$ at times t' later than t , $\chi(\mathbf{r}, t)$ must vanish when $t < 0$. This causality condition is ensured by the small imaginary part in the denominators of eqn (3.43). In turn, this mathematical statement implies the existence of a dispersion relation of the form

$$\chi(k, \omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega' \frac{\chi''(k, \omega')}{\omega' - \omega - i\eta} \quad (3.47)$$

namely, $\chi''(k, \omega)$ serves as the spectral density for $\chi(k, \omega)$. The above relation implies that $\chi'(k, \omega)$ and $\chi''(k, \omega)$ are related by Kramers-Kronig relations. For a classical fluid these relations yield in particular,

$$S(k) = - \frac{k_B T}{\rho} \chi(k, 0) \quad (3.48)$$

as is easily seen from (3.47) and (3.46).

3.3 Moments of van Hove correlation functions and short-time expansions

From the definitions given in section 3.2.2 we have for the second moment of $S_s(k, \omega)$:

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^2 S_s(k, \omega) = - \left. \frac{\partial^2 F_s(k, t)}{\partial t^2} \right|_{t=0} \quad (3.49)$$

Similarly, for the fourth moment we may write

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^4 S_s(k, \omega) = \left. \frac{\partial^4 F_s(k, t)}{\partial t^4} \right|_{t=0} \quad (3.50)$$

Thus, if the second and fourth time derivatives of $F_s(k, t)$ can be found from (3.20), we have the desired expressions for the moments.

To evaluate these derivatives, we find it convenient to develop the small time expansion of (3.20). Then, if we denote by $x_1(t)$ the component of $\mathbf{R}_1(t)$ along \mathbf{k} and use

$$x_1(t) = x_1(0) + t\dot{x}_1(0) + \frac{1}{2!} t^2 \ddot{x}_1(0) + \dots \quad (3.51)$$

we have

$$F_s(k, t) = \langle \exp [ikt\dot{x}_1(0)] \exp [ikt^2 \ddot{x}_1(0)/2!] \exp [ikt^3 \ddot{x}_1(0)/3!] \dots \rangle \quad (3.52)$$

The coefficient of t^2 in the short-time expansion of (3.52) is given by

$$\frac{ikt^2}{2!} \langle \ddot{x}_1(0) \rangle - \frac{k^2 t^2}{2!} \langle \{\dot{x}_1(0)\}^2 \rangle,$$

where the first term clearly averages to zero, while the second term gives the result

$$\left. \frac{\partial^2 F_s(k, t)}{\partial t^2} \right|_{t=0} = -k^2 \langle \{ \dot{x}_1(0) \}^2 \rangle \quad (3.53)$$

But the thermal average of $\langle \{ \dot{x}_1(0) \}^2 \rangle$ is given by

$$\frac{1}{2} m \langle \{ \dot{x}_1(0) \}^2 \rangle = \frac{1}{2} k_B T \quad (3.54)$$

and combining (3.49), (3.53) and (3.54) we find

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^2 S_s(k, \omega) = k^2 k_B T / m \quad (3.55)$$

Actually, from the definition of $F(k, t)$ as

$$F(k, t) = \sum_i \langle \exp [+ik \cdot \{ \mathbf{R}_i(0) - \mathbf{R}_i(t) \}] \rangle$$

the distinct term $i \neq 1$ vanishes to order t^2 , since the velocities of two atoms taken at the same instant of time are uncorrelated. Hence

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^2 S(k, \omega) = k^2 k_B T / m \quad (3.56)$$

for classical fluids. Clearly the behaviour of the fluid to order t^2 is thus described by a free particle model.

We show in appendix 3.1 that the fourth moments for classical fluids in terms of the radial distribution function $g(r)$ and the pair potential $\phi(r)$ are (de Gennes, 1959):

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^4 S_s(k, \omega) &= 3k^4 (k_B T)^2 / m^2 + \frac{\rho k^2 k_B T}{3m^2} \int d\mathbf{r} g(r) \nabla^2 \phi(r) \\ &= 3k^4 (k_B T)^2 / m^2 + \frac{4\pi \rho k^2 k_B T}{3m^2} \int_0^{\infty} dr r^2 g(r) \left\{ \phi''(r) + \frac{2}{r} \phi'(r) \right\} \end{aligned} \quad (3.57)$$

and

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^4 S(k, \omega) = 3k^4 (k_B T)^2 / m^2 + \frac{\rho k^2 k_B T}{m^2} \int d\mathbf{r} g(r) (1 - \cos kx) \frac{\partial^2 \phi(r)}{\partial x^2} \quad (3.58)$$

Similarly, the higher moments can be expressed in terms of the pair potential and of higher static correlation functions.

3.3.1 Asymptotic form of $G(r, t)$ at large r and short times for van der Waals forces

Using these sum rules, plus the fact that

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S(k, \omega) = S(k)$$

we can immediately expand the intermediate scattering function as

$$F(k, t) = S(k) - k^2 t^2 (k_B T) / 2m + k^4 t^4 (k_B T)^2 / 8m^2 + \rho k^2 t^4 k_B T / 24m^2 \int d\mathbf{r} g(r) (1 - \cos kr) \frac{\partial^2 \phi}{\partial x^2} \quad (3.59)$$

We can employ Fourier transform arguments referred to in section 2.5 for van der Waals forces to show that $\int d\mathbf{r} g(r) (1 - \cos kr) \frac{\partial^2 \phi}{\partial x^2}$ has a term $-\pi^2 A k^5 / 12$ as the first odd power of k in its small- k expansion. Actually the presence of this odd power of k is signalled by examining the coefficient of k^6 in the above integral. This involves $\int d\mathbf{r} g(r) r^6 \frac{\partial^2 \phi}{\partial x^2}$ and at large r the integrand (replacing $d\mathbf{r}$ by $r^2 dr$ for the dimensional argument) behaves as $r^8 \frac{\partial^2 \phi}{\partial r^2} \rightarrow \text{constant}$. Hence the integral diverges and we must have missed out a term in the expansion. Since

$$F(k, t) = \int d\mathbf{r} \exp(ik \cdot \mathbf{r}) G(r, t)$$

it is readily shown from the Lighthill theorem (1958) that the leading term in $G(r, t)$ at large r is precisely

$$G(r, t) \sim -\frac{70At^4}{m^2 r^{10}} (k_B T) \quad (3.60)$$

where, as usual, A is the strength of the van der Waals interactions. Should it prove desirable, the next term can also be calculated by this method for a Lennard-Jones (6-12) potential.

The non-analyticity arising from van der Waals interactions dominates the short-time dependence of $G(r, t)$ at large r .

3.3.2 Moments of van Hove function in quantal fluids

Finally, we shall briefly comment on the extension of the moment sum rules for $S(k, \omega)$ to the case of a quantal fluid. We note, first of all, that the moments (3.56) and (3.58) can be rewritten, in a classical fluid, as sum rules for the imaginary part of the density response function, using eqn (3.46) in the classical limit:

$$-\int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega \chi''(k, \omega) = \rho k^2 / m \quad (3.56')$$

and

$$-\int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^3 \chi''(k, \omega) = \frac{2\rho k^4 t}{m^2} + \frac{\rho^2 k^2}{m^2} \int d\mathbf{r} g(r)(1 - \cos kx) \frac{\partial^2 \phi(r)}{\partial x^2} \quad (3.58')$$

where, in the first term on the right-hand side of (3.58'), we have replaced $\frac{3}{2}k_B T$ in favour of the mean kinetic energy per particle, denoted by t . In this form, the sum rules are in fact valid in general, that is independently of the classical approximation.

If one wishes, the above relations can be rewritten as sum rules on $S(k, \omega)$, using the general form of the relation (3.46) between $\chi''(k, \omega)$ and $S(k, \omega)$. It is preferable, however, to introduce the symmetrised correlation function, $\tilde{S}(k, \omega)$ by

$$\begin{aligned} \tilde{S}(k, \omega) &= \frac{1}{2}[S(k, \omega) + S(-k, -\omega)] \\ &= \frac{1}{2}S(k, \omega)[1 + \exp(-\hbar\beta\omega)] \\ &= -\frac{\hbar}{\rho}\chi''(k, \omega)\coth(\frac{1}{2}\hbar\beta\omega) \end{aligned} \quad (3.61)$$

in terms of which the sum rules can be written as

$$\frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega \tgh(\frac{1}{2}\hbar\beta\omega) \tilde{S}(k, \omega) = k^2/m \quad (3.56'')$$

and

$$\frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^3 \tgh(\frac{1}{2}\hbar\beta\omega) S(k, \omega) = \frac{2k^4 t}{m^2} + \frac{\rho k^2}{m^2} \int d\mathbf{r} g(r)(1 - \cos kx) \frac{\partial^2 \phi(r)}{\partial x^2} \quad (3.58'')$$

These are immediately seen to reduce to (3.56) and (3.58) in the classical limit, where, $\tilde{S}(k, \omega) = S(k, \omega)$ and $\tgh(\frac{1}{2}\hbar\beta\omega) = \frac{1}{2}\hbar\beta\omega$.

Similarly, the proper expression for the zero-moment sum rule, that is the static structure factor $S(k) = \frac{1}{N} \langle \rho_k \rho_{-k} \rangle$, is

$$\begin{aligned} S(k) &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \tilde{S}(k, \omega) \\ &= -\frac{\hbar}{\rho} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \chi''(k, \omega) \coth(\frac{1}{2}\hbar\beta\omega) \end{aligned} \quad (3.24')$$

The Ornstein-Zernike relation for $S(k)$ in the long-wavelength limit is in general no longer true, but it remains obviously true that the static density response of the fluid in the long wavelength limit is related to its compressibility,

$$\lim_{k \rightarrow 0} \chi(k, 0) = -\rho^2 K_T \quad (1.27')$$

In the classical limit, using (3.48), this reduces to the Ornstein-Zernike relation (1.27).

3.4 Simple models for $S_s(k, \omega)$ and $S(k, \omega)$

Before we begin to enquire into the general structure and properties of the dynamic structure factors $S_s(k, \omega)$ and $S(k, \omega)$, it will be instructive to evaluate these functions for a few simple models of the dynamics of fluids. The models actually approach the behaviour of real liquids under certain conditions of wave vector and frequency, as we shall see.

3.4.1 Free-particle model

The first simple model that we shall consider is that of a classical perfect gas. We expect that a real fluid will behave as an assembly of free particles in a scattering process at high momentum and energy transfer, or, in other words, that its dynamics will approach this model in the limit of extremely small distances and times.

From (3.20) we find that for a classical perfect gas, using $R_1(t) = R_1(0) + p_1 t/m$, the intermediate scattering self-function is

$$F_s(k, t) = \langle \exp(i\mathbf{k} \cdot \mathbf{p}_1 t/m) \rangle = \left[\int d\mathbf{p}_1 \exp[-p_1^2/(2mk_B T)] \exp(i\mathbf{k} \cdot \mathbf{p}_1 t/m) \right] / \int d\mathbf{p}_1 \exp[-p_1^2/(2mk_B T)] = \exp[-k^2 t^2 k_B T / 2m] \quad (3.62)$$

and correspondingly

$$S_s(k, \omega) = \int_{-\infty}^{\infty} dt \exp(-i\omega t) \exp(-k^2 t^2 k_B T / 2m) \\ = \left(\frac{2\pi m}{k_B T k^2} \right)^{1/2} \exp[-m\omega^2/(2k^2 k_B T)] \quad (3.63)$$

These are Gaussian functions with half-width determined by $k^2 \langle v_x^2 \rangle$, where $\langle v_x^2 \rangle \equiv k_B T / m$ is the mean square thermal velocity along \mathbf{k} . Furthermore, since no correlations between positions or velocities of different particles exist in a classical perfect gas, we immediately find that in this model $G_d(r, t) = 0$ and $S(k, \omega) = S_s(k, \omega)$.

From the above results for a classical perfect gas it is easily found that

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^2 S_s(k, \omega) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^2 S(k, \omega) \\ = k^2 k_B T / m \quad (3.64)$$

in agreement with the exact results (3.55) and (3.56). Obviously, only the kinetic parts of the higher moments will be reproduced by this model.

3.4.2 Diffusion equation for $G_s(r, t)$

We can make contact with the macroscopic diffusional behaviour of the fluid by arguing that the self-correlation function $G_s(r, t)$ must be related to the solution of the diffusion equation, for it represents the meanderings of a particle initially at the origin at time $t=0$. Actually, this particle can exchange energy and momentum with its neighbours and we then fundamentally have only one conservation law for particle number. This is why the self-diffusion problem is much easier than viscosity and heat conduction.

The diffusion equation should be obeyed by $G_s(r, t)$ for times long compared with the collision time and for distances long compared with the mean free path. Bearing this in mind for later purposes, we write

$$D\nabla^2 G_s(r, t) = \frac{\partial G_s(r, t)}{\partial t} \quad (3.65)$$

As we have seen, we need a solution satisfying the condition

$$G_s(r, 0) = \delta(r) \quad (3.66)$$

and such that, for the probabilistic interpretation of G_s ,

$$\int g(r, t) dr = 1, \text{ for all } t \quad (3.67)$$

Actually, (3.65) has the form of the Bloch equation for the density matrix (which is also useful for quantal fluids) and we obtain the desired solution from that equation in appendix 3.2. The result is

$$G_s(r, t) = \{4\pi D|t|\}^{-3/2} \exp\left(-\frac{r^2}{4D|t|}\right) \quad (3.68)$$

which is soon shown to satisfy (3.66) and (3.67).

From the results of appendix 3.2 we can immediately extract the intermediate scattering function $F_s(k, t)$ as

$$F_s(k, t) = \exp(-k^2 D|t|) \quad (3.69)$$

From phenomenological theory, we expect the diffusion coefficient to be related to some mean square distance over a characteristic time and so we next calculate the mean square displacement $\langle r^2 \rangle$ as

$$\langle r^2 \rangle = \int dr r^2 G_s(r, t) = 6Dt \quad (3.70)$$

from eqn (3.68). This result is valid for times long compared with collision times and we must expect that, for a $G_s(r, t)$ correctly calculated from a force law, $\langle r^2 \rangle$ will be proportional to t , the slope yielding the diffusion constant. Machine calculations have been made for a number of cases and figure 3.2 shows typical results for two different potentials for liquid sodium. These

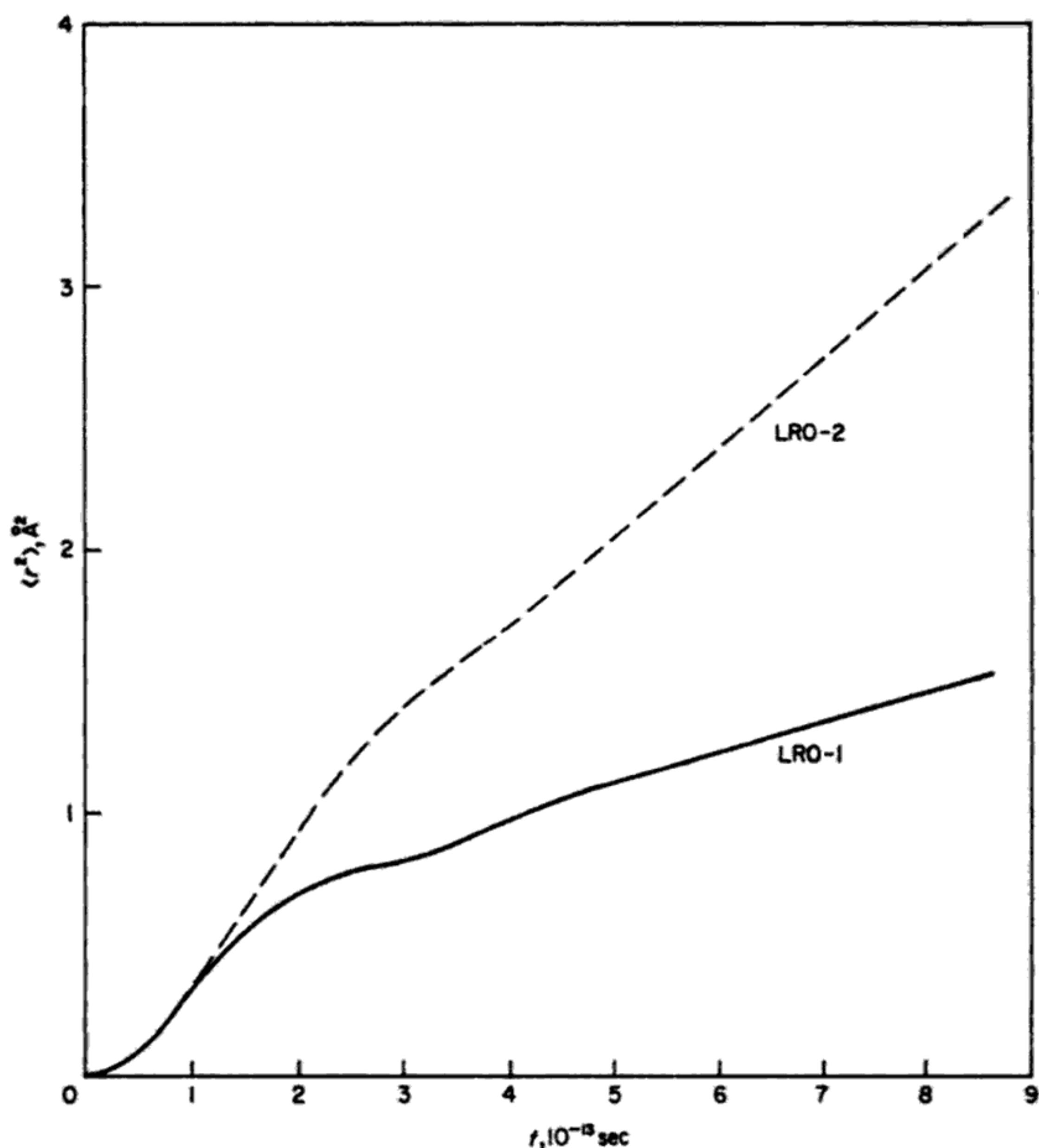


Figure 3.2 Mean square displacement in liquid sodium as a function of time, as obtained by computer experiments for two different assumptions on the pair potential (from Rahman and Paskin, 1966)

potentials were of truncated oscillatory character and the marked differences between curves 1 and 2 show that the diffusion constant is sensitive to the pair potential.

We turn now to obtain an important expression for D in terms of $S_s(k, \omega)$. To do so, we recall that

$$S_s(k, \omega) = \int dt \exp(-i\omega t) F_s(k, t) \quad (3.71)$$

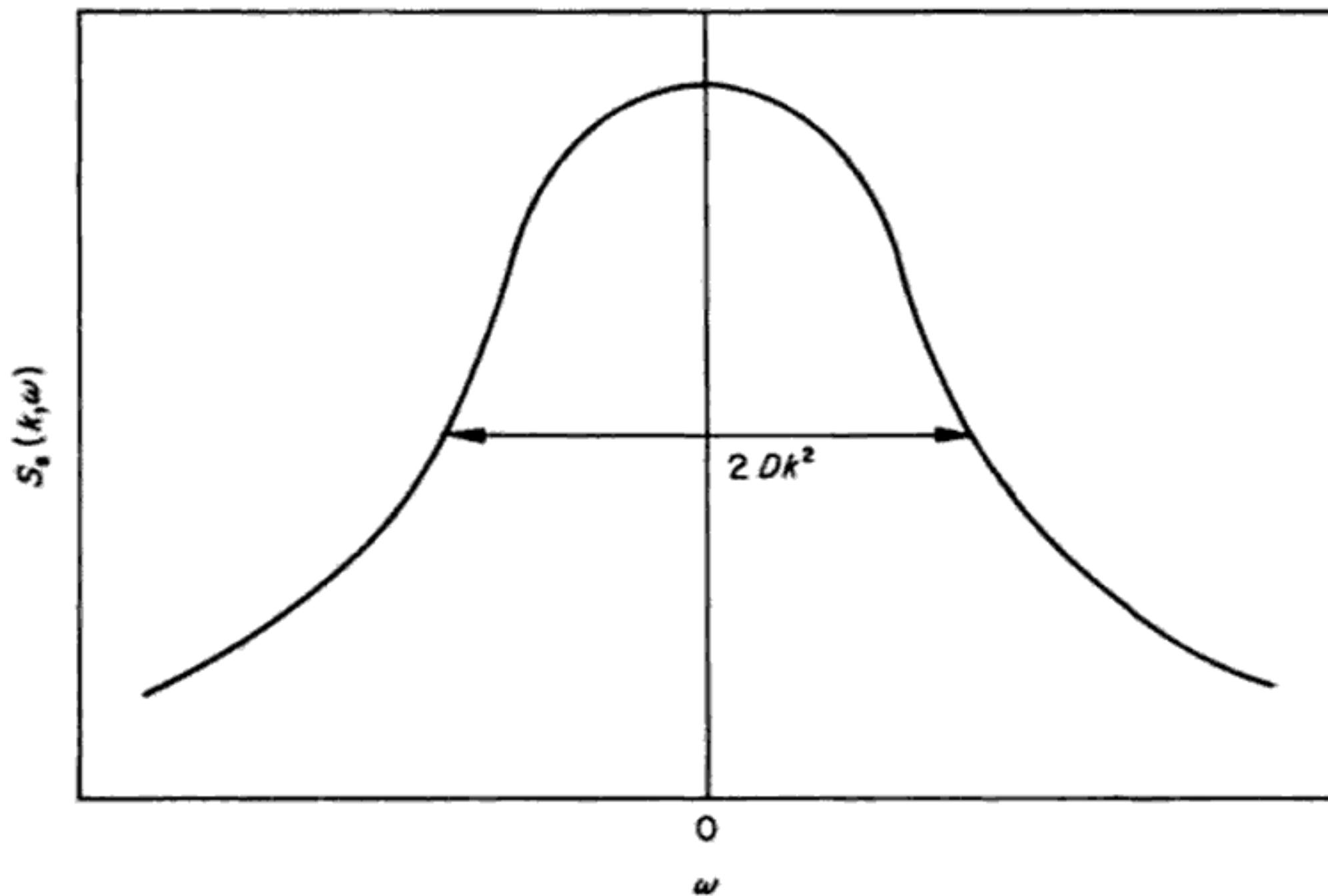


Figure 3.3 Schematic form of $S_s(k, \omega)$ for diffusion

and using (3.69) we find

$$\begin{aligned} S_s(k, \omega) &= 2 \int_0^\infty dt \cos \omega t \exp(-k^2 D t) \\ &= \frac{2 D k^2}{\omega^2 + (D k^2)^2} \end{aligned} \quad (3.72)$$

The form of $S_s(k, \omega)$ as a function of ω is shown in figure 3.3 and it may be seen that the total width at half maximum is determined by the diffusion constant D . Notice that $S_s(k, \omega)$ in a real liquid should change from the Lorentzian form (3.72) at small k and ω to the Gaussian form (3.63) at large k and ω .

We have already seen that the above theory can only work for long times or small ω and, in general, we expect macroscopic arguments to work in the long wavelength or small k limit. While, therefore, we cannot trust (3.72) in general, it is perfectly proper for the limiting case of small k and ω . If we wish to obtain a non-zero limit as $k \rightarrow 0$ we must, from (3.72), consider $S_s(k, \omega)/k^2$, and in the limit we have

$$\lim_{k \rightarrow 0} S_s(k, \omega)/k^2 = \frac{2D}{\omega^2} \quad (3.73)$$

In general, for a proper calculation of $S_s(k, \omega)$ the left-hand side of (3.73) will be a function of ω which will only become proportional to ω^{-2} as $\omega \rightarrow 0$. Thus,

a general result for D may be written

$$D = \frac{1}{2} \lim_{\omega \rightarrow 0} \omega^2 \lim_{k \rightarrow 0} S_s(k, \omega) / k^2 \quad (3.74)$$

So far, no precise use of this result for any realistic interaction has been made, but it clearly gives interesting information about the structure of $S_s(k, \omega)$ near the origin of the (k, ω) plane, which any approximate theory should embody. The long-time behaviour of the self-motions in a liquid will be discussed in more detail in section 4.2.

3.4.3 Contribution of a collective mode to $S(k, \omega)$

As another important model for the calculation of the dynamic structure factor, we consider the case where the collective coordinate $\rho_k(t)$ describes a pure collective mode. This situation is closely realised at long wavelengths, both in quantal fluids (zero sound in liquid He³ and phonon branch of the excitation spectrum in liquid He⁴; see chapter 8) and in charged fluids (plasmon excitation; see chapter 7).

As a result of the standard transformation to normal coordinates in a problem of vibrations, the density fluctuation operator describing a pure collective mode can be written through boson creation and annihilation operators, a_k^+ and a_k , as (see for example Ziman, 1972)

$$\rho_k = N^{1/2} A_k (a_k + a_k^+) \quad (3.75)$$

where A_k is an appropriate *c*-number giving the strength of the mode. The processes involved in the density fluctuation clearly are emission and absorption processes of one quantum. From (3.18) we find

$$\begin{aligned} F(k, t) &= |A_k|^2 \sum_m w_m \langle \Psi_m | (a_{-k} + a_k^+) \exp(iHt/\hbar) (a_k + a_{-k}^+) \exp(-iHt/\hbar) | \Psi_m \rangle \\ &= |A_k|^2 \sum_{m,m'} w_m \exp[i(E_{m'} - E_m)t/\hbar] |\langle \Psi_m | a_{-k} + a_k^+ | \Psi_{m'} \rangle|^2 \\ &= |A_k|^2 \sum_{m,m'} w_m \{ \exp(i\omega_k t) |\langle \Psi_m | a_{-k} | \Psi_{m'} \rangle|^2 + \exp(-i\omega_k t) |\langle \Psi_m | a_k^+ | \Psi_{m'} \rangle|^2 \} \\ &= |A_k|^2 \{ \exp(i\omega_k t) \langle a_{-k} a_k^+ \rangle + \exp(-i\omega_k t) \langle a_k^+ a_k \rangle \} \end{aligned} \quad (3.76)$$

In the above derivation we have taken account of the selection rules for the harmonic oscillator, which ensure that the state $\Psi_{m'}$ differs from the state Ψ_m by the addition or subtraction of a quantum of energy $\hbar\omega_k$, ω_k being the eigenfrequency of the mode. Since $\langle a_k^+ a_k \rangle$ represents the mean number of quanta at equilibrium,

$$\langle a_k^+ a_k \rangle \equiv n_k = [\exp(\hbar\omega_k/k_B T) - 1]^{-1} \quad (3.77)$$

we can finally write the intermediate scattering function as

$$F(k, t) = |A_k|^2 \{ (n_k + 1) \exp(i\omega_k t) + n_k \exp(-i\omega_k t) \} \quad (3.78)$$

and the corresponding dynamic structure factor as

$$S(k, \omega) = 2\pi |A_k|^2 \{ (n_k + 1) \delta(\omega - \omega_k) + n_k \delta(\omega + \omega_k) \} \quad (3.79)$$

If we recall the interpretation of $S(k, \omega)$ as the probability of inelastic scattering of neutrons from the liquid, we can interpret the two terms in the brackets as representing, respectively, the emission and the absorption of a quantum by the neutron in a scattering process. The factor $(n_k + 1)$ in the emission term accounts, of course, for stimulated and spontaneous emission. We also note that (3.79) implies the relation

$$S(-k, -\omega) = \exp(-\hbar\omega/k_B T) S(k, \omega) \quad (3.80)$$

This is (cf. p. 44) a general property of the dynamic structure factor of a fluid, being just a consequence of the principle of detailed balancing, as can be proved by repeating the calculation of section 3.2.3 for the probability $P(-k, -\omega)$. Of course, in the classical limit ($\hbar\omega \ll k_B T$) we have $S(-k, -\omega) = S(-k, \omega)$.

Needless to say, all the simple models described above have a limited range of validity. To get a full microscopic theory of $S(k, \omega)$ which correctly includes the hydrodynamic (e.g. in $S_s(k, \omega)$ diffusion) regime remains a major goal of the theory. To do this from a given pair potential, it seems clear, will at least for a long while yet only be feasible by machine calculations (see for example Alder, 1973 for hard spheres). Therefore the philosophy pioneered by Vineyard (1958) of relating $S(k, \omega)$ to $S_s(k, \omega)$ and the static correlation functions still appears to be a worthwhile direction for further study.