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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

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STRUCTURE AND FORCES IN LIQUIDS AND LIQUID MIXTURES

Additional notes

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efinition of distribution functions

Since both Professor Enderby (appendix to his notes) and Dr Finney have referred to distribution functions and the configurational integral specifically, this introduction to distribution functions can be brief.

We might state the basic theoretical problem of the liquid state as calculating the liquid properties from the intermolecular potential energy function $\Phi(\mathbf{r}_1 \cdots \mathbf{r}_N)$.

Canonical ensemble

We shall first treat classical monatomic liquids like argon. Since the probability distribution in phase space is given by

$$\exp(-H/k_BT)$$

where H is the classical Hamiltonian, we can readily integrate over momenta and hence can confine our attention to distribution functions in coordinate space.

With N atoms in volume V at temperature T, the probability $P^{(N)}(\mathbf{r}_1 \mathbf{r}_2 \cdots \mathbf{r}_N) \prod d\mathbf{r}_i$ that atom 1 will be found in volume element $d\mathbf{r}_1$ around $\mathbf{r}_1$, atom 2 in $d\mathbf{r}_2$ around $\mathbf{r}_2$ etc, atom N in $d\mathbf{r}_N$ around $\mathbf{r}_N$, is given by

$$P^{(N)}(\mathbf{r}_1 \mathbf{r}_2 \cdots \mathbf{r}_N)\, d\mathbf{r}_1\, d\mathbf{r}_2 \cdots d\mathbf{r}_N = \frac{\exp\left[-\Phi(\mathbf{r}_1 \cdots \mathbf{r}_N)/k_BT\right] d\mathbf{r}_1\, d\mathbf{r}_2 \cdots d\mathbf{r}_N}{\int_\Omega \cdots \int \exp\left(-\Phi/k_BT\right) d\mathbf{r}_1\, d\mathbf{r}_2 \cdots d\mathbf{r}_N}, \quad (1.1)$$

the denominator in (1.1) being the configurational integral Q.

Next, we define the probability that a given number n $(n \leqq N)$ atoms will be in $d\mathbf{r}_1$ around $\mathbf{r}_1$, $\cdots$ $d\mathbf{r}_n$ around $\mathbf{r}_n$, regardless of the positions of the remaining $N-n$ molecules. To get this, we integrate (1.1) over coordinates $\mathbf{r}_{n+1}$ to $\mathbf{r}_N$ to find

$$P^{(n)}(\mathbf{r}_1 \mathbf{r}_2 \cdots \mathbf{r}_n) = \frac{\int \cdots \int \exp\left[-\Phi(\mathbf{r}_1 \cdots \mathbf{r}_N)/k_BT\right] d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N}{Q}. \quad (1.2)$$

Convenient normalization of distribution functions

Since one generally works in the so-called thermodynamic limit in which $N \to \infty$, $\Omega \to \infty$, such that $N/\Omega = \rho^{(1)}$ remains finite, $N P^{(1)}$ is a more convenient quantity than $P^{(1)}$, since $N P^{(1)} = \rho^{(1)}$, the number density of the molecules. In general,

$$\rho^{(n)} = \frac{N!}{(N-n)!} P^{(n)} \quad (1.3)$$

defines more conveniently normalized distribution functions. The reason the factor $N!/(N-n)!$ is introduced is to avoid labelling the molecules. In other words, there are N choices for the molecule at $\mathbf{r}_1$ in volume $d\mathbf{r}_1$, $(N-1)$ for $d\mathbf{r}_2$, $(N-n+1)$ for $d\mathbf{r}_n$. Thus the total number of possibilities is $N(N-1) \cdots (N-n+1)$ which is just the factor relating $\rho^{(n)}$ and $P^{(n)}$ in (1.3).

In a bulk liquid, neglecting surface effects, as emphasized above, $\rho^{(1)} = \text{constant} = N/\Omega = \rho$ say, and the first non-trivial distribution is $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$, the importance of which can hardly be overemphasized in the theory of liquids. This is such that $\rho^{(2)}(\mathbf{r}_1 \mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2$ is the probability that one molecule of the liquid will be found at $\mathbf{r}_1$ in $d\mathbf{r}_1$ and another at $\mathbf{r}_2$ in $d\mathbf{r}_2$. In a fluid, $\rho^{(2)}$ depends on the distance $|\mathbf{r}_1 - \mathbf{r}_2|$.

When we switch off the interatomic forces, ie put $\Phi = 0$, the configurational integral Q is simply Ω^N, then $P^{(n)} = \Omega^{N-n}/\Omega^N$ and therefore we have that $\rho^{(2)}$ for a random system is

$$\rho^{(2)} = \frac{N!}{(N-2)!} P^{(2)} = \frac{N(N-1)}{\Omega^2} \quad (1.4)$$

and thus as $N \to \infty$, it follows from (1.4) that (to $O(1/N)$; we return to this point later) $\rho^{(2)} \to \rho^2$. Since it is to be expected that this becomes true, with real interatomic forces, as $|\mathbf{r}_1 - \mathbf{r}_2| = r_{12}$ gets very large, it is useful to write

$$\rho^{(2)}(r_{12}) = \rho^2 g(r_{12}) \quad (1.5)$$

which ensures that $g(r_{12}) \to 1$ at very large interatomic separations. Prof.

Enderby has discussed fully how $g(r)$ can be measured, via the structure factor $S(k)$, related to $g(r)$ by

$$S(k) = 1 + \rho \int [g(r) - 1]\, e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r} \qquad (1.6).$$

Internal energy in terms of $g(r)$ and pair potential $\phi(r)$

As a first use of the radial distribution function $g(r)$, we calculate below the internal energy E, under the simplifying assumption that the intermolecular potential energy Φ can be decomposed into a sum of pair potentials ~~Φ~~ $\phi(r_{ij})$ between atoms i and j : ie we write

$$\Phi(\mathbf{r}_1 \cdots \mathbf{r}_N) = \sum_{i<j} \phi(r_{ij}). \qquad (1.7)$$

For liquid argon, for example, we can consider $\phi(r)$ to be essentially the potential energy of interaction of two argon atoms in vacuo. (However, three body forces are then required for a fully quantitative description of liquid argon).

The kinetic energy of a monatomic fluid at temperature T is evidently $\frac{3}{2} N k_B T$ from equipartition, and hence we require to determine the mean potential energy $\langle \Phi \rangle$ to complete the calculation of E. $\langle \Phi \rangle$ is given by

$$\langle \Phi \rangle = \int \cdots \int e^{-\Phi/k_BT}\, \Phi\, d\mathbf{r}_1 \cdots d\mathbf{r}_N \,/\, Q \qquad (1.8)$$

and from (1.7) the sum consist of $N(N-1)/2$ terms contributing equally to (1.8). One then obtains

$$\langle \Phi \rangle = \frac{N(N-1)}{2} \iint \phi(r_{12}) \left[\frac{\int \cdots \int e^{-\Phi/k_BT}\, d\mathbf{r}_3 \cdots d\mathbf{r}_N}{Q} \right] d\mathbf{r}_1\, d\mathbf{r}_2 \qquad (1.9)$$

Using the definition of the distribution functions, the quantity in square brackets in (1.9) is simply $p^{(2)}(\mathbf{r}_1 \mathbf{r}_2)$ and hence

$$\langle \Phi \rangle = \frac{\rho^2 \Omega}{2} \int_0^\infty \phi(r)\, g(r)\, 4\pi r^2\, dr, \qquad (1.10)$$

one of the integrations giving simply the volume Ω of the fluid. Hence

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

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 doubling counting of pair interactions ϕ, the form (1.11) is easily interpreted.

Equation of state

The virial of the pressure p is $3p\Omega$ giving for a perfect gas

$$2\bar{K} = 3 N k_B T = 3 p \Omega. \qquad (1.12)$$

When we include the virial of a force $\mathbf{F}_i$ acting on the ith molecule at $\mathbf{r}_i$, we have to calculate the average of $-\sum_i \mathbf{r}_i \cdot \mathbf{F}_i$, the sum extending over all the molecules. For central forces, this becomes again the average of $N(N-1)/2$ terms, each of which is

$$\int r_{12} \frac{\partial \phi(r_{12})}{\partial r_{12}} \left[\frac{\int \cdots \int e^{-\Phi/k_BT}\, d\mathbf{r}_3 \cdots d\mathbf{r}_N}{Q} \right] d\mathbf{r}_1\, d\mathbf{r}_2$$

and as for E we can write this in terms of $g(r)$ to obtain the desired generalization of eqn (1.12) as

$$3p\Omega = 3 N k_B T - \frac{N(N-1)}{2} \int r_{12} \frac{\partial \phi(r_{12})}{\partial r_{12}} \frac{(N-2)!}{N!} \rho^2 g(r_{12})\, d\mathbf{r}_1\, d\mathbf{r}_2$$

or

$$p = \rho k_B T - \frac{\rho^2}{6} \int r \frac{\partial \phi}{\partial r}\, g(r)\, d\mathbf{r}. \qquad (1.13)$$

In principle then, from an assumed (or, ideally, quantum mechanically calculated) law of force and a measured $g(r)$, we can estimate the internal energy from (1.11) and the fluid pressure from (1.13).

Structure and forces

The major objective of a theory of the liquid state is to derive the pair function $g(r)$ from the pair potential $\phi(r)$. The theory of distribution functions developed above can be shown to relate $g(r)$ and $\phi(r)$ via the three-particle distribution function $\rho^{(3)}(\mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3)$. We shall present a simple physical argument here, leading to the exact statistical result for a classical liquid. In this latter case, we can usefully write $g(r_{12})$ in the Boltzmann form

$$g(r_{12}) = \exp\left(-U(r_{12})/k_BT\right) \qquad (1.14)$$

Here $U(r_{12})$ is known as the potential of mean force and the objective below is to relate it to the pair potential $\phi(r_{12})$. From the potential of mean force we calculate the total force $-\partial U(r_{12})/\partial \underset{\sim}{r}_1$ on atom 1 as the sum of a direct force $-\partial\phi(r_{12})/\partial \underset{\sim}{r}_1$ and an indirect contribution which we show immediately below depends on the three-atom correlation function $\rho^{(3)}(\underset{\sim}{r}_1 \underset{\sim}{r}_2 \underset{\sim}{r}_3)$. This latter contribution is in fact readily written down as

$$-\int \frac{\partial\phi(r_{13})}{\partial \underset{\sim}{r}_1} \frac{\rho^{(3)}(\underset{\sim}{r}_1 \underset{\sim}{r}_2 \underset{\sim}{r}_3)}{\rho^2 g(r_{12})}\, d\underset{\sim}{r}_3$$

since, given atoms at $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$, the probability of finding atom 3 at $\underset{\sim}{r}_3$ is evidently $\rho^{(3)}(\underset{\sim}{r}_1 \underset{\sim}{r}_2 \underset{\sim}{r}_3)/\rho^2 g(r_{12})$, since there are, by assumption, atoms 1 and 2 at $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$. Thus we have the so-called force equation

$$-\frac{\partial U(r_{12})}{\partial \underset{\sim}{r}_1} = -\frac{\partial\phi(r_{12})}{\partial \underset{\sim}{r}_1} - \int \frac{\partial\phi(r_{13})}{\partial \underset{\sim}{r}_1} \frac{\rho^{(3)}(\underset{\sim}{r}_1 \underset{\sim}{r}_2 \underset{\sim}{r}_3)}{\rho^2 g(r_{12})}\, d\underset{\sim}{r}_3 , \qquad (1.15)$$

which is the basic equation relating structure and (pair) forces. It is immediately seen that the three-particle function is at the heart of such a theory, and to date we have pretty incomplete knowledge of it.

Kirkwood approximation

Because of this, we introduce immediately one of the simple approximations one might contemplate to express $\rho^{(3)}$ in terms of $g(r)$. Kirkwood long ago proposed to write:

$$\rho^{(3)}(\underset{\sim}{r}_1 \underset{\sim}{r}_2 \underset{\sim}{r}_3) \doteq \rho^3 g(r_{12})\, g(r_{23})\, g(r_{31}). \qquad (1.16)$$

We caution that great care is needed in the use of this simple approximation in detailed calculations: it is useful for some purposes, but quite inadequate for others. One of its troubles is that it can lead to severe thermodynamic inconsistency, for example for the fluid pressure. We shall exhibit one method, due to Abe, of rectifying at least in part, this thermodynamic inconsistency. But, bearing in mind these limitations, it will nevertheless be helpful to motivate further directions for progress to insert (1.16) into (1.15) and examine the consequences, known as the Born – Green theory of structure.

As Rushbrooke has shown, with the approximation (1.16) the force eqn. can be integrated to yield

$$U(r) = \phi(r) - \rho\int E(\underset{\sim}{r}-\underset{\sim}{r}')\, h(\underset{\sim}{r}')\, d\underset{\sim}{r}' \qquad (1.17)$$

where we have introduced the total correlation function $h(r) = g(r) - 1$ and the quantity E defined by

$$E = \frac{1}{k_BT}\int_r^\infty g(s)\,\phi'(s)\, ds . \qquad (1.18)$$

Since $g(s) \to 1$ for large s, it is clear from eqn (1.18) that at large r $E(r) \to -\phi(r)/k_BT$, a result we shall make use of below.

Ornstein – Zernike direct correlation function

Though eqn (1.17) is approximate, we use it now to motivate the introduction of an exact equation, namely that defining the Ornstein–Zernike, or direct, correlation function, $c(r)$ say. Whereas we have already stressed the decomposition in eqns (1.15) and (1.17) into a 'direct' part and an indirect part, the idea behind the Ornstein–Zernike work was, in essence, to decompose the total correlation function $h(r)$ into a direct part $c(r)$ and an indirect part. As in the (admittedly now approximate) eqn (1.17) in the Ornstein – Zernike definition of $c(r)$ the indirect part is also written as a convolution; namely:

$$h(r) = c(r) + \rho\int c(\underset{\sim}{r}-\underset{\sim}{r}')\, h(\underset{\sim}{r}')\, d\underset{\sim}{r}' \qquad (1.19)$$

That there is considerable similarity between the exact result (1.19) and the approximate eqn. (1.17) is made clear by noting that in the convolution in (1.17), $E \to -\phi(r)/k_BT$ at large r, ie E is related asymptotically to the direct pair interaction, while $h(r) = e^{-U/k_BT} - 1 \to -U(r)/k_BT$ at large r, ie h is related asymptotically to the total interaction U.

If we combine eqns (1.6) and (1.19) we can write in $\underset{\sim}{k}$ space

$$\tilde{c}(k) = \frac{S(k)-1}{S(k)} \qquad (1.20)$$

where $\tilde{c}(k)$ is evidently the Fourier transform of $c(r)$. An example given in summary of lectures is $\tilde{c}(k)$ for liquid thallium, which, because of the small value of $S(0)$ (for the theory see summary of lectures I–IV), is very difference in range from $S(k)$. $\tilde{c}(k)$ is much more directly related to $\phi(r)$ than is $S(k)$, as the above arguments make quite clear. This is a major reason for introducing $c(r)$: we shall see later that it is also of great importance in describing the liquid-solid transition, as seems first to be clear from the work of Ramakrishnan and Yussouff.

Thermodynamic consistency and long-range behaviour of c(r)

In the summary notes of lectures I–IV, the grand canonical ensemble is used to establish that

$$S(k=0) = \rho k_B T K_T \qquad (1.21)$$

where K_T is the isothermal compressibility. Combining this with eqn (1.20), we have an alternative route into the calculation of the equation of state, which does not require the assumption of a pair potential, namely via

$$\left(\frac{\partial p}{\partial \rho}\right)_T = \frac{k_B T}{S(0)} = k_B T\left(1 - \tilde{c}(0)\right). \qquad (1.22)$$

We set out in the summary notes an argument which is suggestive that at large r,

$$c(r) \to -\phi(r)/k_B T. \qquad (1.23)$$

This is believed to be the exact asymptotic behaviour of $c(r)$ provided we are far from the critical point, though only in special examples (eg Lebowitz and Percus 1963) has a rigorous proof been given.

One trouble of the Kirkwood approximation is that it does not give back the asymptotic form (1.23) as shown by Gaskell.

Abe's approximation (equivalent to hypernetted chain approximation)

Because of this difficulty of the Kirkwood approximation, it is worth stressing that an approximation due to Abe goes some way towards correcting thermodynamic inconsistency of the Born-Green theory. Essentially, his approximation is equivalent to replacing $E(r)$ in eqn (1.17), which tends to $-\phi(r)/k_BT$ at large r, by $c(r)$, which has the same asymptotic behaviour according to eqn (1.23). Of course, this replacement $E(r) \to c(r)$ is made for all r. If then use eqn (1.17) with $E \to c$ and remove the convolution using (1.19) we find the Abe (HNC) equation

$$\frac{U-\phi}{k_BT} = c(r) - h(r) \qquad (1.24)$$

which consistently gives back (1.23) at large r, since $h \to -U/k_BT$.

Molecular dynamical test of Born-Green and Abe theories for liquid argon

G.G. Robinson and N.H. March (unpublished work) have used molecular dynamical data (kindly supplied by Drs Hutchinson and Schofield) to test the above approximate theories based on eqns (1.17) and (1.24). This is done by writing the integral of the force eqn (1.15) as

$$\frac{\partial g}{\partial r} + \frac{g}{k_BT}\frac{\partial \phi}{\partial r} = f(r). \qquad (1.25)$$

From the molecular dynamic data for $g(r)$, for a Lennard-Jones $\phi(r)$, $f(r)$ was calculated from eqn (1.25) and is plotted in the summary notes (I–IV).

But from the Legendre polynomial expansion of $\rho^{(3)}$ in same summary notes, $f(r)$ depends only on p term ($l=1$) and is explicitly given by

$$f(r) = \qquad (1.26)$$

Using the same ϕ and $g(r)$, plus the Kirkwood approximation, $f(r)$ has been calculated ~~at~~ [illegible] from eqn (1.26) and is plotted for comparison in the notes. For the Abe approximation

$$f_{Abe} \equiv f_{HNC} = \frac{\partial}{\partial r}(h-c) \qquad (1.27)$$

and using molecular dynamics data for h and c, (1.27] is also plotted. The large r behaviour of $f_{HNC}(r)$, as expected from thermodynamic consistency arguments, is better than $f_{Born-Green}$, but the opposite is true at r values inside the first peak of $g(r)$.

$\underset{\sim}{k}$ space theories of structure

It will be valuable, especially for some simple liquid metals, to rewrite structural theories of liquids in $\underset{\sim}{k}$ space, by means of the density fluctuations $\rho_{\underset{\sim}{k}}$. These are defined from the particle density; atoms now at $\underset{\sim}{R_i}$,

$$\rho(\underset{\sim}{r}) = \sum_{i=1}^{N} \delta(\underset{\sim}{r} - \underset{\sim}{R_i}) \qquad (1.28)$$

by taking its Fourier transform, to find

$$\rho_{\underset{\sim}{k}} = \sum_{i=N}^{N} e^{i\underset{\sim}{k}\cdot\underset{\sim}{R_i}} \qquad (1.29)$$

Since the density fluctuation $\rho_{\underset{\sim}{k}}$ depends on the position vectors $\underset{\sim}{r_i}$ of all the atoms, it can be regarded as a collective variable. This, when generalized to dynamics, will prove very useful in discussing collective modes in the liquid alkali metals. However, for the present we are interested in the static structure factor $S(k)$. Corresponding to eqn (1.28) we can form the pair function

$$\rho^{(2)}(\underset{\sim}{r_1}\,\underset{\sim}{r_2}) = \sum_{i\neq j=1}^{N} \delta(\underset{\sim}{r_1} - \underset{\sim}{R_i})\,\delta(\underset{\sim}{r_2} - \underset{\sim}{R_j}) \qquad (1.30)$$

and using translational invariance we find

$$\rho g(\overset{|\underset{\sim}{r_1}-\underset{\sim}{r_2}|}{r}) = \frac{1}{N}\Big\langle \sum_{i\neq j} \delta(\underset{\sim}{r_1} - \underset{\sim}{r_2} - \underset{\sim}{R_i} + \underset{\sim}{R_j}) \Big\rangle \qquad (1.31)$$

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

$$\rho_k \rho_{-k} = \sum_{i=1}^{N} e^{i\underset{\sim}{k}\cdot\underset{\sim}{R_i}} \sum_{j=1}^{N} e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R_j}} \qquad (1.32)$$

or

$$\rho_k \rho_{-k} - N = \sum_{i\neq j} \exp(i\underset{\sim}{k}\cdot\underset{\sim}{R_i} - \underset{\sim}{R_j}) \qquad (1.33)$$

Thus by Fourier transform of (1.31) we find

$$S(k) = \frac{1}{N}\langle \rho_k \rho_{-k} \rangle \qquad (1.34)$$

In a similar manner we can obtain the higher order distribution functions in terms of the ρ_k. We now return to the force equation and converting it into $\underset{\sim}{k}$ space we find

$$S(k) = 1 + \frac{1}{Nk^2}\sum_{\eta} \frac{\tilde{\phi}(\eta)}{k_BT} \langle \rho_{\underset{\sim}{k}+\underset{\sim}{\eta}}\, \rho_{\underset{\sim}{k}}\, \rho_{\underset{\sim}{\eta}} \rangle\, \underset{\sim}{k}\cdot\underset{\sim}{\eta} \qquad (1.35)$$

where we have assumed, for the moment, that the pair potential $\phi(r)$ has a Fourier transform $\tilde{\phi}(k)$. Eqn (1.35) is an exact classical equation for a potential that can be Fourier transformed. $\langle \rho_{\underset{\sim}{k}+\underset{\sim}{\eta}}\, \rho_{\underset{\sim}{k}}\, \rho_{\underset{\sim}{\eta}} \rangle$, involving three $\rho_{\underset{\sim}{k}}$'s, stems from the three-body correlation function.

Random-phase approximation

We know from the $\underset{\sim}{r}$ space theories based on the force equation that we must now approximate in eqn (1.35). Since the aim is to relate $S(k)$ and $\tilde{\phi}(k)$, $\langle \rho_{\underset{\sim}{k}+\underset{\sim}{\eta}}\, \rho_{\underset{\sim}{k}}\, \rho_{\underset{\sim}{\eta}} \rangle$ must somehow be reduced to $S(k)$ given by (1.34). If we pick out from the sum the term $\underset{\sim}{\eta} = -\underset{\sim}{k}$ in (1.35), this is evidently related to $S(k)$. This is, in fact, the random phase approximation, which turns out on further examination to be a long wavelength approximation. Collecting the terms in $S(k)$ we obtain

$$S(k) = \left[1 + \frac{\rho\tilde{\phi}(k)}{k_BT}\right]^{-1} \qquad (1.36)$$

and comparing this with the Ornstein-Zernike definition of c in $\underset{\sim}{k}$ space we see that

$$\tilde{c}(k) = -\rho\,\tilde{\phi}(k)/k_BT \qquad (1.37)$$

or in $\underset{\sim}{r}$ space

$$c(r) = -\phi(r)/k_BT, \qquad (1.38)$$

which is the same result as the Abe (HNC) approximation yields for large r.

Actually, without going through the $\underset{\sim}{k}$ space analysis, the same form arises from replacing $\rho^{(3)}$ inside the integration over $\underset{\sim}{r}_3$ in the force eqn by $h(r_{23})$.

Percus - Yevick theory

The crippling limitation of the above approximation is that it assumes the pair interaction has a Fourier transform. For many liquids, the interaction has almost a hard core and therefore the Fourier transform does not exist. The Percus - Yevick (1958) method is an attempt to produce an effective potential which will replace the Fourier components $\tilde{\phi}(k)$ above.

We stressed above the collective character of the density fluctuations ρ_k. We might transform the original Hamiltonian into centre of mass coordinates and $(3N-3)$ ρ_k's. Suppose we consider the potential energy as an example, given in terms of $g(r)$ and $\phi(r)$ in eqn (1.11). In $\underset{\sim}{k}$ space we find

$$\text{Potential energy} = \frac{1}{2}\sum_{\underset{\sim}{k}} \tilde{\phi}(k)\left\langle\left[\rho_{\underset{\sim}{k}}\rho_{-\underset{\sim}{k}} - N\right]\right\rangle \qquad (1.39)$$

We might at this stage ask whether we can choose some effective interaction which has Fourier transform $\tilde{\phi}_{\rm eff}(\underset{\sim}{k})$ to get the 'best' possible approximation. There is ambiguity in this statement, but we might determine the effective potential

$$\phi_{\rm eff}(r) = \sum_{(3N-3)\,k\text{s}} \tilde{\phi}_{\rm eff}(k)\exp(-i\underset{\sim}{k}\cdot\underset{\sim}{r}) \qquad (1.40)$$

by insisting that the mean square difference

$$\left\langle\left\{\phi(\underset{\sim}{R}_i-\underset{\sim}{R}_j) - \sum_{(3N-3)\,k\text{s}}\tilde{\phi}_{\rm eff}(k)\exp\left[-i\underset{\sim}{k}\cdot(\underset{\sim}{R}_i-\underset{\sim}{R}_j)\right]\right\}^2\right\rangle$$

be a minimum. A first-order approximation to this leads to the choice

$$\tilde{\phi}_{\rm eff}(k) = FT\left[\phi(r)g(r)\right] \qquad (1.41)$$

where, by the right-hand side, one means the Fourier transform of the product of $\phi(r)$ and $g(r)$. This expression already avoids 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 $\underset{\sim}{r} = \underset{\sim}{R}_i - \underset{\sim}{R}_j$.

Since the aim here is a theory of structure, it is better to minimize averages of $\rho_k\rho_{-k}$ with respect to the exact distribution function (involving ϕ) and the approximation to it (involving $\phi_{\rm eff}$). One then finds, though only after numerous approximations, that

$$\tilde{\phi}_{\rm eff}(k) = k_BT\ FT\left[g(r)\left\{\exp\left[\phi(r)/k_BT\right]-1\right\}\right] \qquad (1.42)$$

If we combine this with the random phase approximation result, and assume that is true for all k (a somewhat doubtful procedure as it is basically a small $\underset{\sim}{k}$ approximation) then we obtain for the $\underset{\sim}{r}$ space direct correlation function

$$c(r) = g(r)\left[\exp\{\phi(r)/k_BT\} - 1\right], \qquad (1.43)$$

which is usually referred to as the Percus - Yevick equation. It satisfies, as is immediately verified, $c(r) \to -\phi(r)/k_BT$ as $r \to \infty$.

This equation can be solved exactly for hard spheres (Wertheim, 1973; Thiele, 1973).

Theory of small angle scattering from liquid argon

Enderby, Gaskell and March (1966) discussed the small angle scattering from liquid argon near the triple point on the basis of the asymptotic property $c(r) = -\phi(r)/k_BT \simeq c_6/r^6 k_BT$ where c_6 is the usual van der Waals coefficient of the non-retarded dispersion interaction. This leads to the expansion

$$\tilde{c}(k) = \tilde{c}(0) + b_2k^2 + b_3k^3 \qquad (1.44)$$

where the term k^3 comes at small k from Fourier transform theory when $c(r) \propto r^{-6}$ at large r. Another way of saying the same thing is that $\int_0^\infty c(r) r^6 dr$ diverges, the k^2 term reflecting the value of $\int c(r) r^2 d\underset{\sim}{r} = 4\pi\int_0^\infty c(r) r^4 dr$. We shall see below that though this moment is finite near the triple point, if we use the Born-Green theory near the critical point, this second moment $\int c(r) r^2 d\underset{\sim}{r}$ diverges, which is not a property of the forces (which lead as seen to the divergence of the 4th moment), but of critical fluctuations. b_3 in the above expansion is determined by c_6 and hence we find

$$S(k) = S(0) + a_2k^2 + a_3k^3 + \ldots \qquad (1.45)$$

where $a_3 = \pi^2\rho\{S(0)\}^2 c_6/k_BT$. This theory can be tested by comparison with the neutron data of Yarnell on liquid argon (see p5 of summary notes of lectures I to IV).

Collective modes in simple liquid metals and small angle scattering

In contrast to liquid argon, the simple liquid metals show evidence from their observed specific heats that they are 'harmonic' in behaviour. Thus the ratio of the specific heats γ just above the freezing point is ~ 1.1-1.3 while $C_V \geq 3R$, whereas $\gamma = 1$ and $C_V = 3R$ are purely harmonic theory predictions. Roughly speaking, we can think of independent density fluctuations $\rho_k(t) \simeq \rho_k(0)e^{i\omega_k t}$, where ω_k is then the dispersion relation of the collective mode. Put another way, we can follow the Feynman argument in liquid helium but, and write as a model for the dynamical structure factor of a liquid metal

$$S(k\omega) = 2\pi S(k)\,\delta(\omega - \omega_k) \qquad (1.46)$$

in terms of the static structure factor $S(k)$ and the dispersion relation ω_k. The classical expression for the second frequency moment of $S(k\omega)$ is given by

$$\int \frac{d\omega}{2\pi}\, \omega^2 S(k\omega) = k_BTk^2/M, \qquad (1.47)$$

This relates $\omega(k)$ and $S(k)$ in the Feynman manner, the result in the classical liquid being

$$\omega^2(k) = k_BTk^2/MS(k) \qquad (1.48)$$

where M is the atomic mass.

Such a collective mode has been observed for liquid Rb by Copley and Rowe and the above theory is compared with experiment on p14 of summary notes (lectures I-IV). Turning the argument round, the small angle scattering (i.e. small k expansion of $S(k)$) can be found from the dispersion relation $\omega(k)$. As Figs on p15 of summary notes (Lectures I-IV) demonstrate, the small angle scattering is totally different from liquid argon, as pointed out by Matthai and March (1982). The difference is due to the correlations arising from the collective oscillations. In particular the dispersion of these leads to

$$S(k) = S(0) + a_1k + a_2k^2 + \ldots \qquad (1.49)$$

and hence to $c(r) \sim r^{-4}$. This means the second moment $\int c(r) r^2 d\underset{\sim}{r}$ will diverge in a simple liquid metal.

Critical point behaviour of Born-Green theory

Before turning to mixtures, we want to point out that Kirkwood superposition, while deficient as a basis for a quantitative theory of liquid structure, does lead to critical behaviour. According to Green et al (1980), at the critical point the total correlation function $h(r)$ falls off as r^{-2}, from the Born-Green theory, which as we saw was based on the Kirkwood approximation. This theory is expressed quantitatively in eqn (1.7). Gaskell has shown that the Fourier transform $\tilde{E}(k)$ of $E(r)$ defined in eqn (1.18) can be related to the fluid pressure p, in the long wavelength limit by

$$\tilde{E}(k=0) = 2\left[1 - \frac{p}{\rho k_B T}\right], \qquad (1.50)$$

which is a general prediction from Born-Green theory. If we denote the Fourier transform of $\phi - U/k_BT$ by $\tilde{\nu}(k)$, then eqn (1.17) involving a convolution has been solved by Gaskell, to give

$$\tilde{\nu}(k) = \tilde{E}(k)\,\tilde{h}(k). \qquad (1.51)$$

But at the critical point, ϕ is short range compared with U and $h(r) \sim -U(r)/k_BT$. Hence $\tilde{\nu}(0) = \tilde{h}(0)$ at the critical point and hence $\tilde{E}(0) = 1$. Thus, from the above result, $p_c/\rho_c k_B T_c = \frac{1}{2}$, where c labels the critical point. This is not quantitatively good for the liquids composed of rare gas atoms, the van der Waals prediction $p_c/\rho_c k_B T_c = 3/8$ already being too large. But it is of considerable interest that the Kirkwood approximation has some merit as a starting point for a (semi-quantitative) discussion of critical point behaviour. Since $h(r) \sim 1/r^2$, $S(k) = \cancel{S(0)} + a_1 k^{-1}$ at small k at T_c (Kumar, March and Wasserman, 1982) ~~and~~ and $\tilde{c}(0) = 1 + a_1 k + \ldots$, again at T_c. Thus, $c(r) \sim 1/r^4$ at T_c. As for simple metals near freezing, but for totally different reasons, the second moment $\Sigma = \int c(r)\, r^2\, d\mathbf{r}$ diverges. Linear Ornstein-Zernike theory relates the critical indices $c_2 = (T-T_c)^{-\Gamma}$, and the usual γ and ν by $\Gamma = \nu = \gamma$. Green et al set $\gamma = 1.23$ for a square well fluid from Born-Green theory.

Mixtures: especially thermodynamics

We turn now, from monatomic systems, to liquid mixtures. We shall rely much more on models in the mixtures case, and a convenient starting point is the Gibbs free energy G of regular solution theory (see, for example, J. S. Rowlinson's book on Liquids and liquid mixtures). This can be written

$$G = (1-c)G_1 + cG_2 + RT\left[c\ln c + (1-c)\ln(1-c)\right] + c(1-c)w. \qquad (2.1)$$

Here G_1 and G_2 refer to pure species, while the third term on the right-hand side is the entropy of mixing. Let us discuss the final term with a liquid binary metal alloy in mind. w is an interchange energy such that if we start with 2 pure metals A and B and exchange an interior A atom with an interior B atom, the total decrease of the energy of the metals is $2w$.

An important contribution to statistical mechanics of solutions was that of Longuet-Higgins (1951), who showed that G written above followed from first principles from a model known as that of conformal solutions. At the heart of this model is the idea of a monatomic reference liquid with pair potential $\phi(r)$. Then the potentials $\phi_{\alpha\beta}$ are generated in the mixture by scaling:

$$\phi_{\alpha\beta}(r) = A_{\alpha\beta}\,\phi(\lambda_{\alpha\beta} r). \qquad (2.2)$$

The result for G above follows if $A_{\alpha\beta}$ and $\lambda_{\alpha\beta}$ are near to unity. This evidently restricts the model to

(i) size differences that are not too large. Na-K, where the volumes differ by a factor of 2 seems all right, for instance whereas Na-Cs, where the volume ratio is 3, is certainly not conformal.

(ii) force laws that are not very different. Valence differences should therefore be zero, or at very least small, in metallic mixtures.

The other point that emerges from Longuet-Higgins work is that the interchange energy w is calculable from (a) the deviations of $A_{\alpha\beta}$ & $\lambda_{\alpha\beta}$ from unity and (b) the properties (pair function $g(r)$ and pair potential $\phi(r)$) of the reference liquid. Thus w is to be treated as a function of thermodynamic variables, say $w = w(p,T)$.

Can we use the Gibbs free energy G to gain information about liquid partial structure factors in the long wavelength limit. We shall see below that this is so, and in particular that the concentration fluctuations in the mixture are essentially determined by $\partial^2 G/\partial c^2$. This quantity can, of course, be calculated immediately from the above model of conformal solutions. We shall see that interesting results for the k dependent structure factors can be calculated also from this model (Parrinello, Tosi and March, 1974).

Number-concentration structure factors

An important advance in treating the thermodynamics of mixtures came in 1970 with the introduction of number and concentration structure factors by Bhatia and Thornton. Following these workers, consider a binary alloy having N_α atoms of type α, and let $\bar{\rho}_\alpha = N_\alpha/\Omega$ be the mean number density of α ions. Define

$$c = N_1/N_1+N_2 = N_1/N = \bar{\rho}_1/\bar{\rho}_1+\bar{\rho}_2 . \qquad (2.3)$$

If $\rho_\alpha(\underset{\sim}{r}\,t)$ denotes number density at time t for species α, then we write

$$\delta\rho_\alpha(\underset{\sim}{r}\,t) = \rho_\alpha(\underset{\sim}{r}\,t) - \bar{\rho}_\alpha$$
$$= \sum_i \delta(\underset{\sim}{r} - \underset{\sim}{R}_i^\alpha(t)) - \bar{\rho}_\alpha , \qquad (2.4)$$

in an obvious notation. Making the Fourier expansion

$$\delta\rho_\alpha(\underset{\sim}{r}\,t) = \frac{1}{\Omega}\sum_{\underset{\sim}{q}} N_\alpha(\underset{\sim}{q}\,t)\, e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}} ; \qquad (2.5)$$

we find

$$N_\alpha(\underset{\sim}{q}\,t) = \sum_i e^{i\underset{\sim}{q}\cdot\underset{\sim}{R}_i^\alpha(t)} - N_\alpha\,\delta_{\underset{\sim}{q}0} . \qquad (2.6)$$

Similarly, if $N(\underset{\sim}{q}\,t)$ denotes the Fourier transform of the local deviation $\delta\rho(\underset{\sim}{r}\,t)$ in the total number density

$$\rho(\underset{\sim}{r}\,t) = \rho_1(\underset{\sim}{r}\,t) + \rho_2(\underset{\sim}{r}\,t) , \qquad (2.7)$$

then

$$N(\underset{\sim}{q}\,t) = \sum_{i;\alpha=1,2} e^{i\underset{\sim}{q}\cdot\underset{\sim}{R}_i^\alpha(t)} - N\delta_{\underset{\sim}{q}0}$$
$$= N_1(\underset{\sim}{q}\,t) + N_2(\underset{\sim}{q}\,t) . \qquad (2.8)$$

We next define the local deviation from the mean concentration c by

$$\delta c(\underset{\sim}{r}\,t) = \frac{\Omega}{N}\left[(1-c)\,\delta\rho_1(\underset{\sim}{r}\,t) - c\,\delta\rho_2(\underset{\sim}{r}\,t)\right] \qquad (2.9)$$

so that if $\delta\rho_1$ and $\delta\rho_2$ change in proportion to their respective mean concentrations, namely c and $(1-c)$, then $\delta c(\underset{\sim}{r},t)=0$, as it should be. If we again Fourier analyze we find

$$\delta c(\underset{\sim}{r}\,t) = \sum C(\underset{\sim}{q}\,t)\, e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}} \qquad (2.10)$$

where

$$C(\underset{\sim}{q}\,t) = \frac{1}{\Omega}\int \delta c(\underset{\sim}{r}\,t)\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}}\, d\underset{\sim}{r}$$
$$= N^{-1}\left[(1-c)N_1(\underset{\sim}{q}\,t) - cN_2(\underset{\sim}{q}\,t)\right] \qquad (2.11)$$

We now define dynamical structure factors in terms of number and concentration variables by

$$S_{NN}(q,\omega) = (1/2\pi N)\int e^{-i\omega t}\,dt\,\langle N^{\dagger}(q,0)N(q,t)\rangle \qquad (2.12)$$

$$S_{cc}(q,\omega) = (N/2\pi)\int e^{-i\omega t}\,dt\,\langle C^{\dagger}(q,0)\,C(q,t)\rangle \qquad (2.13)$$

and

$$2S_{Nc}(q,\omega) = (1/2\pi)\int e^{-i\omega t}\,dt\,\langle N^{\dagger}(q,0)C(q,t) + C^{\dagger}(q,0)N(q,t)\rangle \qquad (2.14)$$

Of these dynamical structure factors, $S_{NN}(q,\omega)$ is similar to the $S(q,\omega)$ for a pure metal, since it is, like $S(q,\omega)$ associated with the fluctuations in the number density of ions.

Defining

$$S_{NN}(q) = \int S_{NN}(q,\omega)\,d\omega\,, \text{ etc} \qquad (2.15)$$

we set

$$S_{NN}(q) = N^{-1}\langle N^{*}(q)\,N(q)\rangle \qquad (2.16)$$

$$S_{cc}(q) = N\,\langle C^{*}(q)\,C(q)\rangle \qquad (2.17)$$

and

$$S_{Nc}(q) = \mathrm{Re}\,\langle N^{*}(q)\,C(q)\rangle \qquad (2.18)$$

where all the $N(q)$ and $C(q)$ now refer to the same lines.

Sum rules

We can show from these definitions that

$$\frac{1}{(2\pi)^3}\int [S_{NN}(q)-1]\,dq = -\frac{N}{\Omega} \qquad (2.19)$$

$$\int [S_{cc}(q) - c(1-c)]\,dq = 0 \qquad (2.20)$$

$$\text{and } \int S_{Nc}(q)\,dq = 0\,. \qquad (2.21)$$

From these definitions, it follows that as $q \to 0$, the structure factors defined above have simple physical significance, namely

$$S_{NN}(0) = \langle (\Delta N)^2\rangle/N \qquad (2.22)$$

$$S_{cc}(0) = N\langle (\Delta c)^2\rangle \qquad (2.23)$$

$$\text{and } S_{Nc}(0) = \langle \Delta N \Delta c\rangle \qquad (2.24)$$

The relation to thermodynamics is given in summary notes of Lecture V.

Conformal solution results for number-concentration correlation functions

In the summary notes of Lecture VII, the effect of scaling a pair potential $\phi(r)$ to $A\phi(\lambda r)$ for a monatomic fluid is given. In particular, the scaling of the pair function can be applied immediately to the density-density correlation function $g_{NN}(r)$ in the mixture in the conformal solution theory:

$$g_{NN}(r,\beta,\Omega) = g(\lambda r, A\beta, \lambda^3\Omega, A^{\frac{3}{2}}z) \qquad (7.1)$$

provided we take A and λ as

$$A = \sum_{\alpha,\beta} c_\alpha c_\beta A_{\alpha\beta}\,;\quad \lambda = \sum_{\alpha\beta} c_\alpha c_\beta \lambda_{\alpha\beta}\,. \qquad (7.2)$$

This scaling of g_{NN} is in fact true to arbitrary λ and A. But in a conformal solution, the deviations of A and λ from unity are treated only to lowest order. Thus, one can expand $g_{NN}(r)$ above in a Taylor series in $(A-1)$ and $(\lambda-1)$, obtaining to first order

$$g_{NN}(r) = g(r) + (A-1)\left[\beta\left(\frac{\partial g}{\partial\beta}\right)_{\rho} + \frac{3}{2}z\left(\frac{\partial g}{\partial z}\right)_{\beta}\right] + (\lambda-1)\left[r\frac{\partial g}{\partial r} + 3\Omega\left(\frac{\partial g}{\partial\Omega}\right)_{\beta}\right]. \qquad (7.3)$$

Using the thermodynamic identities

$$z\left(\frac{\partial g}{\partial z}\right)_{\beta} = \frac{\rho}{\beta}\left(\frac{\partial g}{\partial p}\right)_{\rho} : \ \Omega\left(\frac{\partial g}{\partial\Omega}\right)_{\beta} = -\rho\left(\frac{\partial p}{\partial\rho}\right)_{\beta}\left(\frac{\partial g}{\partial p}\right)_{\beta} \qquad (7.4)$$

we can write

$$g_{NN}(r) - g(r) = (A-1)\beta\left(\frac{\partial g}{\partial\beta}\right)_{\rho} + 3\rho\left[\frac{A-1}{2\beta} - (\lambda-1)\left(\frac{\partial p}{\partial\rho}\right)_{\beta}\right]\left(\frac{\partial g(r)}{\partial p}\right)_{\rho} + (\lambda-1)\,r\,\frac{\partial g}{\partial r}\,. \qquad (7.5)$$

This result agrees precisely with the result of direct application of perturbation theory to the mixture when one writes $\partial g/\partial\beta$ and $\partial g/\partial p$ in terms of g_3 and g_4. There is agreement with thermodynamics in that

$$S_{NN}(k=0) \doteq \rho k_B T \chi_T \qquad (7.6)$$

where K_T is now the isothermal compressibility of the modified one component liquid with pair potential $A\phi(\lambda r)$.

Concentration-concentration correlation function.

Since, by taking linear combinations of g_{11}, g_{12}, g_{22} to get $g_{cc}(r)$, differences $g_{11}(r) - g_{12}(r)$ and $g_{22}(r) - g_{12}(r)$ appear, we expect strong cancellation to occur, as a change of the temperature and pressure will not affect these differences. In fact, the 3 and 4 atom correlation functions g_3 and g_4 cancell out, and one is left with the very simple result

$$g_{cc}(r) = c_1^2 c_2^2 \beta d_{12}\, g(r)\phi(r) \qquad (7.7)$$

with the corresponding structure factor

$$S_{cc}(k) = c_1 c_2 \left[1 + c_1 c_2 \beta d_{12} (\overline{\phi g})_k\right] \qquad (7.8)$$

where

$$(\overline{\phi g})_k = \rho \int d\underset{\sim}{r}\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} \phi(r) g(r) \qquad (7.9)$$

One can plot out easily the Fourier transform of $g(r)\phi(r)$ for some reasonable choices of the reference liquid. We get curves for this which qualitatively resemble the direct correlation function $\tilde{c}(k)$ of the reference liquid. This should occasion no surprise since in an elementary version of Percus - Yevick theory, the effective interaction $\phi_{eff}(k) \simeq FT(g\phi) \simeq -\tilde{c}(k) k_B T$, as discussed earlier in these lectures. In this treatment, there is a direct relation between the presence in $\underset{\sim}{k}$ space of the first peak in $S_{cc}(k)$ and the peak in $S(k)$ of the reference liquid.

Professor Enderby discussed the experiments of Ruppersberg on the Li - Pb liquid alloy system. While this is not a conformal solution, the valence difference being 3 and the forces turn too different, the first peak in $S(k)$ for both pure Li and pure Pb occurs at the same k value. The pre-peaks found by Ruppersberg are found not to vary in position in $\underset{\sim}{k}$-space over a substantial range of concentration and S_{cc} relates to this as predicted by conformal solution theory.