

Liquid metals

CONCEPTS AND THEORY

N.H. MARCH



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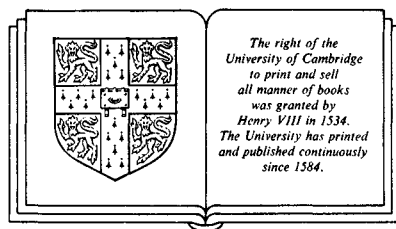
LIQUID METALS

Concepts and Theory

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Preface

The origin of this volume can be traced to a letter from Dr. P. V. Landshoff (PVL), inviting me to write on liquid metals for his series. By then, my earlier book on the subject, published in 1968, described correctly by Professor N. E. Cusack in his generous review as 'Bare bones of liquid metals', was almost 20 years old. Of course, Dr. T. E. Faber's 1972 book was much more extensive, and I immediately recognized that in one important area of the subject: namely, weak scattering theory of electrical transport in liquid metals and alloys (Ziman and Faber-Ziman theory, respectively; see also below), I could not possibly compete with the quality of that.

However, after a long inner debate, I accepted the invitation and sent PVL a proposed outline which already made clear that it would be a large volume. Back came a reply from PVL and an adviser: could I extend it somewhat?! Perhaps this may have been partly motivated by my long-standing interests in matter under extreme conditions of temperature and pressure, but, nevertheless, these additional proposals led me into areas in which I had not contributed myself for more than a decade. In the end, Chapter 16 became the main response to this challenge, and this could not have been written without the help of the 1985 review by Dr. M. Ross of the Lawrence Livermore Laboratory. While mentioning that, I must also acknowledge the 1987 survey by Dr. R. N. Singh, which was used so extensively in Chapter 13. Dr. Singh worked closely with the late Professor A. B. Bhatia, with whom I was also fortunate enough to collaborate over a decade or so.

This leads to acknowledgments of my indebtedness to numerous other people. First, colleagues from my Sheffield University days, Drs. T. Gaskell, W. Jones, J. S. Rousseau and J. C. Stoddart, provided much stimulation and help, while my research students R. C. Brown, G. K. Corless and M. D. Johnson notably influenced my outlook on the subject, the latter two in the general area of effective interionic interactions mediated by conduction electrons. Later, at Imperial College, London University, S. Cusack, through his Ph.D. thesis studies, aided considerably my own understanding

of electronic correlation functions; C. M. Sayers strongly influenced the work in the area of magnetic properties. After moving to Oxford in 1977, my research students J. A. Ascough, R. G. Chapman, A. Ferraz and J. S. McCaskill and my colleague D. P. J. Grout are to be thanked for much help, particularly with transport in strong scattering systems, which has been made the basis for the whole discussion of electrical conductivity in the present volume; leaving T. E. Faber's account of weak scattering theory as the right source of that topic, as has already been mentioned. Though the present book is in the Mathematical Physics Series, I must add that I have been extremely lucky in also having close contact with the experimental groups of Professors J. E. Enderby and P. A. Egelstaff and later with Drs. D. I. Page and M. W. Johnson at Harwell and Rutherford Laboratories.

I owe the greatest debt to Professors M. P. Tosi (MPT) and W. H. Young (WHY) for the strong interactions with them and their research groups over two and three decades, respectively. To both of them I offer my warmest thanks for all the stimulation our group has received from them and also for their readiness to allow me to draw extensively on their own writings (e.g., WHY's 1987 article in Chapters 3 and 13 and my two books with MPT). The influence of them and their colleagues in visiting our group frequently has been of the utmost importance for us. Drs. M. Parrinello and G. Senatore from MPT's group spent extended periods of time with us and, deriving from WHY's influence, Professor J. A. Alonso and Dr. M. Ginoza also paid most valuable visits. It has been a pleasure to be involved with so many fine scientists and to have forged numerous firm friendships in the process.

In a work on this scale and with, at times, considerable theoretical detail, as in Chapter 14, it is almost inevitable that some errors will have crept in. I am, of course, solely responsible for any such, and I trust these will be, at worst, of detail and not of principle. But I shall count it a favour if readers who find my book either useful or interesting, and who spot places where I ought to do better, will write and tell me.

Finally, it is a pleasure to thank Cambridge University Press through the person of Rufus Neal, who gave much friendly and wise advice in seeing this work through to fruition.

NORMAN H. MARCH

1

Outline

This book is about the theory of liquid metals. The interplay between electronic and ionic structure is a major feature of such systems. This should occasion no surprise, as even a pure liquid metal is a two-component system: positive ions and conduction electrons. Therefore, as in a binary liquid mixture such as argon and krypton, where three partial structure factors S_{ArAr} , S_{KrKr} , and S_{ArKr} are required to describe the short-range atomic order, so in liquid metal Na, for instance, one needs $S_{\text{Na}^+\text{Na}^+}$, $S_{\text{Na}^+\text{e}}$, and S_{ee} for a structural characterization.

For a very fundamental treatment, the preceding description would be the correct starting point to treat liquid metal Na. Indeed, the theory of liquid metals has been developed in this manner. However, it is still true that, for many important purposes, a simpler picture suffices. Thus, in the chapter following this outline, attention will be focused on the ion-ion structure factor, which will simply be written as $S(k)$; $k = 4\pi \sin \theta/\lambda$, with 2θ the angle of scattering of X rays or neutrons and λ the wavelength of the radiation. It will be emphasized that it is indeed $S(k)$ that is measured in suitable neutron-scattering experiments.

Then, in the following chapter, the use of this knowledge of structure will be considered in relation to the thermodynamics of liquid metals. Following this, electron screening of ions will be treated with the theme stressed above, the interplay between electronic and ionic structure, leading to a treatment of effective interionic forces. This theory will then be confronted with an approach based on the so-called inverse problem—namely, that of extracting an effective ion-ion interaction from the measured structure factor $S(k)$. Following this study of interatomic forces, in which the Ornstein-Zernike direct correlation function $c(r)$ plays an important role, this same tool will be employed to treat the theory of freezing, following pioneering work of Kirkwood and Monroe (1941) and of Ramakrishnan and Yussouff (1977, 1979). A full discussion of electronic and also atomic transport then follows. This is closely linked to the study of liquids by inelastic neutron scattering; essentially described by the dynamical generalization $S(k, \omega)$ of the static structure factor $S(k)$. The frequency-dependent

dielectric function and its use in treating optical properties will also be briefly considered.

The treatment of critical phenomena in liquid metals follows, this leading into a more detailed study of electron states plus some discussion of magnetism. Then, inhomogeneous systems are considered: the liquid-vapor surface, followed by surface segregation in binary alloys, the bulk properties of which are briefly treated in the penultimate chapter, which also focuses on phase diagrams of binary liquid alloys. This leads into the final chapter, which is concerned with the relevance of liquid metal theory to the hydrogen-helium mixtures in the giant planets, Jupiter and Saturn.

Pair correlation function and structure factor of ions

The most important single tool for dealing with the structural problem of liquid short-range order is the pair correlation function $g(r)$. If the bulk liquid number density is denoted by $\rho = N/\Omega$, for N atoms in volume Ω , then $g(r)$ is defined such that if one sits on an atom at the origin $r = 0$, then the probability of finding a second atom at distance between r and $r + dr$ is given by $g(r)4\pi r^2 dr$ and the density of atoms is found by multiplying this by ρ .

2.1. Liquid structure factor

The pair function is accessible via diffraction experiments, as will now be outlined. Let $I(k)$ be the intensity of, say, X rays of wavelength λ , incident on a liquid sample and scattered through an angle 2θ , with

$$k = \frac{4\pi \sin \theta}{\lambda}. \quad (2.1)$$

Then if N is the number of atoms in the sample, the intensity $I(k)$ is related to the liquid structure factor $S(k)$ by

$$I(k) = N f^2(k) S(k) \quad (2.2)$$

where $f(k)$ is the atomic scattering factor, given in terms of the electron density $\rho(r)$ in the atom (say, argon) by

$$f(k) = \int \rho(r) \exp(ik \cdot r) dr. \quad (2.3)$$

In turn, $S(k)$ is related to the pair function $g(r)$ by

$$S(k) = 1 + \rho \int [g(r) - 1] \exp(ik \cdot r) dr. \quad (2.4)$$

Figure 2.1 shows measured data on liquid Na, K, and Cs at the melting point from the work of Huijben and van der Lugt (1979; see also Greenfield, Wellendorf, and Wiser, 1971).

It is worth considering a number of features of this curve. First, the long wavelength limit of $S(k)$, i.e., $S(0)$, can be related to fluctuations $\langle \Delta N^2 \rangle$ in the number of particles and thereby to the isothermal compressibility K_T , the relation being

$$S(0) = \rho k_B T K_T, \quad (2.5)$$

which is proved in Appendix 2.1. For liquid argon near its triple point, $S(0) \sim 0.06$, whereas for the liquid metal K shown in Figure 2.1, $S(0) \sim 0.02$. This is in sharp contrast to a gas, where $S(0) \sim 1$ except near the critical point (see Section 9.2), where $S(0)$ diverges. In dense liquids the message is that $S(0) \ll 1$, which will later be seen to have important implications.

The second point to be made is that, as is clear from Figure 2.1, $S(k)$ has pronounced oscillations at large k . These come primarily from the

Figure 2.1. Measured structure factor $S(k)$ for liquid metals Na, K and Cs just above the melting point against scaled wave number (Huijben and van der Lugt, 1979; see also March and Tosi, 1984; Greenfield, Wellendorf and Wiser, 1971).

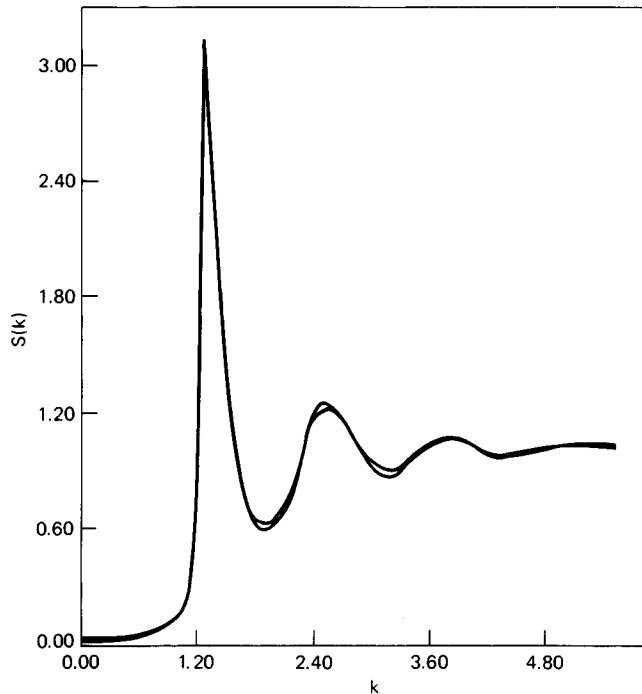
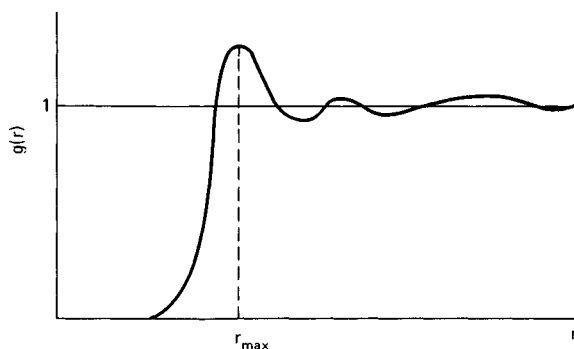


Figure 2.2. Schematic form of $g(r)$, which is related to $S(k)$ in Figure 2.1 by the Fourier transform result (2.4). $r_{\max}$ shows position of first coordination shell.



“hardness” of the core. In Figure 2.2 $g(r)$ is depicted schematically, and the important point is that there is a region inside the core diameter σ for which $g(r)$ is practically zero; then $g(r)$ rises steeply to its first peak. It is this steep rise that leads to the oscillations at large k in $S(k)$, from a basic property of Fourier transforms. The third point to be noted at this stage is that $S(k)$ reaches a first peak height of about 3.0 for the case plotted in Figure 2.1, where the temperature T is quite near the melting temperature T_m . This point will be taken up in the discussion of the theory of freezing in Chapter 6 (see also Ferraz and March, 1980).

Of course, a complete theory will eventually have to reproduce the structure factor $S(k)$ as measured by diffraction experiments (for neutrons, $f(k)$ in (2.2) is replaced by an appropriate scattering length) from a force field: a route that allows this, at least in principle, is set out in Chapters 3 and 4.

Before going on to deal with the relation between structure and forces, there is a further correlation function of central importance for liquid-state theory, namely, the Ornstein-Zernike correlation function $c(r)$.

2.2. Ornstein-Zernike direct correlation function

At this point, it will be useful to give the formal definition of $c(r)$; the definition will then be reexamined later in order to gain deeper insight into the reasons for its important status in liquid-state theories. The pair function $g(r)$ minus its asymptotic limiting value 1 at large r is called the total correlation function $h(r)$, i.e.,

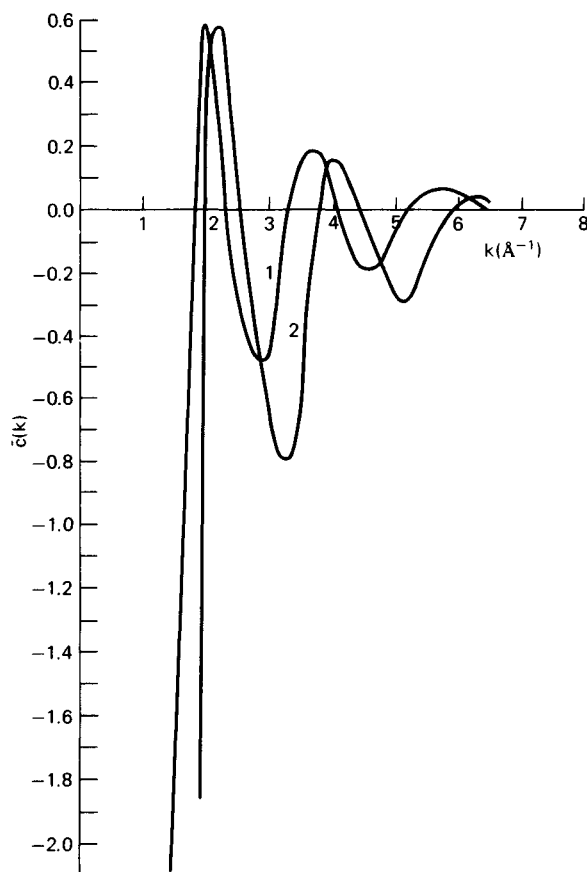
$$h(r) = g(r) - 1. \quad (2.6)$$

$h(r)$, the total correlation function, is now divided into two parts, a direct part described by $c(r)$ and an indirect part. Following Ornstein and Zernike, the indirect part is expressed as a convolution; their definition of $c(r)$ being

$$h(r) = c(r) + \rho \int h(|\mathbf{r} - \mathbf{r}'|)c(r') d\mathbf{r}'. \quad (2.7)$$

The convolution is readily removed by Fourier transform, and (2.7) is then simply equivalent to

Figure 2.3. Schematic form of the Ornstein-Zernike direct correlation function in k -space, denoted by $\tilde{c}(k)$. This is related to $S(k)$ in Figure 2.1 by $\tilde{c}(k) = [S(k) - 1]/S(k)$ (Curve 1 resembles Ar; curve 2, Pb).



$$\tilde{c}(k) = \frac{S(k) - 1}{S(k)}, \quad (2.8)$$

where $\tilde{c}(k)$ is the Fourier transform of $c(r)$. One consequence of (2.8) follows from the small value of $S(0)$ for argon near its triple point or for liquid metals just above their freezing points. It is that for argon, $\tilde{c}(0) \sim -16$, whereas for liquid metals $\tilde{c}(0) \sim -40$ as a typical value. On the other hand, at the peak of $S(k)$, having the value from Figure 2.1 of about 2.9, $\tilde{c}(k) \sim 0.6$. Thus, $\tilde{c}(k)$ has the schematic form shown in Figure 2.3: it is seen to put much greater emphasis on the region of small k , i.e., small-angle scattering, than does Figure 2.1, which is largely dominated by the first peak of $S(k)$. Since, as will be seen shortly, $c(r)$ is more closely related to the microscopic force law than $g(r)$, one must expect small-angle scattering data to be of considerable importance when one wishes to draw conclusions about the force field from liquid structure factor measurements. However, before enquiring as to the precise form of this relation between liquid structure and interatomic forces, let us turn to consider in some detail the thermodynamics of liquid metals.

3

Thermodynamics

The thermodynamic properties of simple s-p bonded liquid metals under normal conditions will be discussed in this chapter. By restricting the range of systems in this way, one is permitted to focus only on those electronic aspects that are describable by nearly free electron (NFE) methods. Some of the theoretical methods and techniques used will be reviewed, and a selection of the results obtained will be presented.

The work of Stroud and Ashcroft (1972) on the melting of sodium indicated how the techniques of classical liquid theory might be combined with the pseudopotential method of calculating interionic forces in metals to produce a successful description of the thermodynamics. It is probably true to say that this problem is understood, albeit in a semiquantitative way; this “solution” is reviewed in this chapter, which follows rather closely the work of Young (1987).

3.1. Simple monatomic fluids

In this section, by way of an introduction, let us leave the problems specific to metals and, instead, consider the statistical mechanics appropriate to a monatomic fluid such as Ar. Many of the results that will be obtained can be applied to simple metals with little or no modification. Such changes as are necessary are dealt with in Section 3.3.

3.1.1. Basic features

Consider a simple classical monatomic fluid of N particles in a volume V , so that the number density is $\rho = N/V$. The Hamiltonian is taken to be

$$H = T + \frac{1}{2} \sum v(|\mathbf{r}_i - \mathbf{r}_j|) \quad (3.1)$$

where T is the kinetic energy and v is a potential energy function independent of density ρ .

Central to the statistical mechanical description afforded by (3.1) is the radial distribution function $g(r)$, which has been defined in Chapter 2 so that $\rho g(r) dr$ is the probability of finding an atomic nucleus in the volume element dr around $\mathbf{r}$ given that there is one at the origin. In terms of this function, application of general theory leads to the expression

$$E = \frac{3}{2}k_B T + \frac{1}{2}\rho \int v(r)g(r) d\mathbf{r} \quad (3.2)$$

for the internal energy per atom and

$$P = \rho k_B T - \frac{1}{6}\rho^2 \int \mathbf{r} \frac{d}{dr} v(r)g(r) d\mathbf{r} \quad (3.3)$$

for the pressure. Other results follow from these, of course, by the application of the various thermodynamic identities.

The structure factor $S(q)^*$ may be defined in terms of $g(r)$ by (2.4), which by Fourier inversion yields

$$g(r) = 1 + \frac{1}{(2\pi)^3\rho} \int \{S(q) - 1\} e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q}. \quad (3.4)$$

For example, (3.2) and (3.3) may be rewritten in terms of $S(q)$ and the (assumed) Fourier transform $\tilde{v}(q)$ of $v(r)$ in (3.1) as

$$E = \frac{3}{2}k_B T + \frac{1}{2}\rho\tilde{v}(0) + \frac{1}{2(2\pi)^3} \int \tilde{v}(q) \{S(q) - 1\} d\mathbf{q} \quad (3.5)$$

and

$$P = \rho k_B T + \frac{1}{2}\rho^2\tilde{v}(0) + \frac{\rho}{2(2\pi)^3} \int \left\{ \tilde{v}(q) + \frac{q}{3} \frac{\partial \tilde{v}(q)}{\partial q} \right\} \{S(q) - 1\} d\mathbf{q} \quad (3.6)$$

where

$$\tilde{v}(q) = \int v(r) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}. \quad (3.7)$$

As discussed in the previous chapters, $S(q)$ is measurable using neutron and other spectroscopies, and such data can be used in (3.5) and (3.6), for example, if $v(r)$ is specified. Such a procedure is of limited value, however, primarily because one wishes to investigate such expressions for varying thermodynamic states T , V , etc. Under such circumstances sufficient experi-

* k and q will be used interchangeably for wave numbers throughout this volume.

mental information is seldom available. What one needs, and what theory provides, are $S(q)$'s and $g(r)$'s compatible, in some approximation, with a given $v(r)$.

An important area of uncertainty with $S(q)$ measurements remains at low q , where, typically, there may be significant error below about $0.5 \text{ \AA}^{-1}$. It is, therefore, worth stressing again that the limit $S(0)$ is known from density fluctuation theory (of Appendix 2.1) to be determined through (2.5), where the isothermal compressibility K_T is given by

$$K_T^{-1} = -V \left(\frac{dP}{dV} \right)_T. \quad (3.8)$$

$S(0)$ is thus accessible from thermodynamics and provides a “target” for the low-argument radiation measurements of $S(q)$.

Integration of (3.8) yields

$$P = k_B T \int_0^\rho \frac{d\rho}{S(0)} \quad (3.9)$$

which is the so-called compressibility equation of state. This is to be compared with the virial pressure equation of state given by (3.3). In an exact theory of $g(r)$ and $S(q)$, these equations of state will be completely equivalent. In practice, however, one has to use approximate theories; thus discrepancies arise (see Appendix 5.2).

3.1.2. Structure factor $S(q)$ as response function

Physical insight into the character of $S(q)$ is obtained by noting its role as a response function (see Young, 1987, whose account is followed closely below). Suppose the fluid atoms are exposed to a small external potential $\delta\varphi(q) \cos \mathbf{q} \cdot \mathbf{r}$ (i.e., a perturbation $\delta\varphi(q) \sum \cos \mathbf{q} \cdot \mathbf{r}_i$ is added to (3.1)). Then, to first order, the density becomes $\rho + \delta\rho(q) \cos \mathbf{q} \cdot \mathbf{r}$, where

$$\delta\rho(q) = -\frac{\rho}{k_B T} S(q) \delta\varphi(q). \quad (3.10)$$

At long wavelengths (small q) this tells us about the ability of the particles to clump, and this process will be assisted by attractions between the particles and hindered by repulsions. This discussion is compatible with the well-known general result (see (2.5)) that K_T diverges at a critical point, for the existence of which attractive interactions are essential (see Chapter 9 for details).

Returning briefly to the direct correlation function $c(r)$ introduced in Chapter 2, it is to be stressed that $c(r)$ is a particularly suitable starting point for theories because of its direct link with the interatomic forces. In fact, statistical mechanics yields the exact result (far from the critical point)

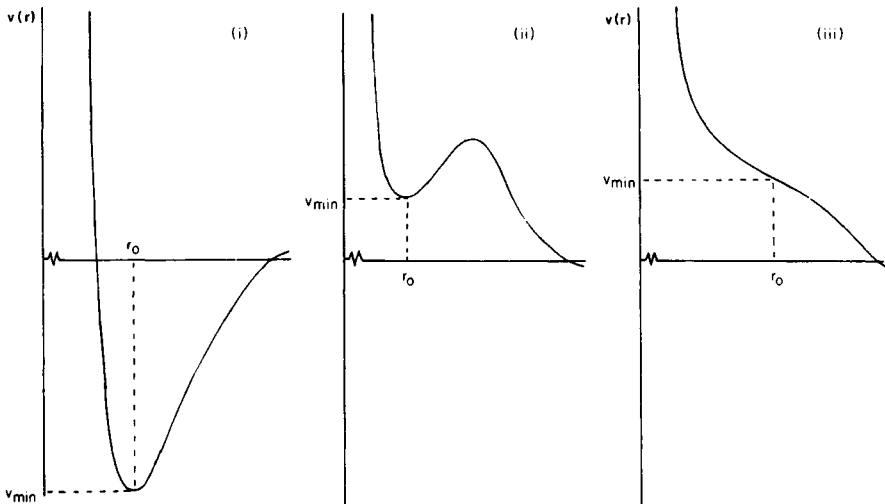
$$c(r) \sim \frac{-v(r)}{k_B T} \quad (\text{large } r). \quad (3.11)$$

This relation will be of considerable importance in what follows.

3.2. Approximate methods

As has been seen, the problem is to estimate $g(r)$, $S(q)$ in some way for use, for example, in such formulae as (3.3) and (3.9). It is, therefore, appropriate to examine next the character of typical interatomic potentials that establish these functions. Possible forms are shown schematically in Figure 3.1, and

Figure 3.1. Possible schematic forms of effective interionic potentials $v(r)$ in liquid metals. It is to be noted that the r axis is broken; there is generally an impenetrable core. The parameters r_0 and $v_{\min}$ play a role in the Weeks-Chandler-Andersen approximation to structure (see Appendix 3.2). In the third part of the figure, to the right, $v_{\min}$ and r_0 are measured at the (assumed) point of inflection (after Young, 1987).



it is evident that in a zeroth approximation the atoms behave as though there is a quite well defined hard sphere diameter. One approach, therefore, is to try to establish a suitable hard sphere reference system and then to incorporate further details of $v(r)$ by suitable “corrections.”

3.2.1. Hard sphere fluids

A good deal is known about hard sphere fluids because of their relative mathematical simplicity. Computer simulation studies (Alder and Wainwright, 1957) have established that they freeze at a packing fraction $\eta \equiv (\pi/6)\rho\sigma^3$ (σ = diameter) of about 0.45–0.46. In the liquid state, their structural and thermodynamic properties have been similarly investigated and found to be quite well reproduced in the Percus-Yevick (1958; PY) approximation, for which analytical results are available (see Appendix 3.1). For example, the Helmholtz free energy per particle of a hard sphere fluid is $\frac{3}{2}k_B T - TS_{hs}$ where machine results are well fitted by (Carnahan and Starling, 1969) an excess entropy (relative to the ideal gas value S_{gas}) of

$$\frac{S_\eta}{k_B} \equiv \frac{S_{hs} - S_{gas}}{k_B} = 3 - \frac{2}{(1 - \eta)} - \frac{1}{(1 - \eta)^2} \quad (\text{CS}). \quad (3.12)$$

This is plotted in Figure 3.2. The Percus-Yevick entropy expressions (differing according to whether the virial or compressibility route is used) are

$$\frac{S_\eta^{\text{vir}}}{k_B} = -2 \ln(1 - \eta) + 6 \left(1 - \frac{1}{1 - \eta} \right) \quad (\text{PY}) \quad (3.13)$$

or

$$\frac{S_\eta^{\text{comp}}}{k_B} = \ln(1 - \eta) + \frac{3}{2} \left(1 - \frac{1}{(1 - \eta)^2} \right) \quad (\text{PY}) \quad (3.14)$$

the latter being the more accurate, as direct substitution shows.

Double differentiation of these expressions with respect to volume and use of (2.5) yields

$$S_{hs}(0) = \frac{(1 - \eta)^4}{(1 + 2\eta)^2 + \eta^4 - 4\eta^3} \quad (\text{CS}) \quad (3.15)$$

and using the more accurate form (3.14) only, one finds

$$S_{hs}(0) = \frac{(1 - \eta)^4}{(1 + 2\eta)^2} \quad (\text{PY}). \quad (3.16)$$

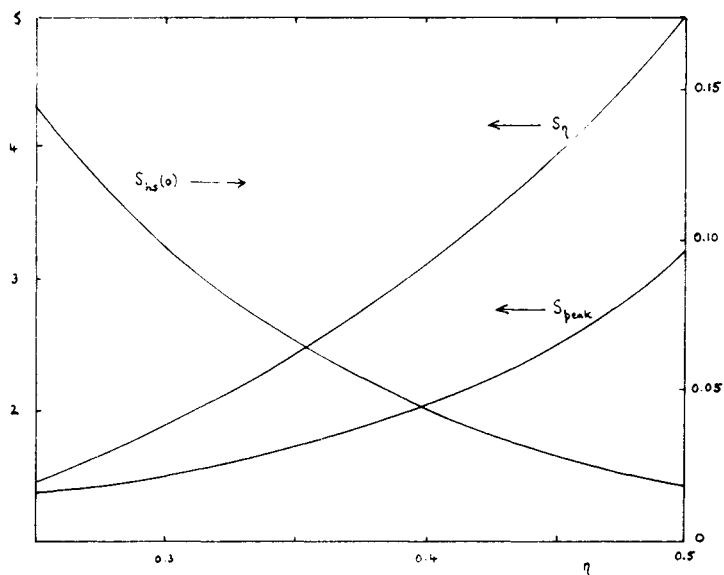
Relationship (3.15) is also plotted in Figure 3.2.

Actually, the whole of $S_{hs}(q)$ is known analytically in the PY approximation (Thiele, 1963; Wertheim, 1963), and this is a major reason for its popularity as a substitute for "exact" machine-generated numerical output. The direct correlation function is obtained in the form

$$c_{hs}(r) = \begin{cases} a + b(r/\sigma) + d(r/\sigma)^3 & (r < \sigma) \\ 0 & (r > \sigma) \end{cases} \quad (\text{PY}) \quad (3.17)$$

where the coefficients are recorded in terms of η in Appendix 3.1. The corresponding structure factor follows using (2.8). The height of the principal peak of this structure factor is also shown in Figure 3.2 as a function of η . The derivation of (3.17) is such that the corresponding structure factor at $q = 0$ agrees with the form (3.16).

Figure 3.2. Three different quantities (given in (3.12), (3.16), (2.8) and (3.14)). These are, respectively, (i) the excess entropy per particle S_η , (ii) the principal peak height S_{peak} of the structure factor, and (iii) $S(k)$ at $k = 0$. All are calculated from (approximate) hard sphere theory and are plotted as functions of the packing fraction η defined by $\eta = \frac{\pi}{6} \rho \sigma^3$, where ρ is the number density and σ the hard sphere diameter.



Two approximate methods have proved particularly useful for proceeding beyond the hard sphere picture to a description of fluids represented by potentials such as are sketched in Figure 3.1. Each of these is reviewed next. The first takes the virial route to the thermodynamics; the second, the compressibility alternative.

GIBBS-BOGOLIUBOV (GB) METHOD

The method outlined below is commonly called the Gibbs-Bogoliubov method (Isihara, 1968; Lukes and Jones, 1968) but is alternatively known as the variational, or high-temperature, method, for reasons that will emerge in the discussion.

Let us begin (see Young, 1987) by writing the interatomic potential in the form

$$v(r) = v_0(r) + v_1(r) \quad (3.18)$$

where $v_0(r)$ is a core part and the remaining contribution $v_1(r)$ is "small." Then the system with interactions $v_0(r)$ becomes the unperturbed, reference system on which the perturbation

$$W = \frac{1}{2} \sum v_1(|\mathbf{r}_i - \mathbf{r}_j|) \quad (3.19)$$

acts. To first order in $W/k_B T$, one obtains a Helmholtz free energy

$$F = F_0 + \langle W \rangle_0 \quad (3.20)$$

where $\langle W \rangle_0$ denotes (3.19) averaged over the reference system. Explicitly,

$$\langle W \rangle_0 = \frac{1}{2} \rho \int v_1(r) g_0(r) \, \mathbf{r} \quad (3.21)$$

or, equivalently, when $v(r)$ is Fourier transformable,

$$\langle W \rangle_0 = \frac{1}{2} \tilde{v}_1(0) + \frac{1}{2(2\pi)^3 \rho} \int \tilde{v}_1(q) \{S_0(q) - 1\} \, \mathbf{q}. \quad (3.22)$$

To the first order indicated, (3.20) is always an upper bound to the exact value. Thus, if $v_0(r)$ contains parameters, these can be varied so as to minimize (3.20) and hence to achieve a "best" free energy estimate.

It is common to take a core of a hard sphere form ($v_0 = v_{hs}$). Then, the diameter σ is the only variable and one requires that

$$\left(\frac{\partial F}{\partial \sigma} \right)_{V, T} = 0. \quad (3.23)$$

When (3.23) applies, one finds (Edwards and Jarzynski, 1972) that (3.20)

yields

$$S = S_{\text{hs}}(\sigma), \quad (3.24)$$

i.e., the entropy estimate is given by the hard sphere expression (e.g., (3.12) or (3.13)) with the optimizing diameter inserted. Furthermore (Watabe and Young, 1974) (3.2) and (3.3) apply with g replaced by $g_{\text{hs}}(\sigma)$ (or, equivalently, (3.5) and (3.6) apply with S replaced by $S_{\text{hs}}(\sigma)$).

For hard spheres, $g_{\text{hs}}v_{\text{hs}} = 0$, since the first factor vanishes when $r < \sigma$ and the second, when $r > \sigma$. Thus, (3.21) can be rewritten, in this case, as

$$\langle W \rangle_{\text{hs}} = \frac{1}{2}\rho \int_{\sigma}^{\infty} v(r)g_{\text{hs}}(r)4\pi r^2 dr \quad (3.25)$$

and solutions using (3.25) then conform quite well to the empirical rule (see Young, 1987)

$$v(\sigma) - v_{\text{min}} \approx \frac{3}{2}k_B T \quad (3.26)$$

where v_{min} is the principal minimum of $v(r)$ (Figure 3.1).

A limitation of this method (at least when used in conjunction with a hard sphere reference system) is its relatively crude treatment of the tail. The latter affects the size of the diameter through its contribution to (3.25) but not the detailed shape of the radial distribution function, which always remains of hard sphere form. A method that rectifies this deficiency is discussed fully by Young (1987). Instead, the approximation

$$S^{-1}(0) = S_{\text{hs}}^{-1}(0) + \frac{\rho \tilde{v}_{\text{tail}}(\sigma)}{k_B T} \quad (3.27)$$

will be employed. This provides an approach to the thermodynamics by the compressibility route (cf. (3.9)).

3.3. Simple liquid metals

A simple liquid metal such as Na is more complicated than, say, Ar, to which the theory so far can be immediately applied. As in Chapter 1, one should really consider liquid Na to be a mixture of Na^+ ions and electrons and proceed by a two-component formalism (see Chapter 14) similar, in many general respects, to that to be given in Section 13.1. Under such circumstances, the $g(r)$ used so far still describes the ion-ion correlations, and (2.4) continues to define the corresponding structure factor, $S(q)$. Now, however, these quantities need to be calculated in the presence of the free

electrons, which must be treated quantum-mechanically. It is interesting to note one simple general result (see Young, 1987) namely, that the requirement of charge neutrality leads to $S(0)$ given by (2.5), where ρ is, as before, the ion number density and K_T is the isothermal compressibility of the entire system of ions and electrons. It follows that observed thermodynamic data can continue to augment radiation measurements of $S(q)$.

3.3.1. Generalities

Notwithstanding the preceding remarks, a fruitful treatment (see also Chapter 1) is to convert the problem into one in which the ions move in an effective force field established by the electron gas (the Born-Oppenheimer approximation). Such a procedure is possible because the electron-ion coupling (the pseudopotential) is weak and can be regarded as merely perturbing the electron gas, assumed to be uniform in zeroth order. To second order, one calculates the energy for a given "frozen" configuration of ions and this acts as the potential energy function for the N ions alone. The resulting Hamiltonian has the form (Hasegawa and Watabe, 1972; see also Corless and March, 1961; Worster and March, 1964)

$$H = T + Nv_0(n) + \frac{1}{2} \sum v(|\mathbf{r}_i - \mathbf{r}_j|, n) \quad (3.28)$$

where n is the mean electron density ($=z\rho$, where z is the valence). In this equation $v_0(n)$, the volume term, is independent of the ionic positions $\{\mathbf{r}_i\}$, and the pair interaction v is density-dependent. Many (≥ 3) body potential energy terms in (3.28) are absent in this approximation.

On comparing (3.28) with (3.1) it is clear that the previous formalism is easily modified, (3.2) and (3.3) becoming, respectively,

$$E = \frac{3}{2}k_B T + v_0(n) + \frac{1}{2}\rho \int v(r, n)g(r) \, \mathbf{dr} \quad (3.29)$$

and

$$P = \rho k_B T + \rho n \frac{dv_0(n)}{dn} - \frac{1}{6}\rho^2 \int \left\{ r \frac{\partial v}{\partial r} - 3n \frac{\partial v}{\partial n} \right\} g(r) \, \mathbf{dr}. \quad (3.30)$$

Further differentiation leads, via (3.8), to a rather complicated expression for the compressibility, K_T . This, as has been noted, is the virial equation route to the thermodynamics.

Alternatively, the compressibility route, as one has seen, requires that $S(0)$ be inserted into (2.5). At constant volume, any standard method of

calculating $g(r)$ requires knowledge of $v(r, n)$ but not of the volume term, $v_0(n)$. Thus, at first sight, (2.4), with $k = 0$ inserted, appears to be incompatible with (3.30), which explicitly depends on the volume term. A resolution of this point is to note (see Young, 1987) that structure-independent $O(\Omega^{-1})$ terms in $g(r)$, invisible when graphed, can be integrated in (2.4) to produce $O(1)$ contributions to $S(0)$, thus restoring compatibility.

The pseudopotential theory of v_0 and v will not be presented in detail at this point. Nevertheless, it will be useful to indicate the form the results take for a local electron-ion pseudopotential interaction, which, in free space, can be written

$$v_{\text{ps}}(r) = v_{\text{ps}}^{\text{core}}(r) - \frac{ze^2}{r}. \quad (3.31)$$

The core part represents a weak short-range-effective interaction between the electron and ion core; outside the core region, only the electrostatic attraction remains. Particularly simple is the Ashcroft (1966) empty core form

$$v_{\text{ps}}(r) = \begin{cases} 0 & (r < r_c) \\ -ze^2/r & (r > r_c) \end{cases} \quad (3.32)$$

$$\tilde{v}_{\text{ps}}(q) = -\frac{4\pi z^2 e^2}{q^2} \cos qr_c \quad (q \neq 0)$$

where r_c is a measure of the ionic radius.

For the ionic array in situ in the electron gas, linear response theory yields a pairwise interaction that can be written in inverse space as: (4.20)

$$\tilde{v}(q, n) = \frac{4\pi z^2 e^2}{q^2} + \frac{q^2}{4\pi e^2} \left\{ \frac{1}{\varepsilon(q, n)} - 1 \right\} \tilde{v}_{\text{ps}}^2(q). \quad (3.33)$$

The first term is clearly the direct coulomb interaction between the ions, whereas the second is the indirect electron-mediated term. In the latter, the dielectric screening function $\varepsilon(q, n)$ appears. This function has been much investigated over three decades, and a variety of forms for it have appeared in the literature (see Chapter 4). Asymptotically, it behaves like

$$\varepsilon(q, n) = \left\{ \frac{(K/K_f)^2 (q_{\text{TF}}/q)^2 + 1}{1 + 16\pi n(1 + G)/q^2} \right\} \quad (3.34)$$

where q_{TF}^{-1} is the Thomas-Fermi screening length,* K/K_f is the ratio of the compressibilities of the associated uniform interacting and noninteracting electron gases, and $1 - G$ is the radial distribution function of the former, evaluated at contact.

* See Section 4.1 below.

The volume term corresponding to the preceding description is

$$v_0(n) = z \left(1 - \frac{1}{2} V^2 \frac{d^2}{dV^2} \right) v_{el} + \frac{1}{2} \int \frac{q^2}{4\pi e^2} \left\{ \frac{1}{\varepsilon(q, n)} - 1 \right\} \tilde{v}_{ps}^2(q) d\mathbf{q} \quad (3.35)$$

where the final term is the self-energy of an ion in the electron gas. The first term arises from the (perturbed) electron gas only, the expression v_{el} being the energy per electron of the uniform gas in a neutralizing background.

The results (3.33) and (3.35) for the pair and volume terms are valid to second order in pseudopotential perturbation theory. Not only would higher-order terms introduce many (≥ 3)-body forces (as indicated earlier), but they would also lead to revised forms of $v_0(n)$ and $v(r, n)$. There has been little investigation of this problem at the time of this writing, the expressions above being almost invariably employed.

3.4. Specifics

In this section, the way in which the above formalism is able to explain some of the properties of liquid metals will be briefly reviewed. The matter largely revolves around the roles and character of the volume and pairwise terms. The former is, in fact, large and is responsible for most of the cohesive energy, as the results of Finnis (1974), shown in Table 3.1, indicate. These data are for the solids but make the point quite satisfactorily, since v_0 is phase-independent and dominantly large. Finnis noted that the first (electron gas) term of (3.35) is quite small compared with the second (self-energy) part and that the latter can be roughly evaluated as

$$\frac{1}{2} \int \frac{q^2}{4\pi e^2} \left\{ \frac{1}{\varepsilon(q, n)} - 1 \right\} \tilde{v}_{ps}^2(q) d\mathbf{q} \approx -\frac{1}{4} \frac{z^2 e^2}{r_c} \quad (3.36)$$

where r_c is the empty core radius of (3.32). In fact, the results of Table 3.1 were calculated by neglecting the electron gas term and applying the self-energy part in the approximate form (3.36).

Since the largest term in $v_0(n)$ has little density-dependence (see (3.36)), one finds that the pairwise term plays a more prominent role in determining the pressure and compressibility derivatives. Any calculation of these quantities requires knowledge not only of $\tilde{v}_{ps}^{\text{core}}(q)$ in (3.31) for $q \neq 0$, but also of $q = 0$. One might plausibly invoke continuity for this purpose, e.g., if the empty core potential (3.32) is employed, one would write

$$\tilde{v}_{ps}^{\text{core}}(0) = \lim_{q \rightarrow 0} \left\{ \frac{4\pi z e^2}{q^2} - \frac{4\pi z e^2}{q^2} \cos qr_c \right\} = 2\pi z r_c^2. \quad (3.37)$$

Table 3.1. Cohesive energies [after Finnis (1974); see also Young, (1987)].

1A	2A	2B	3	4	5	6
Li	Be					
0.512	1.13					
0.33	0.90					
Na	Mg		Al	Si		
0.460	0.892		1.38	1.96		
0.31	0.78		1.39	2.11		
K	Ca	Zn	Ga	Ge	As	Se
0.388	0.733	1.05	1.47	1.97	2.55	3.23
0.24	0.60	1.01	1.52	2.20	2.79	3.57
		Cd	In	Sn	Sb	Te
		0.993	1.36	1.77	2.24	2.73
		0.92	1.38	1.87	2.5	3.04
	Ba	Hg	Tl	Pb	Bi	
	0.617	1.10	1.43	1.81	2.21	
	0.47	1.07	1.40	2.15	2.34	

Note: First entry for each element is the observed value. The second is result of (3.35), calculated using approximation (3.36). The units are Rydbergs per z , where z is the number of free electrons per atom.

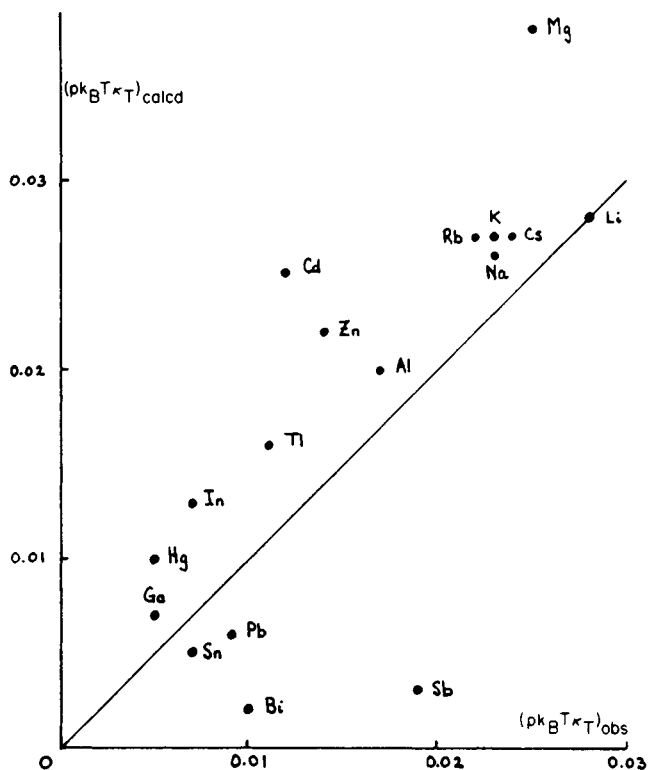
The results so obtained correlate with the experimental data, but it is usual to regard $\tilde{v}_{ps}^{core}(0)$ as an independent parameter to be adjusted to obtain the observed density at zero pressure.

Hasegawa and Young (1981) used the GB hard sphere method (Section 3.2.1) in conjunction with the Ashcroft pseudopotential description to calculate the compressibilities at melting by differentiation of (3.30). They chose r_c to yield a packing of $\eta = 0.45$ and $\tilde{v}_{ps}^{core}(0)$ to give zero pressure; the results are shown in Figure 3.3. Apart from one or two clear failures, these writers found a rough overall correlation between theory and observation. The results are quite sensitive to the pseudopotentials and other features involved, and it is believed (Hasegawa and Young, 1981) that sufficient refinement of these in any given case can bring theory into agreement with experiment.

Table 3.2 shows contributions from the various parts of (3.30) to the total bulk moduli, K_T^{-1} , calculated for Figure 3.3. These and similar calculations for the other metals suggest that volume and pairwise contributions are of comparable magnitude but of opposite sign. Furthermore, the volume dependence of $v(r, n)$ gives rise to only a small fraction of the total pairwise contribution; but for valence 4 and 5 metals, its effect on the final complete sum is important.

The alternative method, using (3.27) to calculate $S(0)$, is more qualitative but provides some further insight. In this case, one relies on the Weeks-Chandler-Andersen (WCA) formalism set out in Appendix 3.2 to obtain $S_{hs}(0)$. The result is about 0.018. This alone does not explain the variety of observed results for $S(0)$, but it is a convenient reference number. For as one knows quite generally ((3.10) and the discussion following) and as

Figure 3.3. Results of Hasegawa and Young (1981) for compressibilities of liquid metals at melting. Calculated versus observed values are plotted. The Gibbs-Bogoliubov hard sphere method, plus the Ashcroft pseudopotential description, was the basis of the calculation.



(3.27) shows specifically, attractive (on average) tails will raise this value and repulsive (on average) ones will lower it.

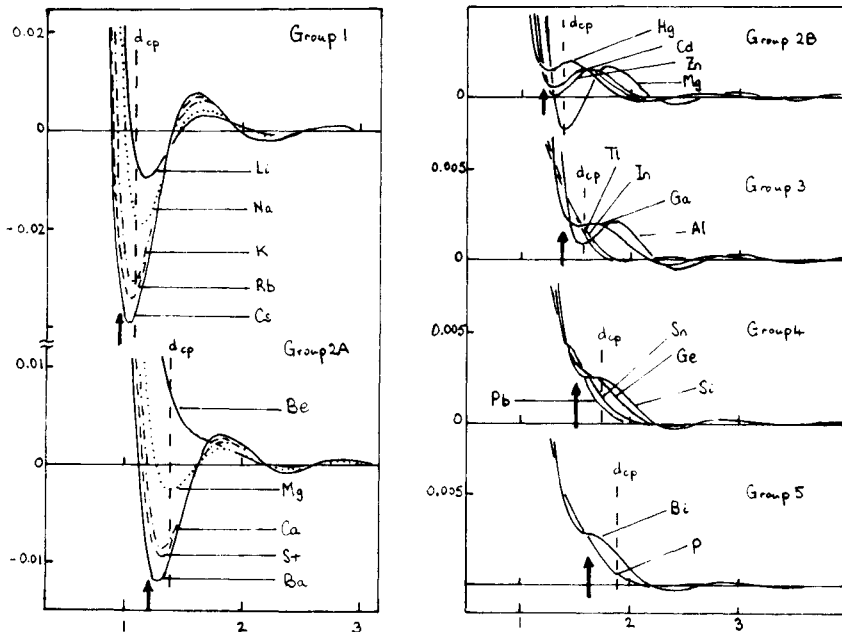
This brings us to the interatomic potentials of Hafner and Heine (1983) shown in Figure 3.4. These were calculated to explain the structures of the

Table 3.2. Contributions to calculated bulk moduli near melting temperature [after Young (1987)].

	Kinetic	Volume	Pair (1)	Pair (2)	Calculated	Experimental
Na	1	-28	60	4	37	43
Al	1	-88	133	5	50	60
Sn	1	-498	598	87	188	150

Note: The kinetic and volume terms arise, respectively, from the application of $\rho d/d\rho$ to the first two terms of (3.30). Similarly, the sum pair (1) + pair (2) comes from the third term, the second contribution being due to the explicit density dependence of $v(r, n)$.

Figure 3.4. A selection of potentials constructed for solid metals by Hafner and Heine (1983). The energy unit is $z^2 e^2 / R_a$, with z the number of free electrons per atom and $R_a = (3/4\pi)^{1/3} \rho^{-1/3}$. The length unit is π/k_f , where $2k_f$ is the diameter of the Fermi sphere. d_{cp} marked on the figure is the interatomic distance in the close-packed solid, while the arrows shown denote liquid-state diameters for 45 and 50% packing (scarcely distinguishable on the scale of the figure) (after Young, 1987).



solids. The essential point here is that when a pronounced minimum exists, many atoms take advantage of it, and a fairly close-packed structure is obtained. On the other hand, when the minimum is lost, closer packing is no longer an advantage, and only detailed further enquiry can establish the lowest energy configuration.

These potentials vary a little (with density) when the liquid is considered (Hafner and Kahl, 1984), but the general characteristics are not altered. In the liquid state, the corresponding structural phenomena to be explained are the three $S(q)$ types, according to Waseda. These are defined through the shape of the principal peaks and are illustrated in Figure 3.5; every liquid metal seems to fit into one such category, and the distribution throughout the periodic table is indicated in Table 3.3. Liquids with well-defined principal minima (Lennard-Jones cases being the prototypes) belong to category (a) but repulsion in the tail (Silbert and Young, 1976) can yield type (c) character; all this is consistent with Figure 3.5.

Figure 3.5. Waseda's attempt to classify liquid-structure factors (after Young 1987). The three types shown can be classified as (a) hard sphere (b) skew peak, and (c) shouldered peak.

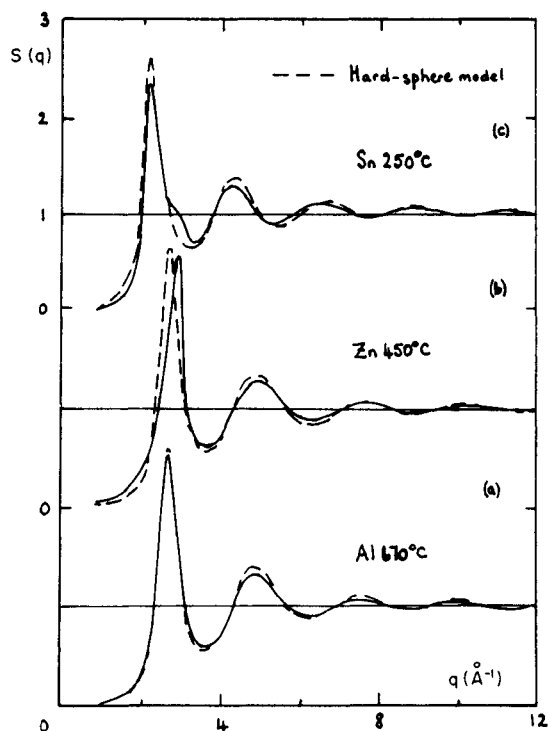


Table 3.3. *Solid (room temperature) and liquid (Waseda) structures. $S(0)$ at melting as deduced from thermodynamic data is also given [after Young (1987)].*

1A		2A		2B		3		4		5	
Li _a	BCC ^a 0.028	Be	HCP ^b			B					
Na _a	BCC 0.023	Mg _a	HCP 0.025			Al _a	FCC ^c 0.017	Si _c	DIA ^d	P	
K _a	BCC 0.023	Ca _a	FCC 0.035	Zn _b	HCP 0.014	Ga _c	ORC ^e 0.005	Ge _c	DIA	As	RHL ^f
Rb _a	BCC 0.022	Sr _a	FCC 0.031	Cd _b	HCP 0.012	In _a	TET* 0.007	Sn _c	TET 0.007	Sb _c	RHL 0.019
Cs _a	BCC 0.024	Ba _a	BCC 0.036	Hg _b	RHL 0.005	Tl _a	HCP 0.011	Pb _a	FCC 0.009	Bi _c	RHL 0.010

Note: Some structures in solid change with temperature, but distinction between closer and looser packing persists.

^a BCC: body centred cubic.

^b HCP: hexagonal close packed.

^c FCC: face centred cubic.

^d DIA: diamond.

^e ORC: orthorhombic.

^f RHL: rhombohedral.

^{*} TET: tetragonal.

In the present context, however, one is mainly interested in the variations in $S(0)$ from metal to metal and, for this purpose, Figure 3.5 continues to be useful. For, as is evident from the diagrams and as is required to explain the details, $S(0)$ lies above $S_{hs}(0) \approx 0.018$ when the tails are (on average) attractive and below when they are (on average) repulsive.

This account of $S(0)$ bears closer analysis (Young, 1987). For example, the increasing attractiveness of the tail (Figure 3.4) through the sequence Hg, Cd, Zn, Mg, Ca, Sr, Ba is reflected in the $S(0)$ trend shown in Table 3.3 (Sr being, perhaps, an exception). Other correct trends are discernable, but one should not attempt to read too much into results that might be sensitive to pseudopotential and screening characterisation.

It is to be noted that the preceding discussion depends on the use of a WCA diameter. If one had relied on the GB packing fraction of 0.45, (3.5) would have given 0.028, which is too high to be compatible with Figure 3.4. However, as discussed by Young (1987), there are good reasons to take an **apparently** larger packing for describing $S(q)$ as $q \rightarrow 0$.

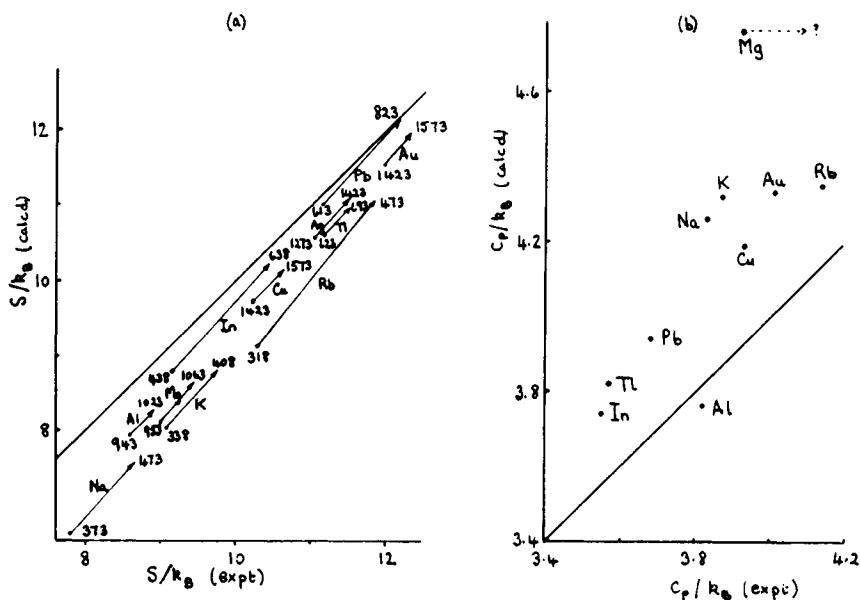
The above discussion has been confined to liquids near their triple points. Before leaving this topic, note that a number of successful calculations have

been made at elevated temperatures and pressures. Details may be found in the original papers (see McLaughlin and Young, 1984).

Finally, there are some properties that are mainly dependent on core size. For example, the GB method of Section 3.2.1, when used with a hard sphere reference system, leads to the conclusion that the structure factor is approximately given by a hard sphere form. It has been seen that there are departures from this result at $q = 0$ and there are others elsewhere, but, overall, a hard sphere shape is quite a fair approximation (with $\eta \approx 0.45$ near the triple point). The corresponding entropy is also given by that appropriate to hard spheres ((3.24) and (3.12)), and it is the case that there is reasonable agreement between the packings deduced from the observed principal peak heights of the structure factors and the measured entropies.

This proposition is illustrated in Figure 3.6(a), where experimentally inferred entropies are compared with those calculated by obtaining packing fractions from the measured first peak heights (Figure 3.2) and using them in (3.12) (Figure 3.2). The calculated values are underestimates presumably

Figure 3.6. (a) Entropies per atom, observed values plotted against the results of calculations. (b) Heat capacities per atom, again observed versus calculated (after Young 1987).



because of inadequate treatment of core softness and tail attraction. The error here diminishes at higher T , since (1) cores become effectively harder (noting (3.26) and the increasing steepness of $v(r)$ as r falls below r_0 in Figure 3.1)) and (2) the influence of $v_{\text{tail}}/k_B T$ on the first peak height decreases (since, although $|v_{\text{min}}|$, for instance, may increase, T increases faster). This is consistent with the behaviour evident in Figure 3.6(a) of the trajectories approaching a 45° asymptote. This figure also carries implications for estimates of the specific heat $C_p = T(\partial S/\partial T)_p$, and these are shown in Figure 3.6(b). As expected from the preceding discussion, the calculated values are overestimates, but there is an overall correlation (Young, 1977). Further discussion of specific heats occurs later (Chapter 8; see also Appendix 5.4).

3.5. One-component plasma as reference liquid

Having discussed the basis of a variational approach to the Helmholtz free energy F afforded by the Gibbs-Bogoliubov inequality, with a detailed example of the use of hard spheres as a reference liquid, it must be added that in the work of Ross et al. (1981; see also Mon et al., 1981), a comparison was made between such results and ones using the one-component plasma (OCP) as a reference liquid. Their conclusion was that for the alkali metals, the OCP is the favourable choice of reference liquid because it yields a lower free energy and better agreement with the Monte Carlo pressures. However, for polyvalent metals (in particular Al), the situation just described is reversed. It is also of interest to mention in concluding this section the calculations of Stroud and Ashcroft (1972) on the melting curve of Na (see also Stishov et al., 1973).

4

Electron screening and effective ion-ion interactions

In this chapter the framework of weak electron-ion coupling theory will be employed to

1. Complete the derivation of effective interactions in liquid metals, discussed in Chapter 3, and
2. Give a simple theory of the structure factor $S(k)$ for the alkali metals.

A useful starting point is the single-centre problem of a charged impurity in an electron liquid. In the following section, one takes a static point charge Ze , with Z sufficiently small (or, alternatively, the electron liquid density high enough) to use first-order perturbation theory in the screened potential round the point charge.

4.1. Screening of impurity centre in electron liquid

If one treats the problem by the linearized Thomas-Fermi approximation, then the self-consistent potential energy $V(r)$ of an electron at distance r from the test charge is obtained from the equation (Mott, 1936)

$$\nabla^2 V(r) = 4\pi Ze^2 \delta(\mathbf{r}) + q^2 V(r) \quad (4.1)$$

where q^{-1} is the Thomas-Fermi screening length l , given by multiplying a characteristic velocity, which in the degenerate electron liquid in molten metals is the Fermi velocity v_f , by a characteristic time τ . This is the period of the plasma oscillations of the electron liquid, $2\pi/\omega_p$, with ω_p the (Langmuir) plasma frequency: i.e.,

$$q^{-1} \doteq l = v_f \frac{2\pi}{\omega_p} = \left\{ \frac{\pi a_0}{4k_f} \right\}^{1/2} \quad (4.2)$$

with k_f the Fermi wavenumber. Equation (4.1) has a solution satisfying the

physical boundary conditions (1) $V(r) \rightarrow -Ze^2/r$ as $r \rightarrow 0$ and (2) $V(r) \rightarrow 0$ faster than $1/r$ as $r \rightarrow \infty$,

$$V(r) = -\frac{Ze^2}{r} \exp(-qr). \quad (4.3)$$

But the Thomas-Fermi approximation is valid for slowly varying potentials, and, as was shown by March and Murray (1960, 1961), one must treat the diffraction of the electron waves off the test charge. This is correctly accomplished by writing the nonlocal generalization of (4.1) as

$$\nabla^2 V(r) = 4\pi Ze^2 \delta(\mathbf{r}) + \int F(\mathbf{r}\mathbf{r}') V(\mathbf{r}') d\mathbf{r}' \quad (4.4)$$

which evidently reduces to (4.1) when the nonlocal response function $F(\mathbf{r}\mathbf{r}') \equiv F(|\mathbf{r} - \mathbf{r}'|)$ in a homogeneous electron liquid is replaced by $q^2 \delta(\mathbf{r} - \mathbf{r}')$. It can be shown (March and Tosi, 1984) that F is in fact given by

$$F(|\mathbf{r} - \mathbf{r}'|) = \frac{2mk_f^2 e^2}{\pi^2 \hbar^2} \frac{j_1(2k_f |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|^2} \quad (4.5)$$

with $j_1(x) = (\sin x - x \cos x)/x^2$ being the first-order spherical Bessel function.

Evidently, it is clear from (4.4) and (4.5) that the charge $\delta n(\mathbf{r})$ displaced by the introduction of the test charge is given in terms of the scattering potential $V(\mathbf{r})$ by

$$\delta n(r) = \frac{mk_f^2}{2\pi^3 \hbar^2} \int \frac{j_1(2k_f |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|^2} V(\mathbf{r}') d\mathbf{r}'. \quad (4.6)$$

To study the form of the displaced charge far from the scattering centre, consider the example of a very localized scattering potential, i.e., $V(\mathbf{r}') = \lambda \delta(\mathbf{r}')$. Inserting this model form into (4.6), one finds

$$\delta n(r) \sim \frac{\cos 2k_f r}{r^3}; \quad r \rightarrow \infty \quad (4.7)$$

when one makes use of the asymptotic form of the spherical Bessel function. Though one needs to obtain the scattering potential self-consistently from (4.4), it turns out that form (4.7) for the asymptotic displaced charge is again recovered for sufficiently large r .

4.2. Lindhard dielectric function

As anticipated, the behavior (4.7) reflects the diffraction of the electron de Broglie waves at the Fermi surface off the test charge, leading to these so-called Friedel oscillations. Equation (4.4), with F given by (4.5), has been solved numerically in $\mathbf{r}$ space for $V(\mathbf{r})$ for various electron densities (March and Murray, 1961), but if one Fourier transforms it, then the solution is obtained immediately in terms of the so-called Lindhard (1954) dielectric function $\epsilon_L(k)$ given by

$$\epsilon_L(k) = 1 + \frac{2mk_F e^2}{\pi \hbar^2 k^2} \left[1 + \frac{k_F}{k} \left(\frac{k^2}{4k_F^2} - 1 \right) \ln \left| \frac{k - 2k_F}{k + 2k_F} \right| \right], \quad (4.8)$$

the Fourier transform $V(k)$ of $V(r)$ then being explicitly

$$V(k) = \frac{-4\pi Z e^2}{k^2 \epsilon_L(k)}. \quad (4.9)$$

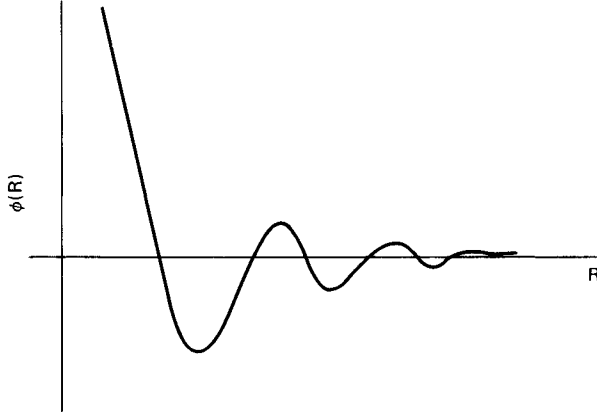
Form (4.8) is established essentially from the form of the Fourier transform of the response function F in (4.5). In $\mathbf{k}$ space, it is the “kink” in $\epsilon_L(k)$ at k equal to the diameter $2k_F$ of the Fermi sphere that is responsible for the long-range oscillations (4.7) in $\mathbf{r}$ space. (See the further discussion in Section 10.6.)

Quite briefly, it should be said that the r space oscillations have been detected in nuclear magnetic resonance experiments on field gradients due to charged impurities in metals (Rowland, 1960; Kohn and Vosko, 1960). Direct evidence for the kink in $\mathbf{k}$ space is provided by the observation of the so-called Kohn anomaly in phonon dispersion relations (Kohn, 1959).

It will be seen later, when strong scattering (for example, off a proton in metallic hydrogen) is treated, that such oscillatory behaviour of the displaced charge persists. The changes are that $\delta n(r)$ has now the asymptotic form $A \cos(2k_F r + \theta)/r^3$ and the amplitude A is changed from the first-order value. But as is evident, the most important point is that a phase factor θ is now introduced into the asymptotic form of $\delta n(r)$. In fact A and θ can be written explicitly in terms of the phase shifts δ_l for scattering of the Fermi surface electrons off the proton.

To discuss the two-centre problem, leading up to the effective pair interaction between ions in simple liquid metals, let us consider the model of two test charges, $Z_1 e$ and $Z_2 e$, separated by a distance R . It turns out that the most elementary electrostatic model is valid in this case. Thus, if one adopts the (oversimplified) form (4.3) of the screened potential, then the

Figure 4.1. Effective ion-ion interaction, with oscillations arising from singularity in the Lindhard dielectric function (4.8) at the Fermi sphere diameter $k = 2k_f$.



pair potential ϕ follows immediately as

$$\phi(R) = \frac{Z_1 Z_2 e^2}{R} \exp(-qR), \quad (4.10)$$

since we can view the charge $Z_2 e$ as sitting in the screened potential of charge $Z_1 e$ (or vice versa). Equation (4.10) is, of course, disappointing, as it tells us that like charges repel at all separations R , even in an electron liquid!

But to correct this (Corless and March, 1961), let us return to the Friedel oscillations. Provided R is taken to be sufficiently large to validate the asymptotic form (4.7) of the displaced charge, then $\phi(R)$ sketched in Figure 4.1 results. This form is, of course, simply the Fourier transform of

$$\phi(k) = \frac{4\pi Z_1 Z_2 e^2}{k^2 \epsilon_L(k)} \quad (4.11)$$

in the Lindhard ($\equiv$ Hartree) approximation.

4.3. Introduction of exchange and correlation

In the presence of exchange and correlation interactions, three modifications of the preceding argument are required, even at linear response level:

1. A one-body potential $V(\mathbf{r})$ exists, which generates the correct displaced charge through (4.6). But (4.4) is restricted to the Hartree approximation.
2. $V(\mathbf{r})$ becomes a functional of the displaced charge, and one may write

$$V(\mathbf{r}) = V_H(\mathbf{r}) + \int U(|\mathbf{r} - \mathbf{r}'|) \delta n(\mathbf{r}') d\mathbf{r}' \quad (4.12)$$

where the Hartree potential is

$$V_H(\mathbf{r}) = \frac{-Z_1 e^2}{r} + \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \delta n(\mathbf{r}') d\mathbf{r}', \quad (4.13)$$

U having subsumed into it exchange and correlation (Jones and March, 1973).

3. The potential $\phi(R)$ felt by a second test charge is determined by Poisson's equation and hence is given by

$$\phi(R) = -Z_2 V_H(\mathbf{R}). \quad (4.14)$$

From (1)–(3) and writing, for convenience,

$$\delta n(\mathbf{r}) = \int \chi_0(|\mathbf{r} - \mathbf{r}'|) V(\mathbf{r}') d\mathbf{r}' \quad (4.15)$$

then one finds

$$\phi(k) = \frac{4\pi Z_1 Z_2 e^2}{k^2 \varepsilon(k)} \quad (4.16)$$

and

$$V(k) = \frac{-4\pi Z_1 e^2}{k^2 \varepsilon_p(k)}. \quad (4.17)$$

Here

$$\varepsilon(k) = 1 - \frac{4\pi e^2}{k^2} \chi_0(k) / [1 - U(k) \chi_0(k)] \quad (4.18)$$

is the usual dielectric function but now corrected, via $U(k)$, for exchange and correlation interactions, whereas

$$\varepsilon_p(k) = 1 - \left[\frac{4\pi e^2}{k^2} + U(k) \right] \chi_0(k). \quad (4.19)$$

This latter screening function enters, through (4.6), the potential energy $V(k)$ of an electron round the test charge and therefore differs from $\varepsilon(k)$ because of exchange and correlation between such an electron and the electrons

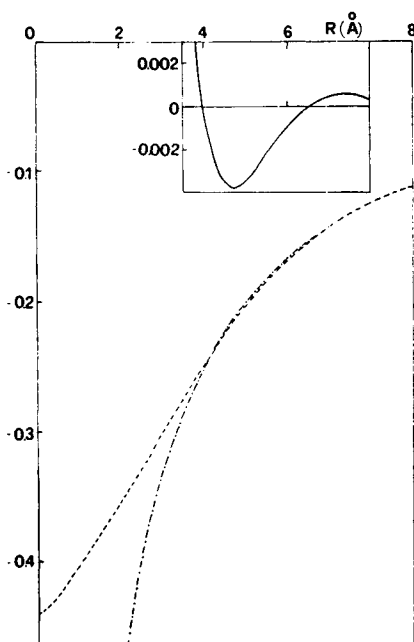
in the screening cloud. The two screening functions coincide, of course, in the Lindhard approximation, in which $V(\mathbf{r})$ is taken to satisfy Poisson's equation (4.4).

Equations (4.16) and (4.17) determine the effective ion-ion interaction and the effective ion-electron interaction, respectively, in the present case in which the ionic point charges are treated by linear response theory.

4.4. Effective ion-ion interactions in simple (s-p) metals

At this stage, one needs to introduce modifications to treat simple s-p liquid metals with ions having core electrons. The procedure adopted is to introduce pseudopotentials to describe the ion cores, and this is best implemented in $\mathbf{k}$ rather than $\mathbf{r}$ space.

Figure 4.2. Components of the effective ion-ion potential in liquid potassium (in units of $e^2 \text{ \AA}^{-1}$). The dot-dash curve is the negative of the direct Coulomb term e^2/R and the dashed curve is the electron-screening contribution. The total potential $\phi(R)$ near its minimum is shown in the inset on an enlarged scale.



To this end, one introduces bare core potentials $v_i(k)$ (cf Chapter 3), which for point ions are simply $-4\pi Z_i e^2/k^2$, to describe the interaction between a bare ion and an electron. The result of (4.16) is then modified to read (see March and Tosi, 1984)

$$\phi(k) = \frac{4\pi Z_1 Z_2 e^2}{k^2} + \frac{v_1(k)v_2(k)}{(4\pi e^2/k^2)} \left[\frac{1}{\epsilon(k)} - 1 \right] \quad (4.20)$$

where the first term has been separated out to represent the direct ion-ion interaction, whereas in the remainder we have replaced the bare coulomb electron-ion interactions by the core potentials, which give the contribution due to electron screening. It may be noted that, in principle, the direct ion-ion term should also be supplemented by ion-core terms, but that these turn out to be normally negligible in practice for metals like Na or K.

The k^{-2} divergence in the direct term in (4.20) is exactly canceled in the limit $k \rightarrow 0$, where $v_i(k) \rightarrow -4\pi Z_i e^2/k^2$. The two components of the effective ion-ion potential in **R** space are illustrated for molten K near freezing in Figure 4.2. This shows the cancellation arising at large R , the oscillations at intermediate R , and the dominance of the direct term at small R . These predictions will be confronted in the following chapter with effective interionic forces extracted using statistical mechanical theory from the measured ionic structure factor $S(k)$. However, this chapter will conclude with a brief discussion of the way $S(k)$ for the liquid alkali metals can be modelled, utilizing the ideas presented above.

4.5. Structure factor of alkali metals modelled in terms of one-component plasma

As will be discussed in Chapter 6, Ferraz and March (1980) noted the relevance of the one-component plasma model to the freezing of liquid Na and K. This model considers classical point ions in a uniform non-responsive neutralizing background of electrons. The model is characterized by a single parameter Γ , measuring the ratio of the mean potential energy e^2/r_s to the thermal energy $k_B T$ (with r_s the mean interionic spacing)

$$\Gamma = \frac{e^2/r_s}{k_B T}. \quad (4.21)$$

Let us denote the structure factor of the ions in this model by $S_0(k)$, which clearly depends on the value of Γ .

Then the work of Tosi and March (1973) (see also Galam and Hansen, 1976; March and Tosi, 1984) allows the liquid alkali metal structure factors $S(k)$ to be modelled in terms of (1) $S_0(k)$; (2) a model potential representing the bare electron-ion interaction; and (3) the static dielectric function $\varepsilon(k)$ of the homogeneous electron fluid, already discussed in Section 4.3. Specifically the result takes the form, with n_i denoting the ionic density:

$$S(k) = \frac{S_0(k)}{[1 + n_i \tilde{v}(k) S_0(k) / k_B T]}. \quad (4.22)$$

Here $\tilde{v}(k)$ is related to the bare electron-ion potential $v(k)$ and $\varepsilon(k)$ by

$$\tilde{v}(k) = \frac{v^2(k)}{(4\pi e^2/k^2)} \left[\frac{1}{\varepsilon(k)} - 1 \right]. \quad (4.23)$$

It is worth noting that (4.22) corresponds to the so-called random phase approximation of the electron screening, referred to in some detail in Section 4.2. A comparison of the long wavelength limit of (4.22) with experiment is worth making as follows (see also Chapter 3). One returns to the fluctuation theory result (2.5), to find (see Chaturvedi et al., 1981; March and Tosi, 1984)

$$\lim_{k \rightarrow 0} S(k) = n_i k_B T K_T. \quad (4.24)$$

This limit can then be taken in (4.22) as follows. For the classical one-component plasma, it can be shown (see March and Tosi, 1984) that

$$\lim_{k \rightarrow 0} S_0(k) = k^2 l_D^2 (1 + k^2/k_s^2)^{-1} \quad (4.25)$$

where $k_s^2 = 4\pi e^2 / (\partial\mu/\partial n)_T$ with μ the chemical potential and l_D the Debye length. The other result one needs is the expansion

$$\lim_{k \rightarrow 0} v(k) = \frac{-4\pi Z e^2}{k^2} \left(1 - \frac{1}{2} k^2 r_c^2 + \cdots \right) \quad (4.26)$$

Table 4.1. *Isothermal compressibility for liquid alkali metals near freezing.*

		Na	K	Rb	Cs
	Theory	0.0215	0.0231	0.0236	0.0235
$n_i k_B T K_T$	Expt.	0.0236	0.0236	0.0220	0.0237

Adapted from March and Tosi, 1984.

for $v(k)$, introducing the parameter r_c which is representative of the core radius. The result from (4.24) is then (March and Tosi, 1984):

$$n_i k_B T K_T = \left(\frac{k_D^2}{k_{se}^2} + \frac{k_D^2}{k_{si}^2} + k_D^2 r_c^2 \right)^{-1}, \quad (4.27)$$

where $k_D^2 = 4\pi n_i Z^2 e^2 / k_B T$, while k_{se}^2 and k_{si}^2 describe the “compressibilities” of the bare electronic and ionic components (March and Tosi, 1984). The first term in this expression (4.27) is essentially the Bohm-Staver result for the velocity of sound but now k_{se}^2 refers to the interacting electron fluid.

The numerical results obtained by Chaturvedi et al. (1981) with values of r_c , the core radius, taken from an analysis of phonon dispersion curves in solid alkalis are recorded in Table 4.1. The values of k_{se}^2 and k_{si}^2 were taken from electron-correlation theory (Vashishta and Singwi, 1972; Singwi and Tosi, 1981) and from computer simulation data on the free energy of the classical one-component plasma (Hansen et al., 1977). The quite good agreement with experiment shows that this simple treatment based on (4.22) is giving a consistent account of sound waves in the liquid.

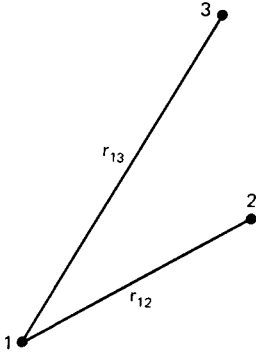
Interionic forces and structural theories

Consider a situation such as depicted in Figure 5.1, in which attention is focused on atom 1 at position $\mathbf{r}_1$ in an environment in which there is a second atom 2 at distance $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$. In a classical liquid, one next writes the pair function $g(r)$ as a Boltzmann factor:

$$g(r) = \exp \left[\frac{-U(r)}{k_B T} \right]. \quad (5.1)$$

This can be viewed as the definition of the potential of mean force $U(r)$, which in general will depend also on the temperature T . Returning to Figure 5.1, one can now write the total force acting on atom 1 as $-\partial U(r_{12})/\partial \mathbf{r}_1$; this can be separated into a direct part $-\partial \phi(r_{12})/\partial \mathbf{r}_1$ due to the assumed pair potential energy $\phi(r)$ acting between two atoms at separation r_{12} and that due to the rest of the atoms. If, as in Figure 5.1, one considers a third atom at $\mathbf{r}_3$, then clearly one must introduce into the theory a three-atom correlation function $g_3(\mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3)$ that measures the probability of finding three atoms simultaneously at $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$.

Figure 5.1. Geometry of three-atom configuration used in setting up the force equation (5.2). The quantity g_3 in that equation measures the probability of finding three atoms simultaneously at $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$.



5.1. Force equation

One can write the so-called force equation:

$$-\frac{\partial U(r_{12})}{\partial \mathbf{r}_1} = -\frac{\partial \phi(r_{12})}{\partial \mathbf{r}_1} - \rho \int \frac{\partial \phi(r_{13})}{\partial \mathbf{r}_1} \frac{g_3(\mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3)}{g(r_{12})} d\mathbf{r}_3. \quad (5.2)$$

The last term has the form shown in (5.2), since one has asserted that there are certainly atoms at $\mathbf{r}_1$ and $\mathbf{r}_2$ and hence the three-body correlation function g_3 must be divided by $g(r_{12})$ to take account of this. This conditional probability must be multiplied by the force $-\partial \phi(r_{13})/\partial \mathbf{r}_1$ on atom 1 due to atom 3 at $\mathbf{r}_3$, and the result must then be integrated over all positions $\mathbf{r}_3$. In (5.2), the total force is evidently expressed as a sum of a direct part, involving $\phi(r_{12})$ and an indirect part. Equation (2.7) is a corresponding decomposition for correlation functions, $c(r)$ evidently reflecting somehow three-body correlations also.

Although the above construction of (5.2) is intuitive, (5.2) is, in fact, an exact consequence of classical statistical mechanics, given that the total potential energy $\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ of the liquid can be expressed solely in terms of pair potentials by

$$\Phi = \sum_{i < j} \phi(r_{ij}). \quad (5.3)$$

Here then, in (5.2), is the desired link between structure and forces. However, it is plain that, since $U(r)$ is related directly to $g(r)$ by (5.1), one can forge an explicit relation between $g(r)$ and the pair potential $\phi(r)$ only if one has knowledge of the three-body correlation function g_3 . This is a characteristic of many-body theories; they lead to hierarchical equations relating correlation functions. To calculate g_3 , one needs to write an equation involving four-body correlations g_4 , etc. (see, for example, Hill, 1956, and Appendix 5.4).

So far, while $g(r)$ can be measured, only limited experimental information can be obtained on the three-particle correlation function $g_3(\mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3)$. As shown in Appendix 5.1, one important result is that integration on g_3 can be related to the density derivative of the pair function. Experiments on this density derivative have been carried out, particularly by Egelstaff and his coworkers (1971; 1980). This already provides valuable constraints that any acceptable theory of g_3 must satisfy.

5.2. Simple structural theories

Following the ideas of Kirkwood, the simplest assumption to make for g_3 is that it is given by the product of pair functions, i.e.,

$$g_3(\mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3) \cong g(r_{12})g(r_{23})g(r_{31}). \quad (5.4)$$

Inserting this approximation (5.4) into the exact form (5.2) leads to the so-called Born-Green theory (see Green, 1952) of liquid structure. Though one must be careful to specify the range of the forces before deciding how to decouple g_3 ((5.4) being a simple example of decoupling), it is now known that the Born-Green theory is not sufficiently refined to yield a quantitative theory of liquid structure from a given pair potential $\phi(r)$. However, a refinement of it leads to the so-called hypernetted chain (HNC) theory, which, as the name implies, had its origins in diagrammatic methods (for a review, see McDonald and O'Gorman, 1978) of handling the classical many-body problem posed by a liquid such as argon.

To see how to reach the HNC theory, one notes that, following Rushbrooke (1960), the Born-Green theory leads to

$$\frac{U(r)}{k_B T} = \frac{\phi(r)}{k_B T} - \rho \int E(\mathbf{r} - \mathbf{r}') h(\mathbf{r}') d\mathbf{r}' \quad (5.5)$$

where

$$E(r) = \frac{1}{k_B T} \int_r^\infty g(s) \frac{\partial \phi(s)}{\partial s} ds. \quad (5.6)$$

In fact, there is a class of structural theories that have a convolution representation of $(U - \phi)/k_B T$, as in (5.5). Since $g(r) \rightarrow 1$ far from the critical point, if one calculates $E(r)$ at large r from (5.6), one has $c(r) \rightarrow -\phi(r)k_B T$,^{*} $E(r) \rightarrow c(r)$. If, in embracing this class of theories, one replaces E in (5.5) by G , then the different members of this class are characterized by different forms of G , as collected in Table 5.1. Included there, in addition to HNC ($G \rightarrow c$) and Born-Green theories ($G \rightarrow E$), are the treatments of de Angelis and March (1976) ($G \rightarrow h$) and a combination of a structural proposal of Liboff (1986) with Born-Green theory. It must be stressed that

^{*} Though no general proof appears to exist to date, this asymptotic result for large r is the basis of the so-called mean spherical approximation (see for instance the book by March and Tosi, 1984), as well as being incorporated in the HNC theory. It ceases though to be valid on approaching the critical point (see (3.11)).