CHAPTER 1

SOME ASPECTS OF THE THEORY OF METALLIC LIQUIDS

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1.1 Introduction

A liquid is considered to be a condensed phase of matter. It has a density very similar to that found in the corresponding solid phase, but has a symmetry more typical of a gas. Many properties of liquids for example specific heat [Faber 1972] are not very different from those of solids at comparable temperatures, but they have generally proved much harder to calculate than either crystalline solid state or gaseous properties. Extended solids normally have both translational and point group symmetries and these lead to enormous simplifications in formulating theoretical descriptions of their various properties. In the case of dense gases, the density is a convenient parameter in terms of which expansions for the thermodynamic functions can be developed. But liquids possess neither obvious symmetry nor obvious expansion parameters and these are serious impediments in formulating theoretical descriptions. Thus liquids differ from gases and solids in that, they are neither completely ordered like solids nor completely disordered like gases. They have only short range order and long range disorder.

The behaviour of liquids exhibits a variety comparable to that found in crystalline solids. For example, liquids, like solids can be classified according to their electronic
transport properties as metals, semiconductors or insulators.

A metallic system is distinguished from other systems by its ductility and by having high values of the electrical and thermal conductivities. These arise from the nearly free motion of some of the electrons—known as the conduction electrons. The remaining electrons, called the core electrons, are bound to the nucleus and the whole is termed as ion: the number $Z$ of electronic charges on an ion is equal to the number of conduction electrons per atom, which is usually set equal to the chemical valence. Thus a liquid metal may be thought of as two intermingled fluids, one composed of the ions and another composed of the conduction electron gas. Liquid metals typically have resistivities of order $10^{-100}$ $\mu$ohm cm and frequently a positive temperature coefficient of resistivity. Liquid semiconductors have much higher resistivities with an activated temperature dependence, and liquid insulators have very large resistivities, which at ordinary temperatures do not show signs of thermal excitation of current carriers.

A liquid metal is composed of charged massive nuclei and light electrons in an electrically neutral admixture. In most liquid metals, some of the electrons are tightly bound to the nuclei and play only a passive role in determining the properties of the metal. The remaining electrons have degrees of freedom which must be explicitly taken into account. The elemental liquid metal is, in
fact properly to be regarded as a two component mixture of interacting electrons and ions. But for many purposes, the two component liquid can be reduced to a quasi-one-component system with suitably redefined effective interactions between the ions. The first requirement in describing a dense fluid of interacting electrons and ions is, of course, a knowledge of interactions. We consider the nature of electron-ion interaction, the quantity which clearly distinguishes simple metals from other metals.

We suppose that the electrons can be unambiguously classified as "valence" or "core" electrons, the latter being so tightly bound that their degrees of freedom can be largely ignored in calculating in thermodynamics of the liquid.

The single particle interaction between an ion and an electron in a simple liquid metal is characterized by a potential \( V(r) \) of the form shown in Fig (1.1). Typically \( V(r) \sim -Z\frac{e^2}{r} \) outside the core, while within it \( V(r) \) is strongly negative and nonconstant. Within the one-electron approximation the eigen spectrum of \( T+V \) (\( T \) being the electron kinetic energy operator) contains both valence and core levels. But since the latter play only a passive role in determining the properties of the metal, it is desirable to eliminate them from the problem. The essence of the pseudo-potential method is to replace the strong potential \( V \) by a much weaker pseudopotential \( V^p \) such that \( T + V^p \) has the same
Fig. 1:1 - Schematic representation of an electron ion potential in a simple metal.

Fig. 1:2 - Local pseudopotential corresponding to potential $V(r)$. 
spectrum of valence eigenvalue as $T + V$, but gives rise to no eigenstates of lower energy. It proves possible to conduct many pseudopotentials of this kind. Indeed, replacing $V$ by any operator $V^P$ having the same phase shifts at the core radius leaves the valence spectrum unchanged. In this way, it is often feasible, for the simple metals to select a pseudopotential that is very small in the core region and is, therefore, capable of being treated by perturbation theory, as has been extensively discussed by Cohen and Heine (1970). Such a pseudopotential is schematically drawn in Figure (1.2).

1.2 Classification of Liquid Metals

Rather than classifying liquids by their transport properties, one can group them according to their prevailing "intermolecular forces" or "bonds". Simple liquids are those composed of spherical or nearly spherical "molecules" and are characterized by predominantly two-body central bonding forces. They include insulating fluids such as liquid argon and even perhaps liquid methane. They also include conducting fluids (such as Na, Cu, liquid Si and Ge) although the forces in these latter substances are functions of density as well as separation. In homonuclear molecular liquids such as $H_2$ and $N_2$ the intermolecular forces include, in addition to a principal central component,
a substantial angular part dependent upon relative molecular orientation.

Associated liquids, such as water and glycerol are characterized by hydrogen bonding, and polar liquids such as HBr and molten salts often have long-range interactions. Finally, liquids made up of large organic molecules may exhibit liquid crystalline order, that is, symmetry elements of a crystalline state while retaining other characteristics of a liquid. Except for simple liquids, all may show strong directional (or steric) effects, or are otherwise complicated by effects of anisotropy and internal degrees of freedom.

Generally, a conducting liquid can exist under only some thermodynamic condition which is specified by thermodynamic variables such as pressure, temperature and volume. Thus, the thermodynamic studies lay the foundations for the understanding of liquid metals. The central problems to be dealt with are those of calculating such measurable quantities as the compressibility, specific heat, entropy and melting curves of metals from the knowledge of fundamental interactions among the electrons and ions. In order to understand this problem, it is necessary to consider both the electronic structure and the "bonding" structure or ionic arrangement. These are closely interrelated. For example, any description of the ionic arrangement must
take into account the presence of conduction electrons. Conversely, the electronic structure must in turn be strongly affected by the physical arrangement of the ions. The interplay between these dual aspects of liquid metals is quite complex. Liquid metals may be further divided into roughly nonoverlapping classes according to their electronic structure. Under normal conditions these classes are broadly defined as follows:

Simple Metals: These have band structures in the crystalline state that are recognizable free electron like. Examples are Na, Mg, Al and Pb. Their valence bands are very well separated in energy from the next lowest core-level bands.

Transition and Noble Metals: In varying degrees these have band structures that exhibit features both of narrow (or tight binding) bands and nearly free electron behaviour. In the noble metals the tight-binding-like structure is contained below energies equal to the highest occupied level (i.e. at T = 0, the Fermi level). In the transition metals this ceases to be the case and the Fermi level lies within a principally d-electron like band structure. In the alkaline earths the tight-binding-like bands lie just above the Fermi energy and it may not be inappropriate to refer to these examples as "near transition" metals.
Rare Earths, Lanthanides, Actinides: In these metals the f-bands are usually split indicating a failure of the independent particle approximation. Between split f-bands lies a set of bands roughly characterized by the atomic s and p (and in some cases, d) levels from which they derive. For certain metals there may also be densities for which mixed valences appear.

From the point of view of electron structure, the range presented by the entire class of molten metals is evidently exceedingly diverse. In the interest of presenting a coherent and relatively compact development of the theory of the thermodynamics of liquid metals, we have chosen the metals whose band structures in the solid state are known to be very free electron like. A large number of elements fall in this class: Some, for example, Pb, Tl, etc. are heavy elements and require a description, which properly takes into account spin–orbit effects.

The central question regarding liquid metals is, of course, why they form simple liquids, or equivalently, why structurally, they have two body central forces. The answer, in the case of free electron metals, lies in the predictions of perturbation theory as applied to an interacting electron gas. The perturbation arises from the metallic ions which carry with them, in an adiabatic
way, the fundamental interaction between the electrons and ions - the pseudopotential.

1.3 Potential Energy of the System

It is now known that the thermodynamics of simple liquid metals is understandable microscopically in terms of both the pseudopotential theory and the liquid state theory, as was reviewed by Young (1977) in the Bristol Conference. This approach becomes increasingly strengthened by refining the details of calculations. It starts from the fact that the potential energy of a metal with N atoms can be written [Shimoji (1977), Evans (1978), Ashcroft and Stroud (1978)]

\[
U(\vec{R}_1, \ldots, \vec{R}_N) = U_g + \frac{1}{2} \sum_{i \neq j} U(\vec{R}_i - \vec{R}_j) \quad (1.1)
\]

where \(\vec{R}_i\) is the ionic co-ordinate, \(U_g\) the potential energy which depends only on the ionic (number) density of the metal, \(n\), and not on the ionic arrangement; \(U(R)\) the effective pairwise potential between the ions. Within the usual framework of pseudopotential theory the interionic pair potential \(U_{ps}(R)\) comes from the direct point charge interaction and the polarization effect of the electron gas to be represented by the electron dielectric function which is also density dependent.
For the ions with large core radii the exchange repulsive energy term, \( U_{\text{rp}}(R) \), caused by core electrons should also be taken into account, e.g. using the equation of Born-Mayer type. Moreover, for highly-polarizable ions the dispersion or Van der Waals forces due to instantaneous dipole-dipole interactions, \( U_{\text{vw}}(R) \), are not always negligible, even though the ions are immersed in the electron gas [Rehr et al (1975), Mahanty and Taylor (1978), Mon et al (1979)]. Thus, an accurate expression for \( U(R) \) in equation (1.1) should be given by

\[
U(R) = U_{\text{ps}}(R) + U_{\text{rp}}(R) + U_{\text{vw}}(R) \tag{1.2}
\]

At normal densities of simple metals both \( U_{\text{rp}} \) and \( U_{\text{vw}} \) are small enough to be ignored, but not always for non-simple metals [Rehr et al (1975), Mon et al (1979)]. The binding energy of a metal is determined largely by the structure-independent energy \( U_g \) in equation (1.1) [Shimoji (1977), Ziman (1969)], which is a sum of the well-known electron gas energy \( U_{\text{eg}} \) in the uniform positive background and the electrostatic energy \( U_{\text{ei}} \) of the electron gas with pseudopotentials embedded with it. The \( U_{\text{ei}} \) is strongly influenced by the pseudopotential used, since it contains the first-order perturbation term.

For transition metals the renormalized-atom method is now developed to describe the binding properties [Gelatt et al (1977)]. From the point of view of the tight binding
method Friedel (1969) and Kajzar et al (1977) proposed another model for the binding of transition metals formed by overlapping of the d-orbitals of free atoms. It would be still reasonable to expect the existence of the strongly structure-dependent pair potential $U(R)$ for such liquid transition metals, whose form is analogous to that in (1.1); for example, the one component plasma model [Minoo et al (1977), Khanna and Lackmann (1979)] is a simple approach for this problem.

Once the potential energy $U$ of a liquid metal is given in (1.1), the microscopic calculation of its thermodynamic properties can be made straightforwardly by employing the technique of the statistical mechanical theory of classical molecular liquids.

The simplest model of a liquid metal is obtained by expressing $U(R)$ in (1.1) by a hard sphere model which is characterized by the diameter $\sigma$ or the packing fraction $\eta = \pi \sigma^3 / 6 \Omega$. Analytical equations of state for the hard sphere fluid are given the form of Percus-Yevick [Thiele (1963), Wertheim (1964)] or Carnahan-Starling (1969) equations, which are in good agreement with computer-simulation studies at packing densities with $\eta$ smaller than ~ 0.5, in consequence, the hard sphere Helmholtz free energy $F_{hs}$ can readily be derived. Thus, the total Helmholtz free energy of a liquid metal is given by [Shimoji (1977)]
F = U_g + F_{hs} \quad (1.3)

from which other thermodynamic quantities can easily be calculated. For example, the entropy ($= -(\frac{\partial F}{\partial T})_V$) may be written in the sum of the electronic part $S_{\text{elec}}$ and the hard sphere part $S_{\text{hs}}$ [Young (1977)].

1.4 Equations for the Direct Correlation Function

(i) Ornstein-Zernike Relation:

The total correlation function $Y(r)$ is defined by

$$Y(r) = g(r) - 1 \quad (1.4)$$

where $g(r)$ is pair correlation function. The total correlation function $Y(r)$ is conveniently regarded as being composed of two terms: a direct correlation function $C(r)$ and an indirect term which describes the correlation of the pair considered through the action of a third particle. Thus

$$Y(r_{12}) = C(r_{12}) + \rho \int C(r_{13}) Y(r_{23}) \, d^3r_3 \quad (1.5)$$

This is known as the Ornstein-Zernike relation.
(ii) Hypernetted Chain (HNC) Approximation:

It is a way to define direct correlation function \( C(r) \) in the Ornstein-Zernike relation

\[
C_{\text{HNC}}(r) = Y(r) - \ln g(r) - \frac{U(r)}{k_B T} \tag{1.6}
\]

(iii) Percus-Yevick Approximation:

It is another way to define the direct correlation function \( C(r) \)

\[
C_{\text{PY}}(r) = g(r) \{ 1 - \exp[-\frac{U(r)}{k_B T}] \} \tag{1.7}
\]

\[
= f(r) \cdot Y(r)
\]

where

\[
Y(r) = g(r) \exp\left[-\frac{U(r)}{k_B T}\right]
\]

1.5 The Percus-Yevick Solution for Hard Spheres

The importance of P-Y approximation in the study of the equilibrium properties of simple fluids stems in part from the fact that this particular integral equation can be solved analytically for the important case of a system of hard spheres. The analytic solution was obtained independently by Thiele (1963) and Wetheim (1963, 1964).

For hard spheres of diameter \( \sigma \) we have the obvious condition that

\[
g(r) = 0, \quad r < \sigma \tag{1.8}
\]
On the other hand the density expansion of \( g(r) \) shows that the function

\[
Y(r) = \exp[\beta v(r)]g(r)
\]  

(1.9)

remains continuous at \( r = \sigma \). In terms of \( Y(r) \), the Percus-Yevick approximation can be written as

\[
C(r) = Y(r)f(r)
\]  

(1.10)

which, in the hard sphere case, reduces to

\[
C(r) = -Y(r) \quad r < \sigma \\
C(r) = 0 \quad r > \sigma
\]  

(1.11)

Inserting (1.8) and (1.11) in the Ornstein-Zernike relation leads to an integral equation for \( Y(r) \)

\[
Y(r) = 1 + \rho \int Y(r')dr' - \rho \int Y(r')Y(|r - r'|)dr' \quad \begin{cases} 
    r' < \sigma & r' < \sigma \\
    |r-r'| > \sigma
\end{cases}
\]  

(1.12)

Thiele (1963) and Wertheim (1963) have shown independently how equation (1.12) can be solved by taking Laplace transform; here we quote only the final result for \( C(r) \)

\[
C(x) = \begin{cases} 
    -\lambda_1 - 6\eta\lambda_2 x - \frac{1}{2}\eta\lambda_1 x^3 & x < 1 \\
    0 & x > 1
\end{cases}
\]  

\[
\lambda_1 = \frac{(1 + 2\eta)^2}{(1 - \eta)^4}
\]  

(1.13)
\[ \lambda_2 = -\frac{(1 + \frac{1}{2} \eta)^2}{(1 - \eta)^4} \]  

(1.15)

The equation (1.13) can be used to solve the compressibility and virial equation of states \[\text{[Thiele (1963) and Wertheim (1963, 64)]}. \] The resulting equations of states are

\[ \frac{\beta_p C}{\rho} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3} \]  

(compressibility equation (1.16))

\[ \frac{\beta_p v}{\rho} = \frac{1 + 2 \eta + 3 \eta^2}{(1 - \eta)^2} \]  

(virial equation)  

(1.17)

These two equations give different results because the Percus-Yevick equation is only an approximation: the difference between the two increases with increasing density. Both give the exact Second and Third virial coefficients, but give different values for higher order coefficients. The expressions for the virial coefficients obtained by expanding (1.16) and (1.17) in powers of density are
\[ B_n^C/b^{n-1} = [1 + \frac{3}{2} n(n-1)](4)^{1-n} \]  
\[ B_n^V/b^{n-1} = 2(3n-4)(4)^{1-n} \]  

where \( b = B_2 = (2\pi/3)\sigma^3 \). It is interesting to note that the Carnahan-Starling relation is recovered by adding the expressions (1.16) and (1.17) with weights, respectively, of \( \frac{2}{3} \) and \( \frac{1}{3} \).

\[ \frac{\beta P^{CS}}{\rho} = \frac{2}{3} \frac{\beta P^C}{\rho} + \frac{1}{3} \frac{\beta P^V}{\rho} \]
\[ = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} \]  

where the subscript \( cs \) indicates the Carnahan Starling result. The fact that \( P^{CS} \) is in such good agreement with the machine calculated data for pure hard spheres indicates that the compressibility relation is more accurate than virial relation, because of its greater contribution in eqn. (1.20). It should be noted that the machine calculated values for compressibility of hard spheres, always stand inbetween the values calculated from compressibility and virial relations.

1.6 Gibb's Bogoliubov Inequality [Approximations for Simple Liquids]

In statistical mechanics variational methods based on minimising the free energy have been used widely. For
many body systems several other variational techniques such as those based on quantum mechanical principles of minimizing the energy have been successfully developed [Feynman and Cohen (1956), Bogoliubov (1958), Kohn (1964), Mermin (1965)].

As one of such variational principles, Peierls (1938) presented an inequality which gave a rigorous lower bound to the exact partition function, namely an upper bound to the free energy. The inequality is of particular importance when one tries to replace the Hamiltonian by its diagonal elements since then several investigations on the inequality have been reported.

The variational approach is based on an exploitation of the so-called Gibb's Bogoliubov inequality which states that if the Hamiltonian for a system is regarded as that for a reference system plus a perturbation then the Helmholtz free energy for the reference system plus the expectation value of the perturbation averaged over the reference system is greater than or equal to the Helmholtz free energy of the actual system.

For simple liquids, the reference system is always chosen to be the hard sphere system. This choice is motivated by the following important considerations:

(ii) The hard sphere system can be accurately treated by the Percus-Yevick Theory (1958) which turns out to be analytically soluble in this case [Wertheim (1963, 1964), Thiele (1963)].

(iii) The properties of the system depend only on a single dimensionless variable \( \rho^* = \rho \sigma^3 \), where \( \rho^* \) is the reduced density, \( \rho \) the number density and \( \sigma \) the hard sphere diameter. So if \( U \) and \( F \) denotes the potential energy and free energy of the real system whereas \( U_0 \) and \( F_0 \) the potential energy and free energy of the reference system then the inequality states that

\[
F \leq F_0 + \langle U - U_0 \rangle v_0
\]  

(1.21)

which means that \( F \) is bounded above by the free energy of the reference system augmented by the potential difference averaged with respect to the distributions of the reference system (Isihara 1968). Evidently the appellations "real" and "reference" are immediately interchangeable in the application of (1.21), so we must also have

\[
F_0 \leq F + \langle U_0 - U \rangle v
\]  

(1.22)
which is a powerful result, particularly if the distribution functions of the reference system are known to be close to those of the real system.

1.7 Thermodynamical Variational Method for Hard Sphere System

Starting from the work of Zwanzig (1954) various forms of perturbation theory have been developed for real fluids. They have in common the underlying assumption that in the zero order, such fluids can be described by hard spheres.

Let $H = K + V$ be the Hamiltonian of a system of interest and $H_{hs} = K + V_{hs}$ be that for a reference system of hard spheres having the same masses and occupying the same volume as the actual particles. Then for any chosen sphere diameter $\sigma$, an upper bound to the Helmholtz free energy per ion, at fixed temperature and volume, is

$$ F = F_{hs} + \langle H - H_{hs} \rangle_{hs} $$

$$ = F_{hs} + \langle V \rangle_{hs} \quad (1.23) $$

Here angular brackets denote an appropriate expectation value per atom and $F_{hs}$ is the free energy per ion of a reference system of hard spheres of packing fraction $\eta$ with the same density $n$ and temperature $T$ as the real ionic system, given by
\[ F_{hs} = \frac{3}{2} k_B T - T S_{hs} \quad (1.24) \]

Now the entropy estimated for the real system contains no contribution from the thermal variation of \( \sigma \) [Edwards and Jarzynski (1972)]. For

\[
S = -\left( \frac{\partial F}{\partial T} \right)_\Omega \]
\[
= -\left( \frac{\partial F}{\partial \Omega} \right)_{\Omega, T} - \left( \frac{\partial F}{\partial \sigma} \right)_{\Omega, T} \left( \frac{\partial \sigma}{\partial T} \right)_{\Omega} \quad (1.25)
\]

One must always minimize the free energy with respect to \( \sigma \) and the best hard sphere reference system will be that conforming to

\[
\left( \frac{\partial F}{\partial \sigma} \right)_{\Omega, T} = 0 \quad (1.26)
\]

Thus final term of equation \(1.25\) vanishes via equation \(1.26\) then

\[
S = -\left( \frac{\partial F}{\partial T} \right)_{\Omega, \sigma} \quad (1.27)
\]

Thus the equation \(1.23\) leads to

\[
S = -\left[ \frac{\partial}{\partial T} \left\{ F_{hs} + \langle V_{hs} \rangle \right\} \right]_{\Omega, \sigma}
\]
\[
= S_{hs} - \left[ \frac{\partial}{\partial T} \langle V \rangle_{hs} \right]_{\Omega, \sigma} \quad (1.28)
\]

\( V \) for metals is non vanishing to the extent that electron gas is non degenerate; to the first order in \( T \) it may be
written (Silbert et al 1975, Meyer et al 1976)

\[ S = S_{hs} + S_{elec} \]  

(1.29)

1.8 The Entropy of the Hard Sphere Reference System

The natural tendency of any physical system consisting of a large number of individual units is to go from a state of order into a state of disorder. In this sense entropy is simply a measure of the disorder of molecular motion. In statistical mechanics we give a precise meaning to disorder and we express its connection with entropy by the relation

\[ S = k_B \ln w \]  

(1.30)

here \( k_B \) is the Boltzman's constant, \( S \) is the entropy of the system, and \( w \) is the disorder parameter. \( w \) gives the probability that the system will exist in the state it is in relative to all the possible states it could be in. The equation connects a thermodynamic, a macroscopic quantity the entropy, with a statistical or microscopic quantity, the probability.

Consider a one component hard sphere fluid at temperature \( T \) with spheres of mass \( M \) and diameter \( \sigma \), so that its volume \( \omega = \pi \sigma^3 / 6 \). If \( \Omega \) is the container volume per sphere, the packing fraction is \( \eta = \omega / \Omega \).

Carnahan and Starling (1969) have proposed a semi empirical
formula for the equation of state of a hard sphere fluid. This leads to an entropy per ion

$$S_{hs} = S_{gas} + S_{\eta} \quad (1.31)$$

where $S_{gas}$ is the ideal gas entropy given by

$$\frac{S_{gas}}{k_B} = 2.5 + \ln \left[ \frac{\Omega \left( \frac{MK_T}{2\pi \hbar^2} \right)^{3/2}}{2\pi \hbar^2} \right] \quad (1.32)$$

while $S_{\eta}$ that depends only upon the packing fraction has been discussed by Jones (1973). It is now well known that different thermodynamic routes lead to different equations of state for a given approximate theory of the radial distribution function. Accordingly, integration of these equations of state (Mansoori and Canfield 1969) give different forms for $F_{hs}$ and therefore $S_{\eta}$. Using the exact Percus-Yevick solutions for the pressure of the hard sphere reference system [Sec. 1.5] derived respectively from the compressibility (Ornstein-Zernike) and pressure (virial) equations, leads to

$$\frac{S_{\text{comp}}}{k_B} (\eta) = \ln (1-\eta) + \frac{3}{2} \left( 1 - \frac{1}{(1-\eta)^2} \right) \quad (1.33)$$

$$\frac{S_{\text{press}}}{k_B} (\eta) = -2 \ln (1-\eta) + 6 \left( 1 - \frac{1}{(1-\eta)} \right) \quad (1.34)$$

but a better (though more empirical) equation for the pressure
of a hard sphere system is known to result from averaging (in the ratio 2/3 to 1/3) the two Percus–Yevick pressures referred to above; the result is the Carnham Starling equation given by

\[
\frac{S \eta}{K_B} = 3 - \frac{2}{(1-\eta)} - \frac{1}{(1-\eta)^2}
\]

\[= -(\xi - 1) (\xi + 3) \quad (1.35)
\]

where

\[
\xi = \frac{1}{1-\eta} \quad \text{and} \quad \eta = \frac{\pi \sigma^3}{6 \Omega}
\]

Equation (1.29) clearly suggests that in addition to the two components of hard sphere entropy, there is an additional contribution \(S_{\text{elec}}\) from electrons

\[
S = S_{\text{gas}} + S_\eta + S_{\text{elec}} \quad (1.36)
\]

In the non interacting electron gas model one can write

\[
S_{\text{elec}} = ZYT; Y = \gamma_{\text{eg}} + \gamma', \quad (1.37)
\]

\(\gamma_{\text{eg}}\) is the Sommerfeld constant for the electronic specific heat and is given by

\[
\gamma_{\text{eg}} = \left(\frac{\pi K_B}{K_F}\right)^2 \quad (1.38)
\]

\(\gamma'\) has been investigated by Silbert et al (1975), they have shown that it represent a small correction to \(\gamma_{\text{eg}}\); so it is
well justified to set $\gamma' = 0$ in general.

Umar, Watabe and Young (1974) pointed out that the entropies of many liquid metals seemed to be explainable, at least in a first approximation on the basis of a hard sphere model. At a crude level, interatomic forces in liquid metals are quite well understood. Simple and transition metals (Young 1977) and also rare earth metals (Harder and Young 1977) can usually be well represented by hard spheres, whose size vary with the temperature and volume. By this device Yokoyama et al (1977) have been able to parametrise empty-core Ashcroft (1966) pseudopotentials in such a way as to explain the observed entropies of the pure liquid metals. Of particular interest, in this respect, is the work of Hodges (1977) who showed how the empirical classification of Miedema et al (1973) of heats of solution for a wide range of solids can be explained rather well by first order perturbation theory provided nonlocal pseudopotentials are used. Sommer (1973) and Hafner (1977), who have used the second order nonlocal pseudopotential perturbation theory to obtain some very promising results for heats of solution. Yokoyama et al (1979) work has taken place largely in parallel with the studies of Hodges (1977) and of Hafner (1977) and conclude that for truly quantitative results, nonlocality in the zeroth Fourier component in the pseudopotential appears to be indispensable. Hafner (1977) and Yokoyama et al (1979)
both used the same hard-sphere description but are otherwise rather complementary. Hafner used an OPW-based first principles pseudopotential approach. With a minimum of arbitrary adjustment he obtained results which are often very good. Yokoyama et al (1979) attempted to explain all the observed data for pure liquid metals. Ohkoshi et al (1980, 1981) were able to obtain accurate entropies for a variety of liquid metals on the basis of two methods: the Percus-Yevick phonon theory (1958) on the one hand and the effective hard sphere packing theory (Young 1977, Ashcroft and Stroud 1978) on the other. Thus we conclude that the hard sphere model provides a basis for understanding the thermodynamic properties of liquid metals microscopically in terms of both the pseudopotential theory and the liquid state theory, as was reviewed by Young (1977) in the Bristol Conference.

1.9 The Hard Sphere Diameter

Metal atoms are of course not hard spheres, we can, however, assign a hard sphere diameter to a liquid metal by consideration of interatomic potential energy curve shown schematically in Figure (1.3). The position of the minimum in the curve is at $\sigma_0$. To the left of the minimum the potential is repulsive and to the right it is attractive. A hard sphere potential energy function is purely repulsive and, so if a hard sphere potential is to
Fig 1.3 - Schematic representation of the potential energy $U(r)$ of interaction between two metal atoms as a function of distance $r$ between the atoms. The distance at which the potential energy is a minimum is $\sigma_0$. 
represent the actual potential, it presumably, should mimic just the repulsive part. When two hard spheres undergo a repulsive collision with one another, their distance of closest approach is \( \sigma \), but when two soft spheres undergo a repulsive collision there is a variety of possible distances of closest approach i.e. they can climb up the potential energy barrier to the left of \( \sigma_0 \) to a variety of heights depending on the relative velocity and other details of the collision. Thus a reasonable way of choosing the hard sphere diameter would be to assign it the value equal to the average distance of closest approach for repulsive collisions in the fluid. At higher temperatures, atoms will collide more vigorously, and hence we would expect that this mean distance would decrease. Therefore, the effective hard sphere diameter for liquid metals should be a decreasing function of temperature. An elementary calculation indicates that the temperature dependence might be expected to be of the following form:

\[
\sigma_T = \sigma_0 \left[ 1 - B \frac{T}{T_m} \right]^{1/2} \tag{1.39}
\]

where \( \sigma_T \) is the diameter at temperature \( T \) and \( T_m \) is the melting temperature of the metal. \( B \) is a dimensionless positive number which is related to the curvature of the interatomic potential at the minimum.
Let \( \eta_m \) denote the packing fraction of a liquid metal at the melting temperature, i.e.

\[
\eta_m = \frac{\pi}{6} n_m \sigma_m^3 
\]

(1.40)

where \( n_m \) is the atom number density for the liquid at the melting temperature and \( \sigma_m \) is the diameter at the melting temperature. Combining equations (1.39) and (1.40) and eliminating \( \sigma_0 \), we obtain

\[
\sigma_T = \left( \frac{6 n_m}{\pi n_m} \right)^{1/3} \left[ \frac{1 - B(T/T_m)}{(1 - B)} \right]^{1/2}
\]

(1.41)

Thus the problem of finding the effective hard sphere diameter for a liquid metal at any temperature is reduced to the problem of estimating two temperature-independent dimensionless numbers \( \eta_m \) and \( B \) for that metal. To a good approximation, \( \eta_m \) and \( B \) each have the same values for all liquid metals, namely 0.472 and 0.112 respectively.

Thus the simplest hard sphere model is expressed by

\[
U(r) = +\infty \quad \text{for} \quad r < \sigma
\]

and

\[
U(r) = 0 \quad \text{for} \quad r > \sigma
\]

(1.42)

This model is of particular importance since it gives a first useful approximation to the effective short range repulsive interaction which governs the geometrical packing at
liquid densities.

The hard sphere perturbation theories of Barker and Henderson (BH) (1971) and Weeks, Chandler and Anderson (WCA) (1971) are the most nearly accurate and widely used for simple fluids.

In BH theory, the hard sphere diameter \( d \) is determined by the expression

\[
d = \int_0^\sigma [1 - \exp(-\beta U)] dr \tag{1.43}
\]

where \( \beta = 1/k_B T \) and \( \sigma \) is the value of \( r \) for which \( U(r) = 0 \). The \( \sigma \) separates the potential into a steep repulsive part, \( r < \sigma \) and a weak, attracting part, \( r > \sigma \). The stiff repulsive part is taken to be the reference state and is approximated by the hard sphere system. The weak attraction is treated as the perturbation.

WCA divide \( U(r) \) at \( r = r_m \) where \( U(r_m) \) is the minimum of \( U(r) \), into a stiff reference potential and a soft perturbation. They, like BH, approximate the reference system by hard sphere function. They approximate

\[
g_o(r/d) = \exp[-\beta U_o(r)] \chi_{HS}(r) \tag{1.44}
\]

where \( \chi_{HS} \) is the hard sphere distribution function. The choice of \( d \) is a little more complicated but is qualitatively
equivalent to $d$ is $r_m$. However, the uncertainty in $g_o(r/d)$ for very high density fluids is one of the limitation of WCA theory.

In contrast, variational theory suffers from no such limitation in density, $d$ is simply chosen as that value of the hard-sphere diameter that minimizes the Helmholtz free energy.

1.10 Structure Factor and Hard Sphere Approximation:

One of the favourite testing ground of liquid state Physics is the calculation of structure factor. The first realistic model of a liquid metal was the hard sphere model proposed by Ashcroft and Lekner (1966). A common way of demonstrating this is to compare them with hard sphere forms characterized by packing fractions chosen to match the observed heights of the principal peaks. It has been known since the work of Ashcroft and Lekner (1966) that $\eta \approx 0.45$ is about right at the melting temperature.

To illustrate this point, Figure (1.4) shows results for Na and Al [Young (1977)]. In Na, significant phase and amplitude differences develop in the structure factors at high scattering angles due to the relatively soft core in this metal [Page et al (1969), Hansen and Schiff (1973)] and similar behaviour occurs in other
Fig. 1.4 Structure factors for Na and Al. Broken lines are the corresponding P-Y hard sphere forms with $\eta = 0.475$ and 0.45 respectively.

Fig. 1.5 Radial distribution functions for Na, Al and Bi near their melting temperatures.

Fig. 1.6 Structure factors for Bi(573K). Crosses are experimental values (Waseda and Suzuki 1973); the dashed line is the P-Y curve for $\sigma = 0.65$ a.u. and dotted line is the RPA corrected version (Silbert and Young 1976).
alkalies. The second case is more typical; quite good hard sphere behaviour occurs in Mg, Al, In, Pb [Waseda and Suzuki (1973)], the alkaline earths [Waseda et al (1974)], the noble and transition metals [Waseda and Ohtani (1974, 1975), Waseda and Tamaki (1975)]. A slight skewness of the first peaks occurs in Zn and Cd [Waseda and Suzuki (1973)] but otherwise these metals are also quite well described by hard spheres.

However, in Ga, Sn, Sb, Bi and (to a very modest extent) in Tl there is a shoulder on the high angle side of the principal peak which cannot be described by hard spheres alone. For the most part, these are the cases which do not form close-packed solids. Heine and Weaire (1970) have shown that the Coulomb forces favour close packing and that other cases can be explained by special circumstances. For example, if the nearest-neighbour distance for close packing occurs near the energetically unfavourable first maximum, it pays for some such neighbours to move inwards and the others to move out. Heine and Weaire (1970) suggested that similar considerations have a role to play in liquid state structure theory. Certainly the implication that the bumps and dips of $g(r)$ will be less pronounced is borne out on Fourier transformation of the observed $a(q)$ for such cases [Waseda and Suzuki (1973)].

The completely typical result for Bi may be contrasted with those for Na and Al in figure (1.5). A calculation by Silbert
and Young (1976) is also relevant. They have performed model calculations for hard spheres with repulsive tails. Their results are of the correct type, as their curve for Bi [Figure (1.6)] shows.

For low-angle region we have the very general result [Watabe and Hasegawa (1973), Chihara (1973), Gray (1973), March and Tosi (1973), Jones (1973)]

\[ a_0 = \frac{k_B T \beta_T}{\Omega} \]  \hspace{1cm} (1.45)

where \( \beta_T \) is the isothermal compressibility. The right side of this equation may be evaluated using observed data for the melting point and for hard spheres with \( \eta = 0.45 \). The agreement is poor for polyvalent metals [Young (1977) Table 1] and in fact there is a good reason for this. Being density-dependent, the interatomic potential contributes to \( \beta_T \) and therefore to the very long wavelength region. Direct calculation [Hasegawa and Watabe (1972)] shows that as a fraction of the total, this contribution is small for the alkalis and large for polyvalents.
1.11 References


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