CHAPTER I

SOME ASPECTS OF THE THEORY OF LIQUID METALS

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1.1 Introduction

The existence of matter in three different phases (solid, liquid and gas) is a fact of everyday experience. Solids are rigid and give sharp Bragg reflections in a diffraction experiment, demonstrating an ordered arrangement of atoms or molecules. Liquids and gases are fluids; they will flow under a shear stress however small. Further, in diffraction experiments they give no sharp Bragg reflections but diffuse rings, showing that there is no-long-range ordered arrangement of molecules. Thus there is a clear distinction between solid and fluid (though this is somewhat blurred by the existence of glasses and amorphous solids).

On the other hand, there is no such qualitative distinction between liquid and gas. Van der Waals pointed out explicitly the continuity of liquid and gaseous states. At temperature below the critical temperature two fluid phases can coexist in equilibrium: the denser phase is called liquid and the less dense phase is called gas. Above the critical temperature coexistence of fluid phases is not observed. One can pass continuously from low temperature gas to low temperature liquid by heating above the critical temperature, compressing and cooling. The difference between liquid and gas is essentially a difference in density.

For roughly spherical molecules, and in particular for the actually spherical rare gases, only one kind of disorder is possible, namely disorder of translational motion.
For molecules which are far from spherical, there is also the possibility of rotational disorder. This may occur in a crystal which retains translational order (plastic crystal). On the other hand rotational order may persist in a temperature range where there is translational disorder; in this case one is dealing with "liquid crystals" and many kinds of phases are observed [1].

The aim of the physics of liquids is to understand why particular phases are stable in particular ranges of temperature and density and to relate the stability, structure and dynamical properties of the fluid phases to the size and shape of molecules, atoms or ions and the nature of the forces between them (which in turn are determined by the electronic properties). For ordinary liquid phases we now have excellent qualitative understanding and in simple cases this can lead to fairly rigorously quantitative predictions.

The interactions which determine the bulk properties of matter are basically electromagnetic, and in fact, apart from small relativistic and retardation effects, electrostatic in character; they arise from the Coulomb interactions between nuclei and electrons. Thus, one way to attempt to predict the properties of a liquid would be to solve, subject to appropriate antisymmetry conditions, the many body Schrödinger equation describing the motion of the nuclei
\[ (- \sum_{i}^{N} \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i<j} \frac{q_i q_j}{\mathbf{r}_{ij}} ) \psi = \frac{\hbar}{i} \frac{\partial \psi}{\partial t}, \quad (1.1) \]

and electrons in which the sums are taken over all nuclei and electrons with appropriate masses \( m_i \) and charges \( q_i \).

There are a number of important simplifications most of which arise from the fact that nuclei are much heavier than electrons.

The first is the Born-Oppenheimer [2] approximation according to which we can solve the electronic problem for a static configuration of nuclei, thus deriving a potential energy function \( U \) depending only on the nuclear coordinates, which can in turn be used to describe the nuclear motions. In fact, if we are prepared to determine this potential energy function experimentally (or semiempirically) we can bypass the electronic problem completely, though naturally we would like to confirm at least for a simplest case that solving the electronic Schrödinger equation leads to results in agreement with experimental determination.

A second simplification arises from the fact that the forces between molecules are often much weaker than intramolecular forces between atoms. Thus for relatively rigid molecules we can often make the approximation of ignoring any coupling between intramolecular vibrations and the motion of the molecules as whole, at least in considering many thermodynamic and transport properties (in spectroscopic
studies, for example, we can certainly see intramolecular effects on intramolecular vibrations, and this is an important experimental probe). For more complex molecules this approximation means that we can treat the molecules as rigid and consider the potential energy function $U_N$ as depending only on the position $\vec{r}_1$ of the centre of mass (say) of the molecules and their orientations $\Omega_1$

$$U_N = U_N (\vec{r}_1, \Omega_1; \vec{r}_2, \Omega_2; \ldots; \vec{r}_N, \Omega_N) \quad (1.2)$$

of course this approximation would not be made in studying molecules with relatively free internal rotations (e.g. polymers).

A third simplification, also arising from the relatively large masses of nuclei, is that in many cases we can describe the behaviour of the molecules by classical mechanics and classical statistical mechanics, supplemented where necessary by quantum corrections. This procedure is certainly inadequate for helium and hydrogen at very low temperatures, but probably adequate for most other liquids.

An other simplification arise from the fact intramolecular potential energies are, to a first approximation, additive. Thus, the potential energy function $U_N$ may be written as

$$U_N = \sum_{i<j} U_2(\vec{r}_i \Omega_i; \vec{r}_j \Omega_j) + \sum_{i<j<k} U_3(\vec{r}_i \Omega_i; \vec{r}_j \Omega_j; \vec{r}_k \Omega_k) + \ldots \quad (1.3)$$
in which the first term is a sum of pair interactions, and second a sum of triplet interactions (which may be chosen to vanish whenever one of the molecules is very distant from the other two). In the case of rare gases, it appears to a good approximation to neglect all the terms beyond the triplet term in equation (1.3) and the effect of triplet term on the thermodynamic properties can be included by perturbative techniques. Whether this will prove to be true for all liquids remain to be seen.

1.2 Intramolecular Forces in Liquids

Let us imagine two molecules separated by a distance \( r \) with no other molecule nearby. We adopt the usual convention that attractive forces are given a negative sign. At large distances the force is attraction but changes to a repulsion at short distances which increases very rapidly with further decrease in \( r \). Figure 1.1 is the plot of mutual potential energy \( \phi(r) \), of the molecule as a function of \( r \). The relation between repulsive/attractive force \( F(r) \) and \( \phi(r) \) is that the work done in producing a small increase in \( r \), that is, \( F \cdot dr \), is equal to the decrease in mutual potential energy, \( -d\phi \), or

\[
F(r) = - \frac{d\phi(r)}{dr} \tag{1.4}
\]

so that the slope of the \( \phi(r) \) vs. \( r \) curve with the sign changed gives the magnitude of the force. The potential
Figure 1.1 The variation with separation of the mutual potential energy of a pair of molecules.
energy is, by convention, chosen to be zero, when the molecules are separated by an infinite distance. At the minimum of $\phi(r)$ vs. $r$ curve,

$$\frac{d\phi(r)}{dr} = 0,$$  \hfill (1.5)

so that the value of $r$, say $r = r_0$, at which this minimum occurs marks the change from attraction to repulsion. This distance, of the order of an Angstrom unit or so, would be the equilibrium distance between a pair of isolated undisturbed molecules. The depth of minimum is the energy required to separate such a pair and so is a measure of the strength of binding forces. From general consideration it would be expected that the strongly bound substances will form relatively hard solids with high melting and boiling points and the large latent heats of fusion and evaporation. When two molecules are close together their mutual potential energy will be due to the following distinct causes. If both molecules are polar there will be a potential energy due to the interaction of their permanent dipoles. This is the electrostatic energy $\phi_s$. It decreases with the increasing temperature. Secondly, there will be a contribution due to the interaction of the dipole induced in each molecule with the permanent dipole of the other. This is induction energy $\phi_i$. Finally, there is a third contribution whose origin is not immediately apparent, known as the dispersion energy $\phi_d$. 
To a good approximation these three contributions of the total energy can be treated separately and added to give the total energy (i.e. \( \varnothing = \varnothing_s + \varnothing_i + \varnothing_d \)). The interaction energies for the three effects all vary as the inverse sixth power of the distance between the molecules. The induction contribution is always small and dispersion effect is always large [3].

The total potential energy of a pair of molecules may be obtained by combining the repulsive and attractive contributions [3]

\[
\varnothing(r) = \frac{c}{r^n} - \frac{d}{r^6}
\]

(1.6)

where \( c, d \) and \( n \) are constants. For many simple substances the best value of \( n \) is in the neighbourhood of 12. Thus equation (1.6) becomes

\[
\varnothing(r) = \frac{c}{r^{12}} - \frac{d}{r^6}
\]

(1.7)

From the figure 1.1 the constants \( c \) and \( d \) may be written in terms of the energy \(-\varepsilon\) (where \( \varepsilon \) is the well depth) and either the distance \( r_o \) or \( \sigma \) from the conditions

\[
\varnothing = 0 \text{ at } r = \sigma; \quad \frac{d\varnothing}{dr} = 0 \text{ at } r = r_o; \quad \varnothing = \varepsilon \text{ at } r = r_o
\]

(1.8)

These give more convenient forms of equation (1.7) as

\[
\varnothing(r) = \varepsilon \left[ \left(\frac{r_o}{r}\right)^{12} - 2\left(\frac{r_o}{r}\right)^6 \right]
\]

(1.9)
\[ \phi(r) = 4 \varepsilon [(\sigma/r)^{12} - (\sigma/r)^6] \] (1.10)

with \( r^6 \).

The distance \( \sigma \), may be regarded as the 'diameter' of the molecules as the term is used in kinetic theory for, by the conservation of energy, it is the closest distance which two molecules attain in a head-on collision if they start far apart with negligibly small velocities. For those ionic liquids in which there is no shielding of the electrostatic forces similar to that found in liquid metals, the dominant contribution to the potential is the Coulombic term. This truce of the OCP (one-component plasma) when neutralizing background is assumed to be rigid and in that simple system there is no other contribution to the interionic force. In the molten salts it is necessary to include an additional short range repulsion between ions of opposite charge so as to prevent collapse of the system.

### 1.3 Direct and Indirect Correlation

A more recent route to the determination of fluid structure is through the concept of direct and indirect correlation. The potential of mean force \( \psi(r_{12}) \) may be resolved into a direct component \( \phi(r_{12}) \) which is straightforward pair potential and a supplement \( W(r_{12}) \) which accounts for the modifying effect of the remaining particles.
An analogous resolution in terms of the correlation rather than the potential is made, although the resolution of the total correlation into a direct and indirect component will, of course have consequences for the potential but these will in general be different to the breakdown in equation

$$\psi(r_{12}) = \alpha(r_{12}) + \omega(r_{12})$$  \hspace{1cm} (1.11)

The total correlation

$$h(r_{12}) = g(r_{12}) - 1$$  \hspace{1cm} (1.12)

is simply the fluctuation about the uniform probability $g(r) = 1.00$ of finding a second particle located at a distance $r$ from another located at the origin. The breakdown of the total correlation into its direct and indirect components is made through the Ornstein-Zernike equation

$$h(r_{12}) = \alpha(r_{12}) + \rho \int h(r_{23}) C(r_{13}) dr_3$$  \hspace{1cm} (1.13)

Total  Direct  Indirect

According to equation (1.13) the total correlation between two atoms arises from a direct effect between 1 and 2, this is modified indirectly through the average effect of a representative particle 3, subject to its remaining correlated with 2, $h(r_{23})$. 
To interpret equation (1.13) a particle 1 is immersed in a uniform molecular system \( g(r) = 1.00 \) initially, the local distribution will be perturbed under the action of the direct and indirect potentials \( \varnothing(r_{12}) \) and \( W(r_{12}) \). A screened or effective direct potential operating in the field may therefore be considered, and the quantity \(-K_B T C(r_{12})\) bears the simple interpretation.

At low densities, it would of course, be expected \(-K_B T C(r_{12})\) to reduce to its unscreened form \( \varnothing(r_{12}) \), and this may be shown as follows: from equation (1.13)

\[
h(r_{12}) = C(r_{12}) \quad \text{as} \quad \rho \to 0 \quad (1.14)
\]

i.e.,

\[
g(r_{12}) \to 1 + C(r_{12})
\]

under these conditions \( \psi(r_{12}) \to \varnothing(r_{12}) \), i.e.,

\[
g(r_{12}) = \exp(-\frac{\psi(r_{12})}{K_B T}) \to \exp(-\frac{\varnothing(r_{12})}{K_B T}) \to 1 - C(r_{12})
\]

(1.15)

where upon

\[
C(r_{12}) \sim \exp(-\frac{\varnothing(r_{12})}{K_B T}) - 1 \quad (1.16)
\]

and

\[-K_B T C(r_{12}) \sim \varnothing(r_{12})\]

when \( K_B T >> \varnothing(r_{12}) \).
The direct correlation function $C(r)$ is important in the theory of fluids in two respects. Firstly it is directly accessible experimentally and the same scattering data can be used to determine both $g(r)$ and $C(r)$. Secondly, the range of the direct correlation function is approximately that of the pair potential which it is relatively simply related. A knowledge of the direct correlation inserted in the Ornstein-Zernike relation (1.13) would enable us to make an analytic determination of the structure.

The diagrammatic representation expresses the total correlation $h(r_{12})$ in terms of indirect effects through all possible chains of direct correlation between particles 1 and 2. This may be seen by repeatedly replacing $h(r)$ by $[C(r) + \text{integral}]$ within the integral of equation (1.13)

$$h(r_{12}) = C(r_{12}) + \rho \int C(r_{13}) C(r_{23}) \, dr_3 +$$
$$\rho^2 \int C(r_{13}) C(r_{34}) C(r_{42}) \, dr_3 \, dr_4 + \ldots$$

(1.17)

1.4 Asymptotic Behaviour of Direct Correlation Function

Much of the informations on the statics of fluid systems can be derived from the knowledge of $g(r)$ or $S(k)$. According to the classical theory of Ornstein and Zernike, $g(r)$ should approach the asymptotic limit of unity in exponential fashion. The work of Enderby et al. [4] emphasized that $S(k)$ is analytic
in \( k \). The theory hinges on the relation

\[
C(r) \sim - \frac{\varphi(r)}{k_B T}
\]  

(1.18)

From the analytic behaviour of \( S(k) \), it emerges that where as in \( A \) for the Van der Waals force, we have

\[
\varphi(r) \sim - A r^{-6}
\]  

(1.19)

and hence

\[
C(r) \sim \frac{A}{k_B T} r^{-6}
\]  

(1.20)

requires the presence of a \( k^3 \) term in the small \( k \) expansion of \( S(k) \)

\[
S(k) = S(0) + a_2 k^2 + a_3 k^3 + \ldots
\]  

(1.21)

Thus \( S(k) \) is not analytic at the origin, due to Van der Waals interaction. It follows that

\[
h(r) \sim \frac{1}{k_B T} \left[ S(0) \right]^2 A r^{-6}
\]  

(1.22)

\[
\sim [S(0)]^2 C(r)
\]

since \( [S(0)]^2 \) is usually small, \( h(r) \ll C(r) \) for large \( r \) according to this argument. Thereby making \( S(k) \) non-analytic at the origin, in liquid metals, the dielectric screening theory yields a singular point at \( k = 2k_F \). For the screened
Coulomb potential, the pair interaction is given by

\[ \phi(r) = \frac{z^2 e^2}{r} \exp(-qr) \]  

(1.23)

where,

\[ q = \left[ \frac{4 k_F e^2}{\pi \hbar^2} \right]^{1/2} \]

Assuming that at large \( r \), in accordance with equation (1.23)

\[ \phi(r) \sim \frac{B \cos(2k_F r)}{r^3} \]  

(1.24)

The oscillatory behaviour arises from the \( k \) space and specially from a term behaving, near \( k = 2k_F \), as

\[ (k - 2k_F) \ln |k - 2k_F| \]  

(1.25)

Using the asymptotic equation (1.18) and that \( C(k) \) and \( S(k) \) are related by equation

\[ C(k) = \frac{s(k) - 1}{S(k)} \]  

(1.26)

it follows that \( S(k) \) has the following expansion around \( 2k_F \)

\[ S(k) = S(2k_F) + S_1 \]  

(1.27)

where \( S_1 \), directly related to equation (1.26) dominates the asymptotic behaviour in \( r \) space. \( h(r) \) is related to
C(r) as follows:

\[ C(k) = \frac{h(k)}{1 + h(k)} \]  \hspace{1cm} (1.28)

since from equation (1.28)

\[ \frac{S_1}{S} \sim \text{constant} + \frac{S_1}{[S(2k_F)]^2} \]  \hspace{1cm} (1.29)

and the Fourier transform of h(r) is given by

\[ S_1 \sim \text{constant} + S_1 \]  \hspace{1cm} (1.30)

since \( S_1 \), leads to the asymptotic form \( r^{-3} \cos 2k_F r \), it may be evidently written from equations (1.29), and (1.30)

\[ C(r) \sim - \frac{B \cos 2k_F r}{K_B T r^3} \]  \hspace{1cm} (1.31)

and

\[ h(r) \sim - \frac{B[S(2k_F)]^2 \cos 2k_F r}{K_B T r^3} \]  \hspace{1cm} (1.32)

since \( S(2k_F) \), from experimental structure data on liquid metals, is always of the order of unity, it is expected that \( h(r) \) and \( C(r) \) to have approximately the same amplitudes at sufficiently large \( r \). One reaches to this conclusion that for liquid metals \( h(r) \) and \( C(r) \) both oscillate about zero
asymptotically. The oscillatory behaviour of $h(r)$ and $C(r)$ which is expected for liquid metals at very large $r$ is in marked contrast to that of classical insulating fluids like Argon, where $h(r)$ and $C(r)$ are expected to approach zero as an inverse power of $r$.

### 1.5.1 Structure Factor

The structure factor is a geometrical factor which can be constructed by the arrangement of ions in case of liquids and the arrangement of atoms in the case of solids. The analysis of this factor for liquids as well as solids is different. For liquids it is known as static structure factor. In past years there have been much progress in the field of liquid metals. A critical description in detail about liquid metals has been described elsewhere \[5-7\]. The study requires the structure factors, which can be determined experimentally with the help of neutron scattering and X-rays measurements. The liquid metals may be considered as binary mixtures of ions and electrons \[8,9\]. Chihara \[10\] has also presented a good theoretical method for the determination of static structure factors with the use of an ion-electron mixture model of liquid metals. Static structure factor for liquids, is defined in the usual way

$$S(k) = \frac{1}{N} \sum_i \exp(-ik \cdot r_i) \quad (1.33)$$

where $N$ is the number of ions, $k$ is the wavevector and $r_i$ is
the position of ion.

1.5.2 Longwavelength Limit of the Structure Factor

A detailed discussion of the density fluctuations argument leading to the relation between the long-wavelength limit of the structure factor and the isothermal compressibility are available elsewhere [11]. An explicit model introduced by Feynman and Cohen [12] is considered here briefly which makes the result plausible. To consider the behaviour of $S(k)$ for small $k$, when longwavelength disturbances are concerned solely, the liquid can be treated as a continuous compressible medium. If $\rho(r,t)$ is the number of atoms per unit volume, in such a medium the normal coordinates $\rho_k$ are defined by

$$\rho_k = \int \rho(r,t) e^{ik \cdot r} \, dr$$

and then the energy is, assuming the $\rho_k$ vary harmonically

$$E = \frac{1}{2} \sum_k (\frac{m}{Nk^2}) [\dot{\rho}_k \dot{\rho}_k^* + \omega_k^2 \rho_k \rho_k^*]$$

where $\omega_k = ck$ and $c$ is the velocity of sound. Passing to quantum mechanics, $\rho(r)$ is replaced by the operator $\Sigma(r-r_i)$ and $\rho_k$ then goes over into the quantum mechanical normal coordinate

$$\rho_k = \sum_i \exp(ik \cdot r_i)$$
Since the average value of kinetic and potential energies are equal, from the virial theorem, for a harmonic oscillator, it follows from equation (1.35) that

\[ S(k) = \frac{<E_k>}{mc^2} \quad (1.37) \]

where \(<E_k>\) is the average energy of the oscillator representing sound wave number \(k\). When \(T = 0^\circ K\), all the oscillators are in their ground states, and hence

\[ <E_k> = \frac{1}{2} \hbar \omega_k = \frac{1}{2} \hbar c k \quad (1.38) \]

Thus it follows from equations (1.37) and (1.38) that

\[ S(k) = \frac{1}{2} \frac{\hbar k}{mc} \quad (1.39) \]

which is true for fluid He\(^4\) at \(T = 0^\circ K\) and small \(k\). The prime interest is the elevated temperature result, since, in this case the probability of finding the oscillator representing phonons of wave number \(k\) in its \(n^{th}\) excited state is proportional to \(\exp(-E_n/K_B T)\), it follows that

\[ S(k) = \left( \frac{\hbar k}{2mc} \right) \coth \frac{1}{2} \beta \hbar c k \quad (1.40) \]

\[ = (\beta mc^2)^{-1} + \frac{\beta \hbar^2}{12m} k^2 + \ldots \ldots \quad (1.41) \]

Here \(\beta = (K_B T)^{-1}\) and as \(k \to 0\) one finds
1.6 Pair Correlation Function and the Structure Factor

The density of particles at a point \( r \) is written as

\[
\rho(r) = \sum_{i=1}^{N} \delta(r-r_i)
\]  

(1.43)

with Fourier transform given by

\[
\rho_k = \int \exp(-ik.r) \rho(r) \, dr
\]

\[
= \sum_{i=1}^{N} \exp(-ik.r_i)
\]  

(1.44)

The average density of particles at \( r \), i.e.

\[
< \rho(r) > = \frac{1}{N} \int \ldots \int \exp(-\beta V_N) \, d^d r
\]

\[
= \rho(r)
\]  

(1.45)

reduces to the mean number density \( \rho \) for a uniform system.

It is evident from equation (1.44) and the known asymptotic behaviour of \( g(r) \) that \( h(r) \to 0 \) as \( |r| \to \infty \); in other words, the positions of distant particles are uncorrelated. The auto-correlation function of the Fourier components of the particle density is called the structure factor, \( S(k) \):

\[
S(k) = \frac{1}{N} < \rho_k \rho_{-k} >
\]  

(1.46)
The structure factor can be expressed as the Fourier transform of the pair distribution function. From equations (1.44) and (1.46)

\[
S(k) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \exp(-ik \cdot r_i) \exp(ik \cdot r_j) \rangle
\]

\[
= 1 + \frac{1}{N} \sum_{i \neq j}^{N} \int \int \exp[-ik \cdot (r-r')] \delta(r-r_i) \delta(r'-r_j) \, dr \, dr'
\]

\[
= 1 + \frac{1}{N} \frac{N(N-1)}{V^2} \int \int \exp[-ik \cdot (r-r')] \ g(r-r') \, dr \, dr' 
\]

\[
= 1 + \rho \int \exp(-ik \cdot r) \ g(r) \, dr 
\] (1.47)

Equation (1.47) can be written as

\[
S(k) = 1 + (2\pi)^3 \rho \ \delta(k) + \rho \ h(k) 
\] (1.48)

where \( h(k) \) is the Fourier transform

\[
h(k) = \int \exp(-ik \cdot r) \ h(r) \, dr 
\] (1.49)

Conversely, \( g(r) \) can be expressed as the Fourier transform of \( S(k) \)

\[
\rho \ g(r) = \frac{1}{(2\pi)^3} \int [S(k) - 1] \ \exp(ik \cdot r) \, dk 
\] (1.50)

The unimportant \( \delta \)-function term of equation (1.48) is ignored, which corresponds experimentally to forward
scattering of radiation, and the relation between \( S(k) \) and \( h(k) \) are taken simply as

\[
S(k) = 1 + \rho h(k) \tag{1.51}
\]

Thus for an isotropic system

\[
\rho h(r) = \frac{1}{(2\pi)^3} \int \left[ S(k) - 1 \right] \exp(ikr) dk
\]

\[
= \frac{1}{2\pi^2} \int \left[ S(k) - 1 \right] \frac{\sin kr}{kr} k^2 dk \tag{1.52}
\]

1.7 Structure Factor and Ornstein-Zernike Relation

The structure factor \( S(k) \) is simply related to the Fourier transform of the total correlation:

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

\[
= 1 + 4\pi \rho \int_0^\infty h(r) \frac{\sin kr}{kr} r^2 dr
\]

\[
= 1 + \rho h(k) \tag{1.53}
\]

The Ornstein-Zernike equation

\[
h(r_{12}) = C(r_{12}) + \rho \int h(r_{23}) C(r_{13}) dr_3 \tag{1.54}
\]

may be Fourier transformed with the aid of the convolution theorem to give
\[ h(k) = C(k) + \rho h(k) C(k) \quad (1.55) \]

so that

\[ \alpha(k) = \frac{h(k)}{1 + \rho h(k)} = \frac{S(k) - 1}{\rho S(k)} \quad (1.56) \]

From which the direct correlation is experimentally accessible through the scattering function \( S(k) \). Alternatively \( S(k) \) may be expressed in terms of direct correlation

\[ S(k) = \frac{1}{1 - \rho C(k)} \quad \text{or} \quad \rho C(k) = 1 - \frac{1}{S(k)} \quad (1.57) \]

Thus a calculation of \( \alpha(k) \) is readily converted into \( S(k) \).

A condition of \( S(k) \), other than that it must, of course, be positive, is provided by a sum rule which follows directly from the inverted form of equation (1.53)

\[ h(r) = \frac{1}{2 \pi^2 \rho} \int_0^\infty [S(k) - 1] \frac{\sin(kr)}{kr} k^2 \, dk \quad (1.58) \]

which at \( r = 0 \) reduces to

\[ 2\pi^2 \rho = \int_0^\infty [S(k) - 1] k^2 \, dk \quad (1.59) \]

This is not a stringent constraint on the detailed form of \( S(k) \) but it does nevertheless provide a criterion of acceptability for model structure factors. There is also a well
known thermodynamic relation between the longwavelength limit \((k \to 0)\) of the structure factor \(S(0)\) and the isothermal compressibility, \(X_T\) \([13]\)

\[
\frac{1}{K_B T} \left( \frac{\partial P}{\partial \rho} \right)_T = 1 - 4\pi \rho \int_0^\infty C(r) r^2 dr
\]

or

\[
\frac{1}{K_B T} X_T = 1 - 4\pi \rho \int_0^\infty C(r) r^2 dr \quad (1.60)
\]

where the integral represents the \(k=0\) form of \(C(k)\)

\[
\rho C(k) = 4\pi \rho \int_0^\infty C(r) \frac{\sin kr}{kr} r^2 dr \quad (1.61)
\]

The compressibility relation may then be rewritten with the aid of equation (1.57)

\[
S(0) = \rho K_B T X_T \quad (1.62)
\]

As the density of the system rises so its compressibility will decrease and \(S(0) \to 0\).

1.8 Pair Potential

The X-ray diffraction in liquids can be demonstrated on the basis of considering the interference effect arising from the two atoms. This effect depends on the relative
separation of two atoms, i.e., on the pair function \( g(r) \). In real sense the function \( g(r) \) can be calculated from statistical mechanics. Johnson and March [14], Enderby et al [15] and Enderby [16] have revealed that X-ray and neutron diffraction techniques may be used in the investigations of structure factor of liquid metals. An information about the atomic distribution and pair potential may be obtained directly from the experimental structural data with the help of March [17]. Ascarelli et al [18] have discussed a relationship between the structure factor and the interatomic potential through the k-space relationship between the Orstein-Zernike direct correlation function and the interatomic potential. It is equivalent to a generalized Debye-Hückel equation and is valid only in special cases, where the potential is of long-range nature. Waseda and Sujuki [19] have discussed relationship between the pair potential obtained by solving the Born-Green equation and from the liquid static structure factor data. In case of many metals the temperature in sensitive long-range oscillatory-type potentials are important. The shape of \( \phi(r) \) (pair potential) curves is generally the similar for all metals. The measure of the steepness of the repulsive core in \( \phi(r) \) can be defined through the \( \delta \) function, which can be described by

\[
\delta = \frac{\sigma}{k} \left[ \frac{\Delta \phi(r)}{\Delta r} \right]_{r = r_0}
\]  

(1.63)
where \( \sigma \) is the hard sphere diameter, \( \xi = \rho_{\text{max}}(r) - \rho_{\text{min}}(r) \) (energy parameter) and \( r_0 \) is the distance of first node in the \( \Phi(r) \) curves. They obtained an average value of \( \delta = 15.1 \) for liquid metals. Thus it can be concluded from the pair potential studies that due to the soft repulsive core part in \( \Phi(r) \), rapidly damped oscillations in the structure factor are obtained which move out of phase with increase of \( k \).

The pair function (radial distribution function) \( g(r) \), which is Fourier transform of \( S(k) \), may be represented by

\[
g(r) = 1 + \frac{1}{2\pi^2 \rho} \int_{0}^{\infty} \left[ S(k) - 1 \right] \frac{\sin kr}{kr} k^2 dk \quad (1.64)
\]

March [17] has discussed that in calculations, total correlation function \( h(r) = [g(r) - 1] \) should be considered which may be split into a pair term, and that due to remaining atoms. Thus \( h(r) \) may be denoted by

\[
h(r) = C(r) + \rho \int C(|r - r'|) h(r') \, dr' \quad (1.65)
\]

where \( C(r) \) is the direct correlation function. The Fourier transform of total correlation function and direct correlation function are related through the equation

\[
C(k) = \frac{h(k)}{1 + \rho h(k)} \quad (1.66)
\]
where \( h(k) = [S(k) - 1] \), which gives \( C(k) = \frac{[S(k) - 1]}{S(k)} \).

Thus, through simple analysis,

\[
C(r) = \frac{1}{12\pi^2\rho} \int_0^\infty \frac{[S(k) - 1]}{S(k)} \cdot \frac{\sin kr}{kr} k^2 dk
\]

may be easily obtained.

Howell's [20] and Ballentine and Jones [21] have fully discussed about the theoretical evaluation of pair potential \( \varphi(r) \) from Percus-Yevick (PY), hypernetted chain (HNC) equations through the following equations

\[
\varphi_{PY}(r) = K_B T \ln \left[ 1 - \frac{C(r)}{1 + h(r)} \right]
\]

\[
\varphi_{HNC}(r) = K_B T \left[ h(r) - C(r) - \ln \{1 + h(r)\} \right]
\]

both of which yield the asymptotic form \([h(r) \sim 0]\)

\[
C(r) \to -\frac{\varphi(r)}{K_B T}.
\]

At the zero of \( h(r) \)

\[
C_{PY}(r) = -\exp \left[ \varphi(r)/K_B T \right]
\]

\[
C_{HNC}(r) = -\varphi(r)/K_B T
\]

These workers determined the pair potential \( \varphi(r) \) for metals and compared the results with the results obtained directly.
from X-ray and Neutron data and with theoretical results obtained by using pseudopotential formalism. The small change in structure factor $S(k)$ in the region of small $k$ lead to a drastic change in the pair potential $\varphi(r)$ which gives an idea that pair potential is highly sensitive to the choice of structure factor used [21]. It appears that the long-range oscillations in the pair potential arises due to the behaviour of the charge density which follows the condition of Friedel oscillations [22]

$$\Delta \rho \propto (1/r^3) \cos(2k_pr)$$

(1.70)

where $\rho$ is the number of atoms per unit volume and $r$ is the distance of the screening charge.

1.9 Random Phase Approximation (RPA)

The potential energy of the system is assumed to be composed of two parts: a "reference system" potential energy and a perturbation potential [23], which is the sum of two particle potentials. The two particle perturbation potential energy is assumed to have a Fourier transform. Collective variables, which are the Fourier transforms of the single particle density, are introduced, and the canonical ensemble partition function is expressed as an infinite series. The mode expansion is a theory [24] which describes the effect of a perturbation energy, $U$, on the equilibrium
properties of a system whose total potential energy is

\[ W = U_0 + U \]  \hspace{1cm} (1.71)

The quantity \( U_0 \) is called the reference system potential energy. Attention is focussed on the correlation among a set of collective coordinates: the Fourier transform of the particle density. We assume that the perturbation can be decomposed into a sum of pair potentials, and that the Fourier transforms of the pair potential exist. The mode expansion expresses the total free energy minus the reference system free energy of an infinite series of terms involving the Fourier transforms of the perturbation potentials and correlation functions in the reference system. The first term neglects correlation among density Fourier components with different wavevectors. This is often called the random phase approximation. The successive terms give a systematic way of correcting that approximation. The series is a formally exact representation of the equilibrium properties of the system. The RPA has a degree of theoretical respectability. It is equivalent to linearized self-consistent field approximation and a well defined many body diagrammatic summations [23], and is first term in a systematic expansion for free energy [24,25]. Further, it has enjoyed significant practical success in predicting properties of system with long-range forces [23 - 25]. The collective
coordinate method for the evaluation of many particle integrals has only been used in its simplest approximation, which is known as RPA. When applied to a system with Coulomb interactions, the RPA leads to Debye-Hückel theory.

A more general problem of a reference system which includes short-range interactions can be treated by a collective coordinate approach [24,26]. In the so-called mode expansion [23,24] the equation of structure factor [27]

\[ S(k) = \frac{S_0(k)}{1 - \rho S_0(k) \phi(k)} \]  

(1.72)

is obtained by neglecting correlation between density components having different wave-vectors. It is therefore appropriate to refer to above equation (1.72) as the "random phase approximation" for the fluid structure in the presence of a perturbation; the perturbation must be sufficiently weak, or the density sufficiently low, to ensure that

\[ \rho S_0(k) \phi(k) < 1 \]  

(1.73)

for all wavevectors in equation (1.72). In the case of Coulombic fluids the RPA reduces to the linearized Debye-Hückel theory.
The pair distribution function is given as

\[ g(r) = g_0(r) + C(r) \]  \hspace{1cm} (1.74)

The RPA equation (1.74) has the drawback that it predicts a pair distribution which can be non-zero for \( r < \sigma \), i.e., inside the hard core, since \( C(r) \) is generally nonzero in that range. It is possible to remedy this unphysical feature of the approximation by means of a self-consistency requirement by an optimization procedure [28].

1.10 Some Useful Thermodynamic Relations

A thermodynamic state is specified by fixing the set of independent thermodynamic variables for which a thermodynamic potential is uniquely given. A single homogeneous substance has two degrees of freedom with a wide possible choice of pairs of independent variables. For condensed materials it is experimentally convenient to choose temperature \( T \) and pressure \( p \). The corresponding thermodynamic potential is the Gibbs free energy, \( G \), defined as follows:

\[ G = U - TS + pV \]
\[ = H - TS \]  \hspace{1cm} (1.75)

where \( U \) is the internal energy, \( S \) is the entropy, \( V \) is the volume and \( H \) is the enthalpy or heat function. The total differential of \( G \) is written as

\[ dG = -S \, dt + V \, dp \]  \hspace{1cm} (1.76)
where
\[
\left( \frac{\partial G}{\partial T} \right)_p = -S,
\]
and
\[
\left( \frac{\partial G}{\partial p} \right)_T = V \tag{1.77}
\]

Equation (1.76) is called the fundamental formula for the variables \( T, p \). The enthalpy is given by
\[
H = G - T \left( \frac{\partial G}{\partial T} \right)_p = -T^2 \left( \frac{\partial (G/T)}{\partial T} \right)_p \tag{1.78}
\]

small change in the energy \( U \), the Helmholtz free energy \( F \) are given by the following equations for systems of constant composition and total mass:
\[
dU = T \, dS - pdV \tag{1.79}
\]
\[
dF = -S \, dT - pdV \tag{1.80}
\]

It follows that
\[
\left( \frac{\partial U}{\partial V} \right)_S = \left( \frac{\partial F}{\partial V} \right)_T = -p \tag{1.81}
\]
and
\[
\left( \frac{\partial F}{\partial T} \right)_V = -S \tag{1.82}
\]

The changes of \( U, S \) and \( F \) are related to the heat capacities at constant volume and constant pressure:
\[ C_V = \left( \frac{\partial U}{\partial T} \right)_V \]
\[ = T \left( \frac{\partial S}{\partial T} \right)_V \]
\[ = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V \]  \tag{1.83}

\[ C_p = \left( \frac{\partial H}{\partial T} \right)_p \]
\[ = T \left( \frac{\partial S}{\partial T} \right)_p \]
\[ = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_p \]  \tag{1.84}

and
\[ U = F - T \left( \frac{\partial F}{\partial T} \right)_V \]  \tag{1.85}

The isothermal changes of \( U \), \( S \) and \( F \) with volume or pressure can be expressed solely in terms of pressure, volume, temperature. Their mutual derivatives are

\[ \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial B}{\partial T} \right)_V \]

and

\[ \left( \frac{\partial S}{\partial p} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_p \]  \tag{1.86}

From equation (1.85)
\[ \left( \frac{\partial U}{\partial V} \right)_T = -p + T \left( \frac{\partial p}{\partial T} \right)_V \]  \tag{1.87}

The equation (1.87) is known as thermodynamic equation of
of state. From equation (1.87)

\[ C_p - C_V = T \left( \frac{\partial p}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_p \]  

(1.88)

\[ C_p = C_V - T V \left[ V \left( \frac{\partial p}{\partial V} \right)_T \right] \left[ \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_T \right] \]  

(1.89)

\( \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \) is the coefficient of thermal expansion and is denoted hereby \( \alpha_p \). \( -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \) is the isothermal coefficient of bulk compressibility and is denoted hereby \( X_T \).

\( \left( \frac{\partial p}{\partial T} \right)_v \) is the thermal pressure coefficient and is denoted hereby \( \nu_v \). The change of \( \alpha_p \) with pressure is the complement of the change of \( X_T \) with temperature:

\[
\left( \frac{\partial \alpha_p}{\partial \nu_v} \right)_T \left( \frac{\partial \nu_v}{\partial p} \right)_T = \left( \frac{\partial \nu_v}{\partial \alpha_p} \right)_I \left( \frac{\partial \alpha_p}{\partial p} \right)_T
\]

(1.90)

Experimental results are often expressed in terms of these coefficients and it is therefore useful to write some of the equations in the following form:

\[ X_T = \alpha_p \nu_V \]  

(1.91)

\[ \nu_V = \left( \frac{\partial S}{\partial V} \right)_T \]  

(1.92)

\[ C_p - C_V = T V \frac{\partial^2}{\partial p^2} X_T \]  

(1.93)

\[
\left( \frac{\partial S}{\partial V} \right)_T = -p + T \nu_V
\]

(1.94)
1.11 References


