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## The entropies and structure factors of liquid simple metals

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**Abstract.** Some results of a systematic study of the entropies and structure factors of fourteen liquid simple metals are presented. The *ab initio* model potentials of Shaw and the dielectric function of Vashista and Singwi have been used to construct effective pairwise interatomic potentials for these liquid metals. These pairwise potentials have then been employed in both the Weeks–Chandler–Anderson (WCA) and the variational thermodynamic perturbation theories to determine appropriate effective hard-sphere diameters. In the variational scheme the excess entropy of the liquid metal consists solely of a hard-sphere contribution while in the WCA approach there are important additional contributions. For ten of the metals, the excess entropies calculated in the WCA theory are in reasonably good agreement with experiment. However, for Li, In, Tl and Pb the calculated hard-sphere diameters are too large and lead to packing fractions and entropies which are non-realistic.

We examine in detail the short-range repulsive part of the pairwise potential in several liquid metals and show, within the WCA theory, how the softness of this influences the form of the liquid structure factor. For Mg and Al, in particular, the combination of our calculated pairwise potentials and the WCA theory leads to structure factors which agree well with those measured experimentally. In the alkali metals, however, the repulsive potentials are softer and the hard-sphere potential is a poor starting approximation for the WCA procedure. We discuss briefly the calculation of the compressibility from the long-wavelength limit of the structure factor.

### 1. Introduction

Over the last decade our understanding of the structure and thermodynamical properties of classical monatomic liquids such as the rare-gas liquids has developed enormously. For these systems it is reasonable to assume that the total energy of interaction  $\Phi$  can be approximated by a pairwise sum of the interatomic potentials  $\phi$ :

$$\Phi = \frac{1}{2} \sum_{i \neq j} \phi(R_{ij}) \quad (1)$$

where  $R_{ij}$  is the separation of the atoms located at  $R_i$  and  $R_j$ . The pair potential  $\phi$  is usually modelled by a Lennard-Jones or related form and there exist many machine calculations (Monte Carlo or molecular dynamics) of the radial distribution function and thermodynamic quantities for such a model. The interpretation of this work has been simplified by the development of the so-called thermodynamic perturbation theories which were originally introduced by Zwanzig (1954). In such theories the Helmholtz free energy is expanded in a rapidly converging series by treating the hard-sphere fluid as a reference system and the difference between the real potential and the hard-sphere

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potential as a perturbation. All the relevant thermodynamic properties can then be evaluated provided the corresponding quantities for the hard-sphere system are known. The method of choosing the diameter of the hard spheres and the detailed structure of the perturbation expansion depend on the particular perturbation theory and the most widely used schemes are those of Barker and Henderson (1967), Mansoori and Canfield (1969) and Weeks *et al* (1971, to be referred to as WCA). The reliability of such perturbation expansions has been well established by comparison with the machine calculations (eg Verlet and Weis 1972). The WCA theory has also been successful in describing the radial distribution function and liquid structure factor of the simple classical liquids in terms of perturbations on a hard-sphere reference system.

Although liquid metals are also monatomic they are complicated by their two-component nature. Here we restrict our discussion to simple metals i.e. those without *d* or *f* electrons in the conduction band, and assume that the core electrons are rigidly fixed to the nuclei, so that the liquid metal consists of *N* ions and *NZ* conduction electrons where *Z* is the valence. If we fix the ions in an arbitrary static configuration and evaluate the corresponding thermodynamic potential of the conduction electron system, we can use this as an effective potential  $\Phi$  for describing the classical statistical mechanics of the ions. This adiabatic approximation reduces the two-component problem to, effectively, a one-component problem. For most liquid metals, at temperatures close to their melting points, the electron distribution is almost degenerate so it is sufficient to replace the thermodynamic potential of the conduction electron system by the ground state energy. In general the problem of calculating an effective potential energy for an arbitrary arrangement of ions is still complex but if the interaction between the conduction electrons and the ions can be replaced by a weak pseudo or model potential  $v_{ps}$ , the required total energy can be written as an expansion in powers of  $v_{ps}$ . It is well known (eg Harrison 1966) that if this expansion is truncated at second order in  $v_{ps}$ , the resultant expression for the total energy can be transformed to the form

$$\Phi = Nu(n_0) + \frac{1}{2} \sum_{i \neq j} \phi(R_{ij}; n_0) \quad (2)$$

where  $n_0 = NZ/V$  is the average conduction electron density and *V* is the total volume of the system.  $\phi(R; n_0)$  is an effective pairwise potential acting between the pseudo-ions. This object includes the direct ion-ion Coulomb repulsion as well as an indirect contribution arising from the dielectric screening of the latter.  $\phi$  can be written explicitly in terms of the pseudopotential and the dielectric function of the interacting, homogeneous electron gas. The quantity  $u(n_0)$  is independent of the positions of the ions but again depends on the pseudopotential and the properties of the uniform electron gas. Most of the binding energy of the metal resides in the term  $u(n_0)$ .

Equation (2) forms the starting point for all recent investigations of the structure and thermodynamical properties of simple liquid metals. Once an appropriate pair potential has been calculated this can be used in a machine calculation of the radial distribution function and various thermodynamical quantities. Price (1971) carried through such a programme for liquid Na. Other authors (Hasegawa and Watabe 1972) used experimental structure factor data to obtain radial distribution functions but then employed calculated pair potentials for the evaluation of the pressure and compressibility of several liquid metals.

Since the pairwise potentials  $\phi(R; n_0)$  have a repulsive 'hard-core' part, thermodynamic perturbation theories have been applied to this model of a liquid metal. Jones (1971 and 1973) and Stroud and Ashcroft (1972) used the Mansoori-Canfield (1969) approach to calculate a wide variety of quantities, including the melting temperature, for a few

metals. For quantities which depend on volume derivatives of the free energy the analysis becomes more complicated than in the rare-gas case since one has to consider differentiation with respect to the average electron density  $n_0$  and terms involving  $du(n_0)/dn_0$  and  $(\partial/\partial n_0)\phi(R; n_0)$  appear—which are absent for rare-gas liquids. Properties which depend on the rearrangement of ions at constant volume are determined solely by the pairwise potential and so the calculation of these is no more difficult than for the rare gases. Several authors (Edwards and Jarzynski 1972, Umar and Young 1974 and Silbert *et al* 1975) have discussed the calculation of constant volume properties such as the entropy, specific heat and effective hard-sphere structure factor. Their work is based on the Mansoori and Canfield perturbation scheme. Wehling *et al* (1972), Hasegawa and Watabe (1974) and Hasegawa (1976) have used the WCA approach to investigate the structure factors of liquid Na and K.

Although many of the above calculations have claimed to be successful in explaining experimental results on liquid metals, it is at present somewhat difficult to assess just how good the combination of the simple pseudopotential scheme with thermodynamic perturbation theory really is. A glance at the various papers will show that the pair potential calculated for a particular element by one author can differ by as much as an order of magnitude, in the region of the first minimum, from the corresponding calculation of another author. Such large discrepancies occur because the pair potential is notoriously sensitive to the choice of pseudopotential and to the form of exchange and correlation correction to the dielectric function. The authors mentioned above have used a wide variety of pseudopotentials and dielectric functions.

In this paper we present some results of a systematic study of the structure factors and entropies of fourteen liquid simple metals. Both the WCA and the Mansoori and Canfield variational theories have been used to calculate the appropriate effective hard-sphere diameters. In the latter scheme the entropy is given solely in terms of a hard-sphere contribution (Edwards and Jarzynski 1972) while in the former there is an additional contribution from the attractive part of the pair potential. We examine in detail the repulsive part of the pairwise potential in liquid metals and show, within the WCA theory, how the 'softness' of this influences the form of the structure factor. In constructing the pair potentials we have employed Shaw's (1968) non-local optimized model potential and the Vashista and Singwi (1972) form of  $f(q)$ , the exchange and correlation correction to the dielectric function. We consider these to be the most realistic *ab initio* prescriptions which are available but we have also calculated pair potentials using various local pseudopotentials and different forms of  $f(q)$  in order to assess the sensitivity and hence the usefulness of the various schemes. For many of the metals which we consider, the pair potential derived from Shaw's model potential leads to a realistic structure factor and a reasonable value for the entropy. However, for the remainder, the calculated effective hard-sphere diameters are too large and produce unphysical results.

The paper is arranged as follows: in §2 we briefly outline the calculation of the entropy in the WCA and in the Mansoori and Canfield perturbation theories. Our calculated pair potentials are presented and analysed in §3 while the results for the entropies and structure factors are given in §4 and §5. The final section contains a discussion of our results.

## 2. Thermodynamic perturbation theories

In this section we derive expressions for the entropy  $S$  in our model of a liquid metal

using two different thermodynamic perturbation theories. The form of the entropy within the Mansoori–Canfield variational procedure has previously been discussed by several authors (see especially Edwards and Jarzynski 1972). We include the present discussion in order to facilitate comparison with the corresponding result from the WCA theory, which to our knowledge has not been given before.

### 2.1. The variational approach

We assume that the total interaction potential  $\Phi$  of any system can be divided into a part corresponding to a reference system,  $\Phi_0$  and a perturbation part  $\Phi_1$ , so that

$$\Phi = \Phi_0 + \Phi_1. \quad (3)$$

It is well known that the Helmholtz free energy  $F$  of the true system satisfies the following inequality:

$$F \leq F_0 + \langle \Phi_1 \rangle_0 \quad (4)$$

where  $F_0$  is the free energy of the reference system and the brackets  $\langle \rangle_0$  denote a configuration average which is to be performed over the reference system. This result is usually referred to as the Gibbs–Bogoliubov inequality. If  $\Phi$  has the form of equation (2) and  $\phi(R; n_0)$  has a strongly repulsive part then it is convenient to define a reference system of hard spheres of diameter  $d$

$$\Phi_0 = \frac{1}{2} \sum_{i \neq j} \phi_0(R_{ij}) \quad (5)$$

where

$$\begin{aligned} \phi_0(R) &= \infty & R \leq d \\ &= 0 & R > d \end{aligned}$$

and then from equation (4) it follows that

$$F \leq F_0 + Nu(n_0) + 2\pi N\rho \int_d^\infty dR R^2 g_0(R) \phi(R; n_0). \quad (6)$$

$F_0$  now refers to a reference fluid of hard spheres whose number density is equal to that of the true fluid i.e.  $\rho = N/V$ .  $g_0(R)$  is the radial distribution function of the hard-sphere reference fluid. In their work on simple classical liquids, Mansoori and Canfield suggested using the diameter  $d$  as a variational parameter to minimize the RHS of the analogue of equation (6). They then used the minimum value of this quantity as a measure of the free energy of the true system. Clearly the same procedure can easily be carried through for the liquid metal since the term  $Nu(n_0)$  is a constant independent of  $d$ . The resultant estimate of the free energy satisfies the condition

$$\left( \frac{\partial F}{\partial d} \right)_{V, T} = 0$$

or alternatively

$$\left( \frac{\partial F}{\partial \eta} \right)_{V, T} = 0 \quad (7)$$

where  $\eta = \pi d^3 \rho / 6$  is the packing fraction of the effective hard spheres. The entropy is

given by

$$\begin{aligned} S &= - \left( \frac{\partial F}{\partial T} \right)_v \\ &= - \left( \frac{\partial F}{\partial T} \right)_{v, \eta} - \left( \frac{\partial F}{\partial \eta} \right)_{v, T} \left( \frac{\partial \eta}{\partial T} \right)_v. \end{aligned} \quad (8)$$

The second term of this equation vanishes by equation (7) and since the last term of equation (6) contains no temperature dependence other than that implicit in  $\eta$ , the entropy in this scheme reduces to

$$S_{\text{MC}} = - \left( \frac{\partial F_0}{\partial T} \right)_{v, \eta}. \quad (9)$$

This is just the entropy of the hard-sphere fluid in which the appropriate diameter has been fixed via equation (7). Once the pair potential has been specified, all that is required to evaluate the entropy is information about the hard-sphere system.

In this analysis we have ignored any contribution to the entropy which might arise from the free energy of the conduction electron distribution. For the simple metals which we consider, such contributions are expected to be very small compared with the ionic terms (e.g. Edwards and Jarzynski).

## 2.2. The WCA approach

Weeks *et al* (1971) have developed an alternative perturbation theory which stresses the role played by the repulsive force part of the interatomic potential. In their approach they separate the potential into a part which gives rise to repulsive forces and a remainder which contains all the attractive forces. For the liquid metal such a division is complicated by the long-range Friedel oscillations in the effective pair potential. However these are not expected to be significant so we simply write

$$\phi(R; n_0) = \phi_0(R; n_0) + \phi_1(R; n_0)$$

where

$$\begin{aligned} \phi_0(R; n_0) &= \phi(R; n_0) - \phi_{\min} & R \leq R_{\min} \\ &0 & R > R_{\min} \end{aligned}$$

and

$$\begin{aligned} \phi_1(R; n_0) &= \phi_{\min} & R \leq R_{\min} \\ &\phi(R; n_0) & R > R_{\min}. \end{aligned} \quad (10)$$

$R_{\min}$  is the position of the first minimum in the pair potential and  $\phi_{\min}$  is the value of the potential at that point. We consider the test interaction

$$\Phi^T = \frac{1}{2} \sum_{i \neq j} (\phi_0(R_{ij}; n_0) + \lambda \phi_1(R_{ij}; n_0)) + \lambda N u(n_0) \quad (11)$$

where  $\lambda$  is a constant:  $0 \leq \lambda \leq 1$ . By manipulation of the canonical partition function, the free energy of the true system (corresponding to the interaction of equation (2)) takes

the form:

$$F = F_0 + \frac{\int_0^1 d\lambda \int \dots \int \exp(-\beta\Phi^T) [\frac{1}{2} \sum_{i \neq j} \phi_1(R_{ij}; n_0) + Nu(n_0)] d\{N\}}{\int \dots \int \exp(-\beta\Phi^T) d\{N\}} \quad (12)$$

where  $\beta = 1/k_B T$  and  $F_0$  is the free energy of the reference system of density  $\rho$  in which particles interact via the potential  $\phi_0(R; n_0)$ . This expression simplifies to

$$F = F_0 + Nu(n_0) + \frac{N\rho}{2} \int_0^1 d\lambda \int d\mathbf{R} g(R; \lambda) \phi_1(R; n_0) \quad (13)$$

where  $g(R; \lambda)$  is the radial distribution function in the test system. So far this analysis is exact. Following WCA we obtain after some manipulation

$$\begin{aligned} F = F_0 + Nu(n_0) + \frac{N}{2} \rho \hat{\phi}_1(0) + \frac{N}{2(2\pi)^3} \int d\mathbf{q} \hat{h}_0(q) \hat{\phi}_1(q) \\ + \frac{N}{2(2\pi)^3} \int_0^1 d\lambda \int d\mathbf{q} (\hat{h}(q; \lambda) - \hat{h}_0(q)) \hat{\phi}_1(q) \end{aligned} \quad (14)$$

where  $h(R) = g(R) - 1$  and  $h_0$  refers to the reference system. The appropriate transforms are defined by

$$\begin{aligned} \hat{\phi}_1(q) &= \int d\mathbf{R} \exp(-i\mathbf{q} \cdot \mathbf{R}) \phi_1(R; n_0) \\ \hat{h}(q) &= \rho \int d\mathbf{R} \exp(-i\mathbf{q} \cdot \mathbf{R}) h(R). \end{aligned}$$

The liquid structure factor  $a(q)$  is given by

$$a(q) = \hat{h}(q) + 1. \quad (15)$$

The essential hypothesis of the WCA treatment is that for a *dense* fluid the behaviour of  $\hat{h}(q)$  even at fairly small wavevectors,  $q$ , should be determined by the repulsive force part of the pairwise interaction. This is simply an assertion that the density correlations in the fluid are almost entirely due to excluded volume effects—provided the average density is large enough. WCA suggest that  $\rho\sigma^3$  should be  $\geq 0.65$  where  $\sigma$  is the position of the first zero of the pair potential. For liquid metals near their melting points  $\rho\sigma^3$  is typically  $\sim 0.95$ .

If we make use of the above hypothesis we can argue that  $\hat{h}(q; \lambda) \approx \hat{h}_0(q)$  (except perhaps at very low values of  $q$ ) and set the last term of equation (14) equal to zero. The free energy then reduces to

$$F \approx F_0 + Nu(n_0) + 2\pi N\rho \int dR R^2 g_0(R) \phi_1(R; n_0). \quad (16)$$

Although this result is identical in form to that of equation (6), the physical content is somewhat different.  $F_0$  and  $g_0(R)$  now refer to a reference fluid in which the interatomic potential is  $\phi_0(R; n_0)$  and *not* the hard-sphere potential which enters directly into the variational method. Further approximations are required in order to express the WCA reference functions in terms of appropriate hard-sphere quantities. Anderson *et al* (1971) have treated this problem by expanding the free energy of the reference system about that of a hard-sphere fluid in a type of cluster expansion. The expansion parameter is the

so-called 'blip function'  $B(R)$  which is defined as

$$B(R) = y_{\text{hs}}(R) [\exp(-\beta\phi_0(R; n_0)) - \exp(-\beta\phi_{\text{hs}}(R))] \quad (17)$$

where

$$y_{\text{hs}}(R) = \exp(\beta\phi_{\text{hs}}(R))g_{\text{hs}}(R)$$

and  $\phi_{\text{hs}}(R)$  is the hard sphere potential and  $g_{\text{hs}}(R)$  is the corresponding radial distribution function. The blip function is only finite for  $R$  close to  $d$ , the diameter of the hard spheres. If the range of  $B(R)$  is denoted by  $\xi d$  it is clear that  $\xi$  depends on the softness of the repulsive potential  $\phi_0$  but, in general,  $\xi \ll 1$ . Anderson *et al* (1971) showed that

$$F_0 = F_{\text{hs}} - \frac{N\rho}{2} k_B T \int d\mathbf{R} B(R) + \text{terms of higher order in } B. \quad (18)$$

It is therefore natural to choose the effective hard-sphere diameter  $d$  such that

$$\int d\mathbf{R} B(R) = 0. \quad (19)$$

For any realistic repulsive potential,  $d$  is a decreasing function of temperature and decreases slowly with increasing density at constant temperature. The free energy obtained with the prescription of equation (19) has the form

$$F_0 = F_{\text{hs}}(1 + O(\xi^4)). \quad (20)$$

It can also be shown that

$$g_0(R) = y_{\text{hs}}(R) \exp[-\beta\phi_0(R; n_0)](1 + O(\xi^2)) \quad (21)$$

so provided we have the hard-sphere quantities  $F_{\text{hs}}$  and  $y_{\text{hs}}(R)$  we have a straightforward scheme for determining both the free energy of the reference system and its radial distribution function. Fourier transforming equation (21) and ignoring the terms  $O(\xi^2)$  we obtain the structure factor for the reference system

$$a_0(q) = a_{\text{hs}}(q) + \rho \int d\mathbf{R} \exp(-i\mathbf{q} \cdot \mathbf{R}) B(R) \quad (22)$$

where  $a_{\text{hs}}(q)$  is the structure factor of the hard-sphere system.

Our final expression for the free energy of the liquid metal in the WCA theory is

$$F = F_{\text{hs}} + Nu(n_0) + F_A \quad (23)$$

where

$$F_A = 2\pi N\rho \int d\mathbf{R} R^2 y_{\text{hs}}(R) \exp[-\beta\phi_0(R; n_0)] \phi_1(R; n_0).$$

$F_A$  is the contribution due to the attractive part of the effective pair potential. The corresponding result for the entropy is

$$S_{\text{WCA}} = -\left(\frac{\partial F_{\text{hs}}}{\partial T}\right)_{V, \eta} - \left(\frac{\partial F_{\text{hs}}}{\partial \eta}\right)_{V, T} \left(\frac{\partial \eta}{\partial T}\right)_V - \left(\frac{\partial F_A}{\partial T}\right)_V \quad (24)$$

which appears somewhat more complex than the result from the variational treatment.



### 2.3. The properties of the hard sphere fluid

The analytic form suggested by Carnahan and Starling (1969) is particularly convenient for describing the free energy of the hard-sphere system. It is designed to fit the results of machine calculations and can be written as

$$F_{\text{hs}} = F_i + Nk_{\text{B}}Tf_{\text{cs}}(\eta)$$

with

$$f_{\text{cs}}(\eta) = (4\eta - 3\eta^2)/(1 - \eta)^2 \quad (25)$$

and  $F_i$  is the free energy of the ideal gas of the same density and temperature. With this form equation (9) for the entropy in the variational scheme yields

$$S_{\text{MC}} = S_i - Nk_{\text{B}}f_{\text{cs}}(\eta) \quad (26)$$

while

$$S_{\text{WCA}} = S_i - Nk_{\text{B}}f_{\text{cs}}(\eta) - Nk_{\text{B}}T \frac{2(2 - \eta)}{(1 - \eta)^3} \left( \frac{\partial \eta}{\partial T} \right)_v - \left( \frac{\partial F_{\text{A}}}{\partial T} \right)_v \quad (27)$$

and  $S_i$  is the entropy of the ideal gas.

The function  $y_{\text{hs}}(R)$  is readily available from the Percus–Yevick treatment of the hard-sphere system but we have chosen to use the tabulated results of Watts and Henderson (1969) for this quantity and for  $g_{\text{hs}}(R)$ .

## 3. The effective pairwise potentials

### 3.1. Formulation of the pair potential

The procedure for calculating the effective pairwise potentials of equation (2) has been well documented. Here we merely quote the relevant results. If the bare electron–ion pseudopotential is assumed to be local i.e.

$$\langle \mathbf{K} + \mathbf{q} | v_{\text{ps}} | \mathbf{K} \rangle = \int d\mathbf{r} v_{\text{ps}}(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) = v_{\text{ps}}(q) \quad (28)$$

then

$$\phi(R; n_0) = \frac{1}{(2\pi)^3} \int d\mathbf{q} \exp(i\mathbf{q} \cdot \mathbf{R}) \phi(q; n_0) \quad (29)$$

where

$$\phi(q; n_0) = \frac{4\pi Z^2}{q^2} (1 - F_{\text{N}}(q)).$$

$F_{\text{N}}(q)$  is the normalized energy wavenumber characteristic:

$$F_{\text{N}}(q) = -\frac{q^4}{16\pi^2 Z^2} \left( \frac{1}{\epsilon(q)} - 1 \right) |v_{\text{ps}}(q)|^2 \quad (30)$$

and the dielectric function  $\epsilon(q)$  is given by the usual result:

$$\frac{1}{\epsilon(q)} = 1 + \frac{4\pi\chi_0(q)}{q^2[1 - \chi_0(q)(4\pi/q^2)(1 - f(q))]} \quad (31)$$

$\chi_0(q)$  is the response function of the non-interacting homogeneous electron gas and  $f(q)$  is the exchange and correlation correction term. The dependence of the pair potential on the average conduction electron density  $n_0$  arises from the dependence of both  $\chi_0(q)$  and  $f(q)$  on this quantity.

If the bare pseudopotential is non-local the physical content of  $\phi(R; n_0)$  remains the same but the above analysis becomes much more complicated. Shaw (1970 and earlier references contained therein) has shown how to derive  $F_N(q)$  for his non-local optimized model potential (OMP). Once  $F_N(q)$  is determined, the effective pair potential is given by equation (29) but with  $Z$  replaced by  $Z^* = Z - \rho_d$  where  $\rho_d$  is the total depletion hole charge. The use of a model wavefunction instead of the real wavefunction in the calculation of the conduction electron charge density in a metal corresponds to a depletion of the electron density in the ion cores. The actual distribution of this depletion hole charge depends on a knowledge of the real wavefunction and only the *total* depletion charge is available from model potential theory (Shaw and Harrison 1967). Shaw assumed that the depletion hole charge was localized at the nuclei ( $\delta$  function distribution) while later Appapillai and Heine (1972) assumed it was distributed uniformly through some ionic sphere. The normalized energy wavenumber characteristic includes information about the distribution of depletion hole charge.

Further complications arise in the non-local treatment when it is recognised that the diagonal term  $\langle \mathbf{K} | v_{ps} | \mathbf{K} \rangle$  which enters the perturbation expansion for the one-electron eigenvalues now has a dependence on the wavevector  $\mathbf{K}$ . Consequently this term cannot be fully absorbed into the non-structural part of the total energy. Shaw (1969) has treated this problem by introducing two  $\mathbf{K}$  dependent effective masses and Appapillai and Williams (1973) have carried through his analysis to obtain the modified  $F_N(q)$ . If the effective masses  $m_E(\mathbf{K})$  and  $m_K$  are slowly varying functions of  $\mathbf{K}$  they can be taken as constant and set equal to the values calculated at the Fermi energy. The effective pair potential is then again given by equation (29) but now  $Z$  is replaced by  $Z^* = Z - \rho_d/m_E$ . We note that the depletion hole charge and the effective masses all depend on the average electron density.

### 3.2. Specification of pseudopotentials and choice of $f(q)$

For our calculations based on Shaw's model potentials we have only considered those metals in which there are no d bands in the close vicinity of the conduction band. Under these circumstances the process of fitting the bare-ion parameters  $A_i(E)$  to spectral term values and interpolating to conduction band energies should be reasonable (e.g. Evans 1970) and we have used the values of  $A_i$  listed by Appapillai and Heine (1972). Three different choices for the distribution of depletion hole charge have been considered. These are: (a) no depletion charge; (b) the  $\delta$  function distribution; and (c) the uniform distribution.

We have also examined three different local pseudopotentials. The first of these is the Ashcroft (1966) empty core (ECM) model potential:

$$\begin{aligned} v_{ps}(r) &= 0 & r < r_c \\ &= -Z/r & r \geq r_c \end{aligned} \quad (32)$$

where the parameter  $r_c$  is treated as an adjustable constant. The second is the modified point ion model (MPIM) due to Harrison (1966)

$$v_{ps}(r) = -\frac{Z}{r} + \frac{\gamma}{8\pi\alpha^3} \exp(-r/\alpha). \quad (33)$$

The parameters  $\alpha$  and  $\gamma$  are usually fitted to experimental data of one kind or another. Our third choice is a local version of the Heine–Abarenkov model potential. This (LHA) model was proposed by Popović *et al* (1974) in their study of the energetics of solid metals:

$$v_{ps}(r) = \begin{cases} -DZ/r_m & r < r_m \\ -Z/r & r \geq r_m \end{cases} \quad (34)$$

The two parameters  $D$  and  $r_m$  are adjustable.

There are many different forms for  $f(q)$ , the exchange and correlation correction, in the literature. We have considered three specific choices for this function, those of Kleinman (1967), Singwi *et al* (1970) (SSTL) and Vashista and Singwi (1972). Of the three, the self-consistent treatment of Vashista and Singwi (VS) probably represents the most accurate form which is presently easily available. The importance of  $f(q)$  in determining the shape of the effective pair potential has been discussed at length by Shaw and Heine (1972).

All of our calculations were performed at the density of the appropriate liquid metal near its melting point. More details can be obtained from the authors.

### 3.3. Results

In figure 1 we plot the pairwise potentials of liquid Na calculated using the three different local pseudopotentials referred to above. For the ECM we have chosen  $r_c = 1.7$  au while for the MPIM we have taken  $\alpha = 0.25$  and  $\gamma = 37$ . The latter values were obtained by

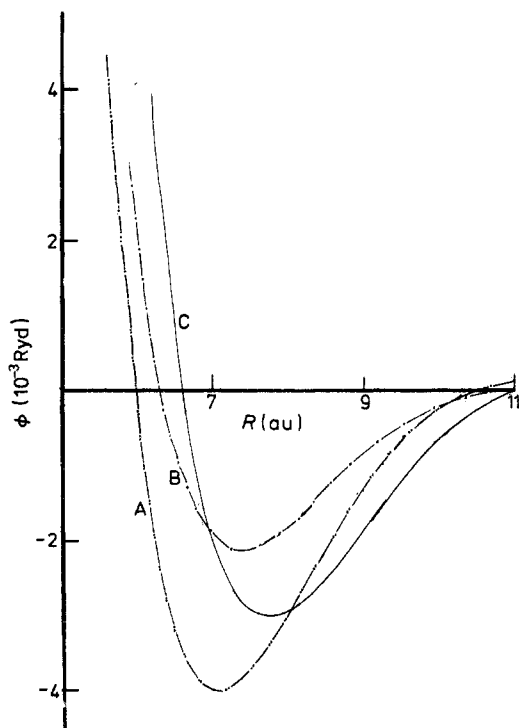


Figure 1. Pair potentials for liquid Na calculated from local model potentials: Curve A (---) ECM; Curve B (-.-.-) MPIM; Curve C (—) LHA. The Vashista and Singwi form of  $f(q)$  has been used in each calculation.

Wallace (1968) by fitting to the measured binding energy and compressibility of crystalline Na at temperature  $T = 0$  K. In the LHA model we have set  $r_m = 1.0133/K_F$  and  $D = 0.3079$  which are the values obtained by Popović *et al* (1974) by fitting to the pressure and compressibility again at  $T = 0$  K. It is clear from the figure that the different local pseudopotentials lead to very different pair potentials, especially in the region of the first minima. Calculations on other metals exhibit essentially the same features.

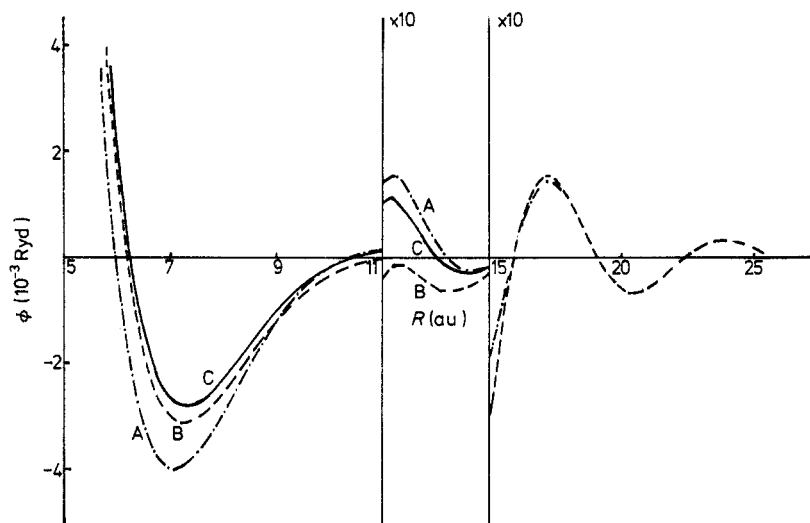


Figure 2. Pair potentials for liquid Na calculated from the ECM with  $r_c = 1.7$  au and different forms of exchange and correlation correction  $f(q)$ : curve A (chain)  $f(q)$  from Vashista and Singwi; curve B (broken) from Kleinman; curve C (full) from Singwi *et al*.

Figures 2 and 3 indicate how the depth of the first minimum is strongly dependent on the form of  $f(q)$ . This sensitivity is especially pronounced in the dense polyvalent

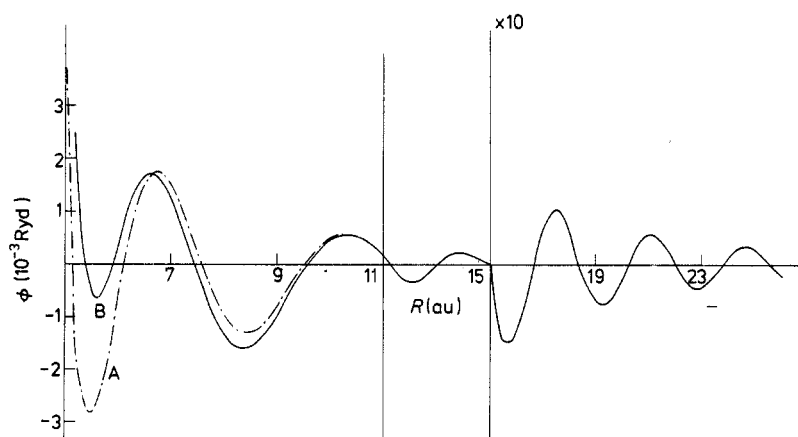


Figure 3. Pair potentials for liquid Al calculated from the ECM with  $r_c = 1.2$  au and different forms of exchange and correlation correction: curve A (chain) Vashista and Singwi; curve B (full) Kleinman.

metals such as Al. In figure 4 the density dependence of the pairwise potential of Al is exhibited. For metals with lower melting points, the difference between the pair potential in the low-temperature solid and in the liquid state is, of course, much less significant.

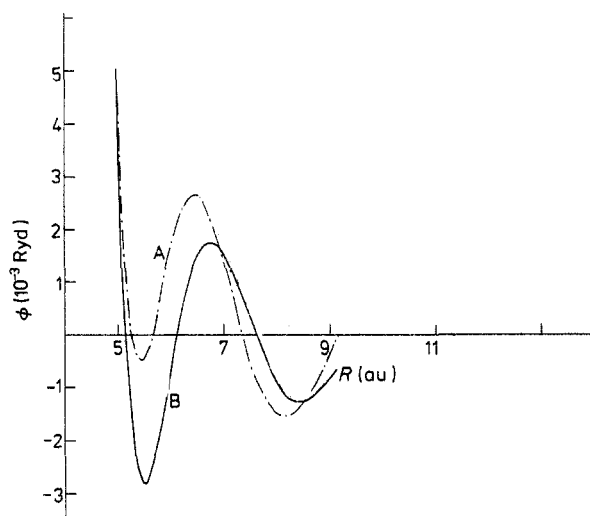


Figure 4. Pair potentials for Al calculated at densities corresponding to the low-temperature solid: curve A (chain), and the liquid; curve B (full). The ECM has been used with  $r_c = 1.2$  au and the Vashista and Singwi form of  $f(q)$ .

Figures 5, 6 and 7 refer to calculations based on Shaw's OMP for liquid Na and demonstrate, in particular, how the repulsive part of the pair potential depends on the assumed

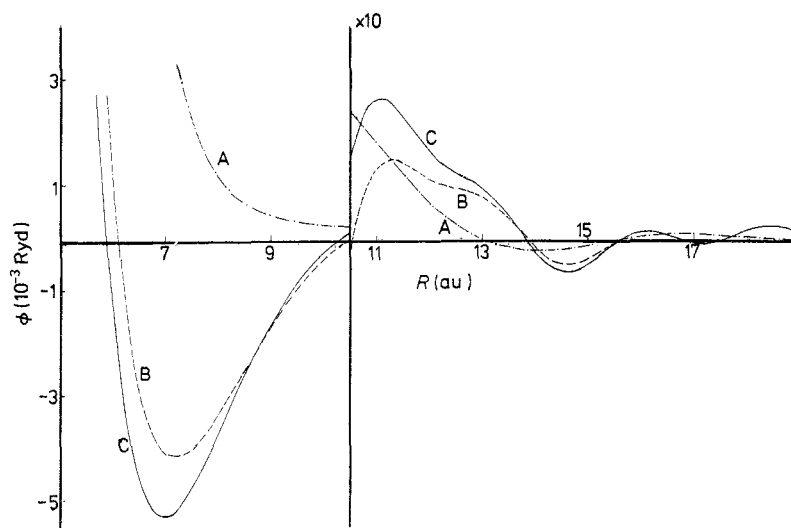


Figure 5. Pair potentials calculated for liquid Na from Shaw's OMP. The depletion hole charge is taken to be zero: Curve A (chain) Hartree approximation ( $f(q) = 0$ ); curve B (broken) includes the Vashista and Singwi  $f(q)$  but no effective-mass correction; curve C (full) includes the Vashista and Singwi  $f(q)$  and the effective-mass correction.

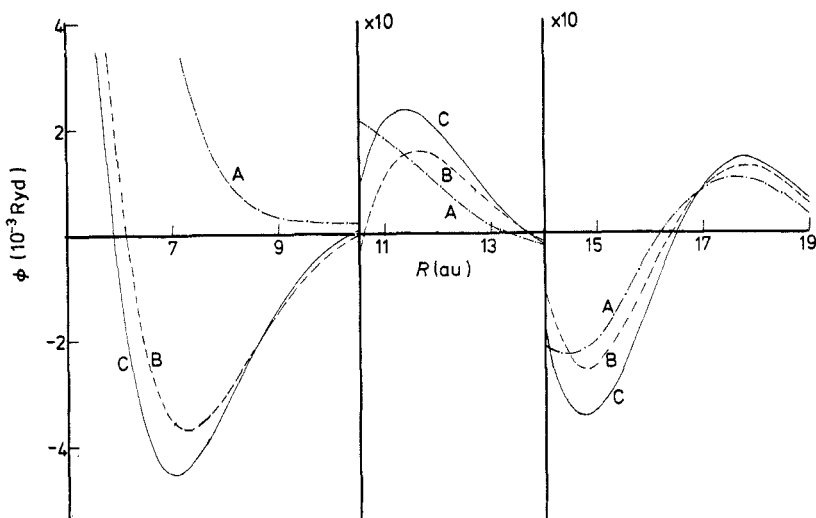


Figure 6. Pair potentials calculated for liquid Na from Shaw's OMP. A  $\delta$ -function distribution of depletion hole charge is assumed. The labelling follows that of figure 5.

distribution of depletion hole charge and on whether or not effective-mass corrections are applied. The inclusion of the latter always lowers the first minimum of the pair potential. Ballentine (1968) has shown that the various contributions to the structure dependent energy which involve  $\rho_d$  cancel to first order in this quantity and he argued that second-order contributions could be neglected because they are small in comparison with other uncertainties in the problem. Our calculations support his argument. Changing the distribution of depletion hole charge from the  $\delta$  function to the uniform distribution brings about variations in  $\phi(R; n_0)$  which are of the same order as the differences between pair potentials calculated with the  $\delta$  function distribution and with no depletion hole

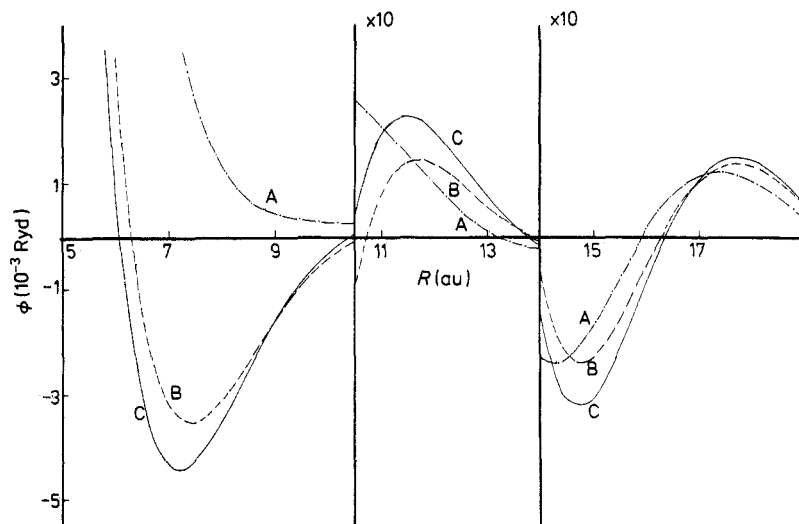
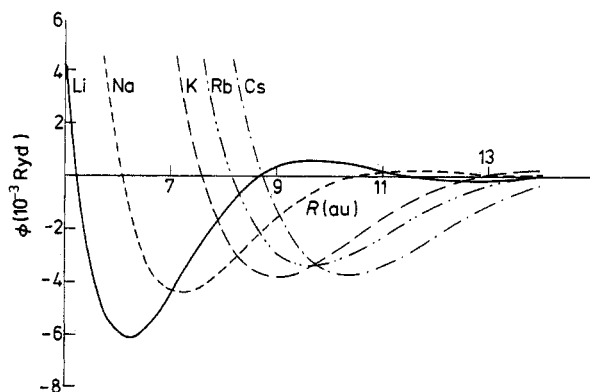


Figure 7. Pair potentials calculated for liquid Na from Shaw's OMP. A uniform spherical distribution of depletion hole charge is assumed. The labelling follows that of figure 5.

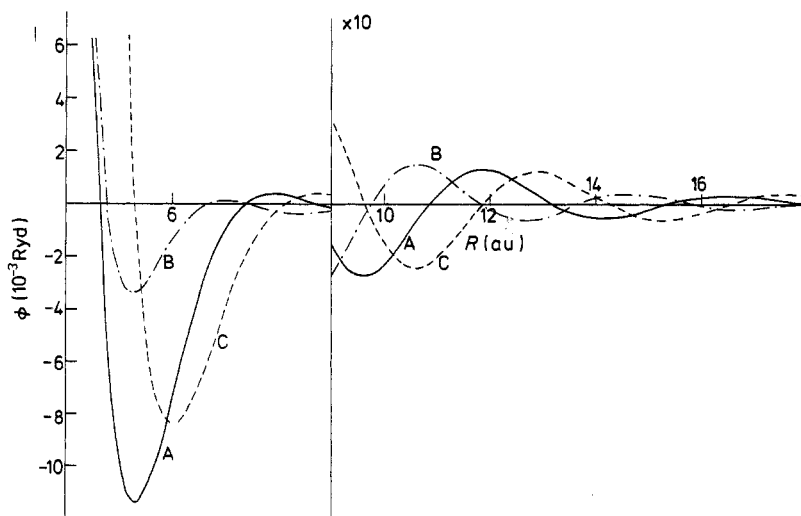
charge at all. In all of the calculations described hereafter, with the exception of Al, the depletion hole charge has been included and assumed to be distributed uniformly through an ionic sphere. For Al, a  $\delta$  function distribution has been assumed. Effective-mass corrections are included.

In figure 8 we present the calculated pair potentials for the alkali metals. These results can be compared directly with those of Rao (1975) who performed what are



**Figure 8.** Pair potentials calculated for the liquid alkali metals from Shaw's OMP. The Vashista and Singwi form of  $f(q)$  has been used and the calculations include effective-mass corrections. A uniform spherical distribution of depletion hole charge is assumed in each case.

essentially equivalent calculations for the solid alkalis. On proceeding down this column of the periodic table the minimum of the pairwise potential shifts progressively to large distances reflecting the increasing 'size' of the atoms. Figures 9 and 10 show the corresponding results for the liquid divalent and trivalent metals. There are no obvious trends



**Figure 9.** Pair potentials calculated for some liquid divalent metals from Shaw's OMP. The details are the same as for figure 8: curve A (full) Cd; curve B (chain) Zn; curve C (broken) Mg.

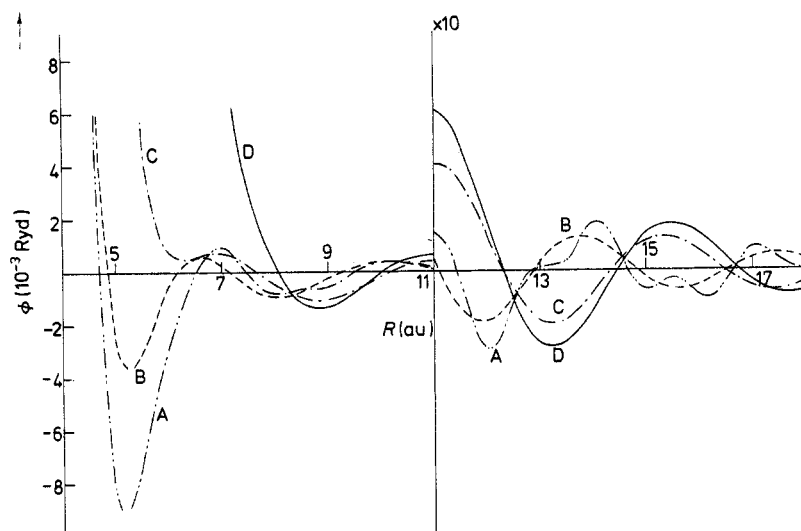


Figure 10. Pair potentials calculated for some liquid trivalent metals from Shaw's OMP. The details are the same as for figure 8 except for Al where a  $\delta$ -function distribution of depletion hole charge is assumed: curve A (---) Al; curve B (-·-·-) Ga; curve C (—) In; curve D (—) Tl.

to be discerned in these groups. In figure 11 we have compared the pair potential of liquid Pb calculated from Shaw's OMP with that obtained from Ashcroft's ECM. These differ enormously. The corresponding results for liquid Sn are shown in figure 12.

It is encouraging that the results for Na indicate that the pair potential calculated from the ECM is in fair agreement with that obtained from the non-local OMP. Furthermore the value of  $r_c = 1.7$  is well accepted for this metal since it seems to give a reasonable

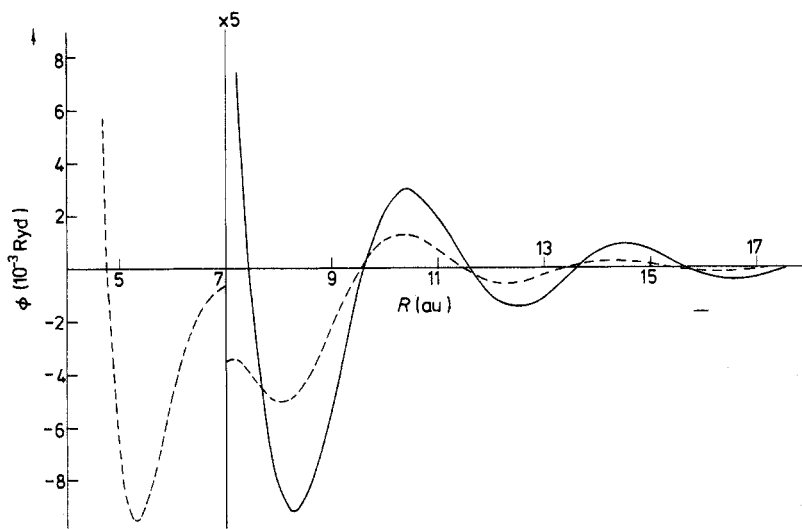


Figure 11. Pair potentials calculated for liquid Pb. The full curve is based on Shaw's OMP and includes effective-mass corrections and assumes a uniform spherical distribution of depletion hole charge. The broken curve is based on the ECM with  $r_c = 1.03$  au. The Vashista and Singwi form of  $f(q)$  is used in each case.



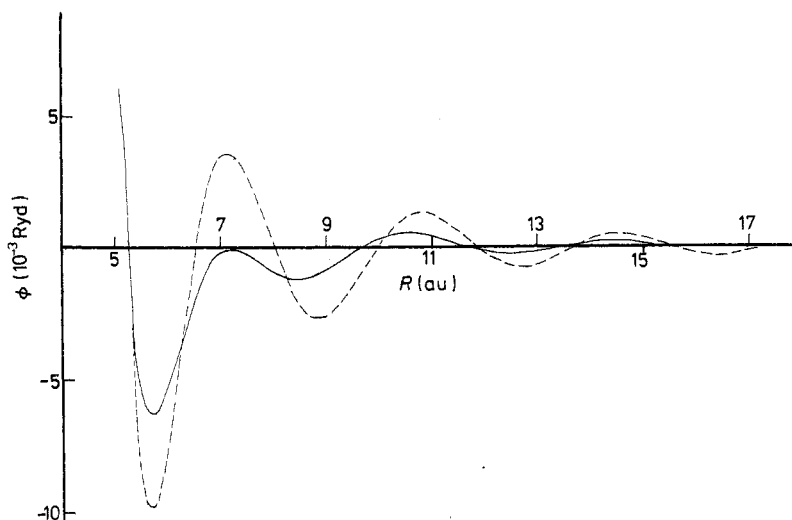


Figure 12. Pair potentials calculated for liquid Sn. The details are the same as for figure 11. In the ECM  $r_c = 1.30$  au.

account of many electronic and structural properties. For the other alkali metals it is probable that judicious selections of  $r_c$  will also produce pair potentials close to those presented in figure 8, and still yield sensible estimates of transport properties etc (see e.g. Cohen and Heine 1970). This does not appear too likely for metals of higher valence. Even for Al where we might expect the ECM to be adequate, the calculated ECM potential of figure 4 differs considerably from the OMP result of figure 10. The other local pseudopotentials which have been used in studies of energetics clearly predict pair potentials which are far removed from those obtained from the OMP (see figures 1, 5, 6 and 7).

For completeness we should mention here other work based on the Shaw OMP. Rao (1975) and Shyu *et al* (1971) have calculated  $\phi(R; n_0)$  for crystalline metals. The latter authors used the SSTL form of  $f(q)$  while Rao considered several different  $f(q)$ . Effective-mass contributions were not taken into account in these papers. Appapillai and Heine (1972) (see also Appapillai and Williams 1973) have calculated their pair potentials using the Toigo and Woodruff (1970)  $f(q)$ . Their calculations, however, appear to contain some programming errors. To our knowledge only Edwards and Jarzynski (1972) and very recently Hasegawa (1976) have calculated pair potentials for liquid metals using the OMP. Again effective masses were not included by these authors. Edwards and Jarzynski used a form of  $f(q)$  which leads to pair potentials that are, in many cases, an order of magnitude deeper at their first minima than the potentials presented above. The work of Hasegawa, and that of Rao can be considered complementary to our present study.

#### 4. Calculations and results for the entropies of liquid metals

In the variational calculation of the entropy, the effective hard-sphere diameter  $d$  is fixed by equation (7). The RHS of equation (6) was evaluated for various values of  $d$  and the minimum determined numerically. Although we did not experience any serious convergence difficulties with the integral, it is probably more efficient to carry out this

procedure in reciprocal space (Jones 1973). The corresponding values of  $d$  and packing fraction  $\eta$  are listed in table 1. The pair potentials which were used are those shown in figures 8–12. For Na we examined several different pairwise potentials. Once  $\eta$  is fixed

**Table 1.** Packing fractions  $\eta$ , effective hard-sphere diameters  $d$ , and excess entropies  $S_E$  calculated by the variational method†. For Na three different forms of the depletion hole charge distribution have been considered as well as the Ashcroft (ECM) model potential (see text).  $T$  denotes the temperature. The experimental values for the excess entropy were taken from Hultgren *et al* (1963).

Metal	$T$ (K)	$d$ (au)	$\eta$	$-S_E/k_B$	$-S_E/k_B$ (Experiment)
Na (ECM)		6.23	0.45	3.94	
Na (No dep. hole)	373	6.23	0.45	3.94	3.45
Na ( $\delta$ -fn dep. hole)		6.31	0.47	4.33	
Na (Uniform dep. hole)		6.35	0.48	4.54	
Cs	303	9.14	0.48	4.54	3.56
Rb	313	8.35	0.47	4.33	3.63
K	338	7.88	0.48	4.54	3.45
Cd	623	5.00	0.42	3.42	4.00
Mg	948	5.41	0.47	4.33	3.29
Zn	723	4.64	0.47	4.33	3.78
Ga	353	4.83	0.46	4.13	4.62
Al	1000	4.77	0.45	3.94	3.49
Sn	523	5.31	0.41	3.26	4.08

† The electronic contribution will reduce the calculated values of  $-S_E/k_B$  by about 0.05 for Na and about 0.11 for Al. These estimates are calculated for the non-interacting electron gas.

in this way the excess entropy per ion  $S_E$  defined by

$$S_E = (S - S_i)/N \quad (35)$$

can easily be obtained from equation (26). The values of  $S_E$  calculated in this scheme are compared with experiment in table 1 and the overall level of agreement is reasonable. However it is significant that, in the alkali metals,  $S_E$  (calculated) is considerably smaller than  $S_E$  (experimental). We will return to this point later.

For all of the metals listed in table 1 the calculated packing fractions are found to be close to 0.45. It is well known that hard-sphere structure factors evaluated with this choice of  $\eta$  are in qualitative agreement with experiment for many simple metals. In the remaining metals i.e. Li, In, Tl and Pb, the values of  $\eta$  calculated from the OMP are  $>0.5$  and lead to unphysical entropies. This implies that in these metals the effective hard-sphere diameters are too large and by inference, the repulsive part of the pair potential extends too far. One could almost have foreseen such behaviour for In, Tl and Pb from figures 10 and 11.

The entropy was obtained in the WCA scheme by evaluating the free energy of equation (23) at different temperatures with fixed density and taking the derivatives numerically. The appropriate packing fractions and the various contributions to the excess entropies are listed in table 2. For Li, In, Tl and Pb the calculated packing fractions are again unrealistically large and yield poor values for the excess entropy.

The values of  $\eta$  calculated in the WCA treatment are close to those obtained in the variational scheme. The WCA values of the excess entropy are, with the exceptions of Cd, Ga and Sn, in better agreement with experiment than the results of the variational

**Table 2.** Packing fractions  $\eta$ , effective hard-sphere diameters  $d$  and various contributions to the excess entropies  $S_E$  calculated in the WCA scheme.  $S_1 = k_B f_{cs}(\eta)$ ;  $S_2 = k_B T[2(2 - \eta)/(1 - \eta)^3](\partial\eta/\partial T)_V$ ;  $S_3 = (1/N)(\partial F_A/\partial T)_V$  and  $-S_E = S_1 + S_2 + S_3$  (see equation 27). The temperatures are the same as those listed in table 1.

Metal	$d$ (au)	$\eta$	$S_1/k_B$	$S_2/k_B$	$S_3/k_B$	$-S_E/k_B$	$-S_E/k_B$ (Experiment)
Na (ECM)	6.229	0.455	4.03	-1.32	0.72	3.43	
Na (No dep. hole)	6.205	0.449	3.93	-1.20	0.62	3.35	
Na ( $\delta$ -fn dep. hole)	6.258	0.461	4.09	-1.20	0.72	3.61	3.45
Na (Uniform dep. hole)	6.356	0.483	4.61	-1.48	0.70	3.83	
Cs	9.147	0.483	4.60	-1.46	0.64	3.78	3.56
Rb	8.464	0.488	4.72	-1.53	0.54	3.73	3.63
K	7.909	0.487	4.70	-1.55	0.69	3.84	3.45
Cd	4.904	0.393	3.01	-0.59	0.40	2.82	4.00
Mg	5.412	0.473	4.40	-1.25	0.53	3.68	3.29
Zn	4.719	0.494	4.86	-1.38	0.32	3.80	3.78
Ga	4.941	0.492	4.82	-0.88	0.11	4.05	4.62
Al	4.804	0.457	4.08	-0.81	0.15	3.42	3.49
Sn	5.374	0.425	3.50	-0.52	0.04	3.02	4.08

method. It is significant that the hard-sphere contribution  $k_B f_{cs}(\eta)$  in equation (27) for  $-S_E$  is reduced by the sum of the terms in  $(\partial\eta/\partial T)_V$  and  $(\partial F_A/\partial T)_V$ . These reductions which are typically 12–20% are absent in the variational treatment (equation 26). The calculated values of  $S_E$  for the alkali metals are in close agreement with experiment. By varying the form of the depletion hole charge distribution the calculated  $S_E$  straddles the experimental value in the case of Na. The ECM also yields a realistic value for the packing

**Table 3.** The specific heat  $C_V$  calculated in the WCA scheme. The calculations were performed at the temperatures listed in table 1. The experimental values of  $C_V$  were obtained from the equation  $C_p - C_V = (\alpha^2 V_0 T / \chi_T)$  and the expansion coefficients  $\alpha$  were taken from Wilson (1965). The constant pressure values  $C_p$  were obtained from Hultgren *et al* (1963), while experimental values of  $\chi_T$  were taken from the compilation of Waseda and Suzuki (1973). For Mg the compressibility data of McAlister *et al* (1974) were used. The values of  $C_V$  (experiment) obtained in this way are probably accurate to about  $\pm 0.1 k_B$  per atom. The numerical accuracy of our calculated  $C_V$  is about the same. The electronic contribution to  $C_V$  should be added to the listed  $C_V$  (calculated). This can be estimated from the non-interacting electron gas and ranges between about  $0.05 k_B$  per atom for Na to  $0.11 k_B$  per atom for Al.

Metal	$C_V$ (Calculated) $k_B$ per atom	$C_V$ (Experiment) $k_B$ per atom
Na (ECM)	3.4	
Na (No dep. hole)	3.5	
Na ( $\delta$ -fn, dep. hole)	3.5	3.4
Na (Uniform dep. hole)	3.3	
Cs	2.5	3.2
Rb	3.2	3.3
K	3.6	3.4
Cd	2.6	2.8
Mg		3.0
Zn	2.9	3.1
Ga	2.5	3.0
Al		2.7
Sn	2.1	3.2

fraction and a good estimate of the excess entropy in this metal. The other local model potentials i.e. the MPIM and LHA lead to values of  $\eta$  which are far too large (see figure 1) in both the WCA and the variational theories. They predict very poor entropies and non-realistic structure factors.

We have also attempted to calculate the constant volume specific heat  $C_v = T(\partial S/\partial T)_v$  in the WCA scheme and the results are shown in table 3. Since  $C_v$  is the second derivative of the free energy, numerical differentiation leads to inaccuracies and we were unable to obtain stable results for Al and Mg. The level of agreement between theory and experiment is fair for the other metals. We should note that the ideal gas contribution to  $C_v$  is  $\frac{3}{2}k_B$  per atom.

## 5. The liquid structure factors

Although the WCA theory is primarily designed for calculating the free energy and its derivatives, it can be used to study the structure factor or radial distribution function. The structure factor of the repulsive reference system  $a_0(q)$  can be obtained direct from equation (22) once the hard-sphere diameter has been determined. We have used this scheme to calculate  $a_0(q)$  for several metals. For convenience we have used the Percus–Yevick approximation for  $a_{hs}(q)$ . This is known to be quite accurate for wavevectors in the neighbourhood of the first two peaks.

In figure 13 we compare the results obtained by the WCA procedure with the hard-sphere structure factor for liquid Na. The experimental data for this metal are also plotted. The large  $q$  oscillations in  $a_0(q)$  are more damped than those of  $a_{hs}(q)$  and this reflects the softness of the repulsive potential  $\phi_0(R; n_0)$  (see also Schiff 1973). There is

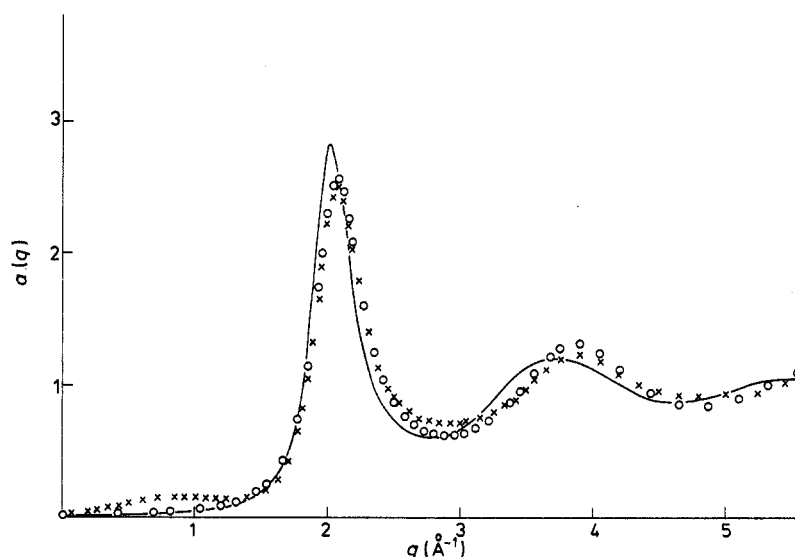


Figure 13. The liquid structure factor of Na calculated from the WCA approach using the pair potential obtained from the ECM with the Vashista and Singwi form of  $f(q)$ . The crosses denote the WCA calculation  $a_0(q)$ ; the open circles denote the Percus–Yevick hard-sphere structure factor and the full curve represents the experimental results of Greenfield *et al* (1971). The calculated packing fraction is 0.454.

some evidence that the experimental results are also damped in this fashion. The WCA procedure leads to spurious behaviour at values of  $q \leq 1.4 \text{ \AA}^{-1}$  and this can also be seen in the earlier work by Wehling *et al* (1972) and Hasegawa and Watabe (1974). The large values of  $a_0(q)$  obtained in this region result from the fairly large range of the blip function  $B(R)$  for this 'soft' Na potential. This can be ascertained from equation (22).

A better test of the WCA approach is to compare its results for  $a_0(q)$  with those obtained from a full machine calculation. In figure 14 we show such a comparison for

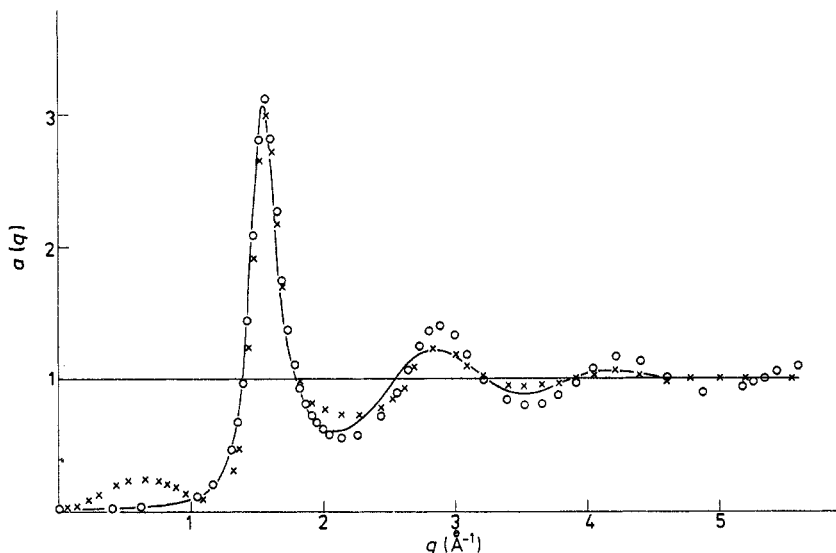


Figure 14. The liquid structure factor of Rb calculated from the WCA approach using the repulsive part of the pair potential of Price (1971). The crosses denote the WCA calculation  $a_0(q)$ , the open circles denote the Percus-Yevick hard-sphere structure factor and the full curve is the result of a molecular dynamics calculation by Rahman (1974) using the same (complete) pair potential. The calculated packing fraction is 0.493.

liquid Rb. Rahman (1974) calculated  $\hat{a}(q)$  from molecular dynamics using the pair potential of Price (1971). Our WCA results for  $a_0(q)$  were calculated from the repulsive part of the same potential. They agree reasonably well with Rahman's for large values of  $q$  and both exhibit weaker oscillations than the corresponding hard-sphere calculation. For small values of  $q$  the WCA treatment again yields spurious behaviour. We have calculated  $a_0(q)$  for liquid Mg and Al and in figures 15 and 16 we compare the WCA results with the experimental data for these metals. The overall level of agreement between theory and experiment is reasonable and the low  $q$  discrepancies are less pronounced than in Na and Rb.

In figure 17 we plot the radial distribution function  $g_0(R)$  calculated by the WCA method for Rb alongside that from Rahman's molecular dynamics calculation. The hard-sphere result is shown for comparison.

It is clear from these figures that the WCA prescription for both  $a(q)$  and  $g(R)$  is much less satisfactory when employed with our calculated liquid-metal pair potentials than when it is used for the Lennard-Jones type of potential (WCA and Anderson *et al* 1971). This does not mean that our initial WCA hypothesis, i.e.  $a(q) \approx a_0(q)$  is incorrect. It is more probable that hard spheres do not constitute a very good starting approximation for the blip function expansion of the reference system in liquid metals since the

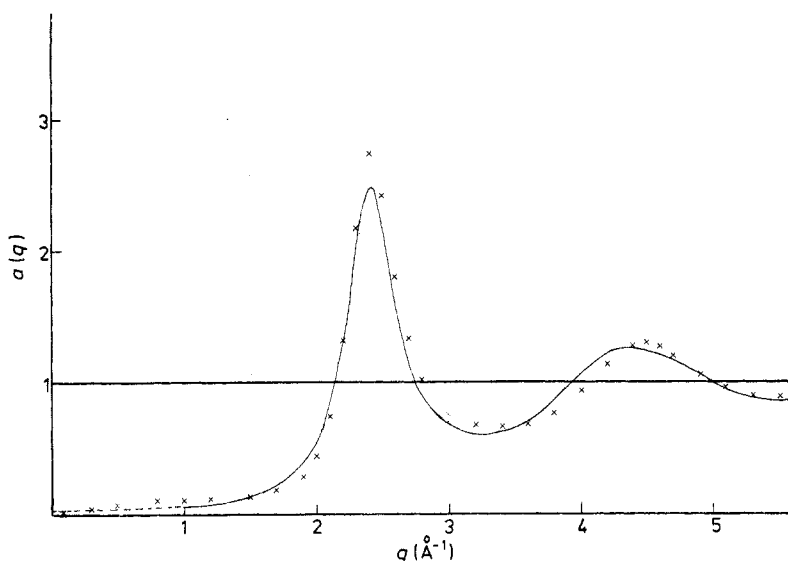


Figure 15. The liquid structure factor of Mg calculated from the WCA approach using the pair potential from Shaw's OMP (figure 9). The crosses denote the WCA calculation  $a_0(q)$  and the full curve represents the experimental results of Woerner *et al* (1965). The calculated packing fraction is 0.473.

quantity  $\xi$  which measures the range of  $B(R)$  is much larger than for the Lennard-Jones potential. An indication of the relative softness of the potentials is given in figure 18, where appropriately normalized repulsive potentials  $\phi_0$  are plotted. All the metallic

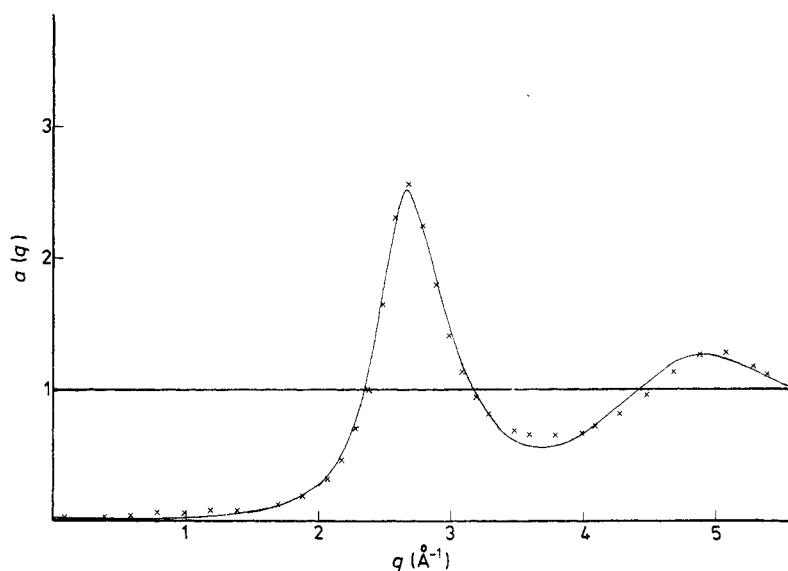


Figure 16. The liquid structure factor of Al calculated from the WCA approach using the pair potential from Shaw's OMP (figure 10). The crosses denote the WCA calculation  $a_0(q)$  and the full curve represents the experimental results of Ruppertsberg and Wehr (1972). The calculated packing fraction is 0.457.

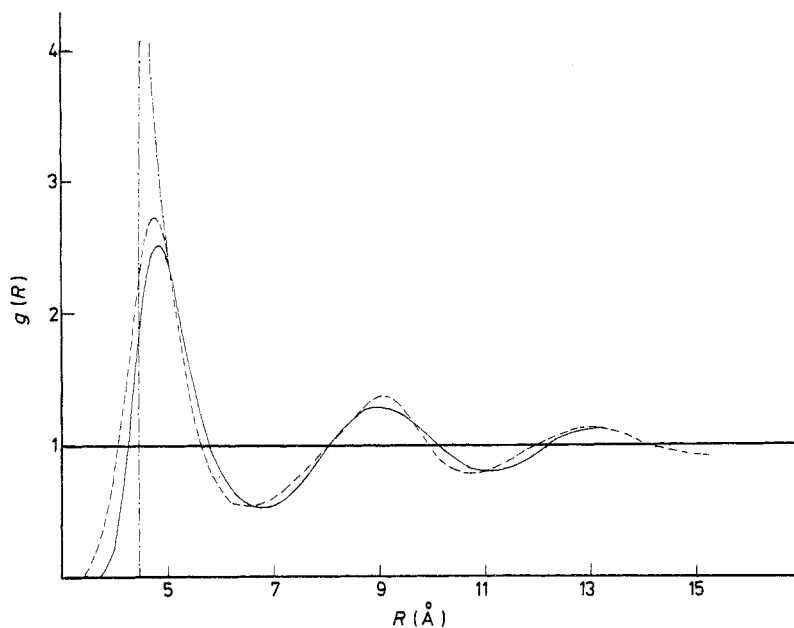


Figure 17. The radial distribution function of liquid Rb: (---) WCA calculation  $g_0(R)$ ; (-.-.-) Percus-Yevick hard-sphere result; (—) molecular dynamics result of Rahman (1974).

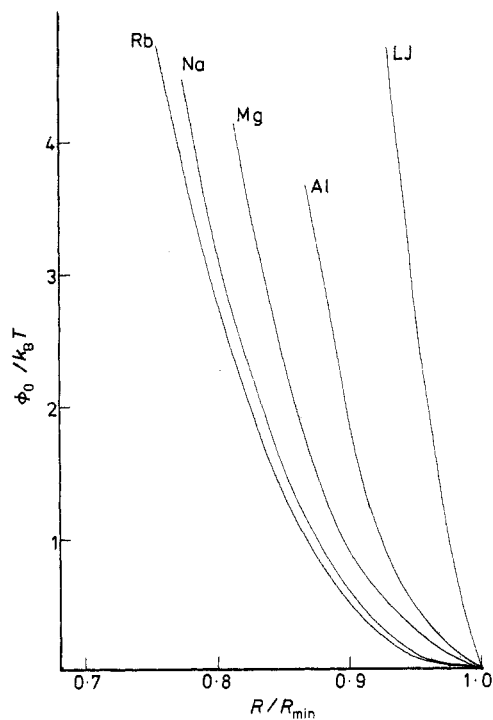


Figure 18. A comparison of the repulsive force part  $\phi_0$  of the pairwise potentials used in the calculations described in figures 13–16.  $R_{\min}$  denotes the position of the first minimum (see equation 10). Curve LJ is calculated for a 'typical' Lennard-Jones 6–12 pair potential.

potentials are considerably softer than a typical Lennard-Jones potential but it is significant that the potentials for Mg and Al are harder than those for the alkalis. This explains why the results for  $a_0(q)$  in figures 15 and 16 are somewhat better than the corresponding results for Na and Rb. The calculated pair potentials for other polyvalent metals are also harder than those for the alkalis.

We should note that the WCA result, equation (20) for the free energy  $F_0$  of the repulsive reference system may still be reasonably accurate though the calculated  $a_0$  or  $g_0$  is poor since the corrections to the former are of a higher order in  $\xi$  than the corrections to the distribution function.

The isothermal compressibility  $\chi_T$  can be obtained from the long-wavelength limit of the liquid structure factor. For a two-component system of ions and conduction electrons charge neutrality (Watabe and Hasegawa 1973, Chihara 1973 and Gray 1973) ensures that

$$\lim_{q \rightarrow 0} a(q) = a(0) = \rho k_B T \chi_T \quad (36)$$

where  $a(q)$  refers to the ion-ion structure factor. If we accept the WCA hypothesis that  $a(q)$  is very close to  $a_0(q)$ , the structure factor of the repulsive reference system, even for small values of  $q$  then we can attempt an approximate evaluation of  $\chi_T$ . It is clear from equations (19) and (22) that the WCA prescription for the effective hard-sphere diameter  $d$  implies

$$a(0) \approx a_0(0) \approx a_{hs}(0) \quad (37)$$

where terms  $O(\xi^2)$  etc have again been ignored, and thus the compressibility of the metal is approximately equal to that of the hard-sphere fluid at the same density and temperature. The latter can be calculated by double differentiation of the Carnahan and Starling result (equation 25) for the free energy and we have

$$a_{hs}(0) = \frac{(1 - \eta)^4}{(1 + 2\eta)^2 + \eta^4 - 4\eta^3} \quad (38)$$

which differs slightly from the well known Percus-Yevick result

$$a_{hs}^{PY}(0) = \frac{(1 - \eta)^4}{(1 + 2\eta)^2} \quad (39)$$

When the WCA prescription is applied to a standard Lennard-Jones 6-12 model of liquid Ar it yields a packing fraction of about 0.46 (Salter and Davis 1975). This gives in equation (38)  $a_{hs}(0) \approx 0.025$  which is much smaller than the value of 0.052 obtained from the measured compressibility. Such a result may indicate that the attractive part of the pair potential plays an important role at  $q = 0$  or, what is more likely, that the Lennard-Jones potential is not a very accurate model potential for liquid Ar. For liquid metals we have further complications because of the softness of the repulsive part of the pair potential. Leaving these aside we have investigated the validity of equation (37) for the simple liquid metals. We have obtained  $a(0)$  using equation (36) and experimental values of the compressibility. These values are compared with those from equation (38) in table 4. The corresponding results obtained from equation (39) are smaller by about 0.002.

For the four listed alkali metals, the experimental values of  $a(0)$  are remarkably constant and are close to our estimates obtained from WCA theory. The latter are, of course, somewhat dependent on the prescription used for the pseudopotential. Of the



polyvalent metals only  $a(0)$  for Mg seems to fit within the hard-sphere description and our model appears to be fairly realistic in this case.

Most previous authors (Price 1971, Stroud and Ashcroft 1972, Hasegawa and Watabe 1972, Jones 1973) have calculated  $\chi_T$  by double differentiation of the free energy of the metal. As mentioned in the Introduction this procedure involves knowledge of the density dependence of the self-energy and the pair potential *and* how  $g(R)$  varies with density. In general such a calculation will lead to a value for  $\chi_T$  which is different from that obtained via equation (36) (eg Price 1971 and W Jones 1973).

**Table 4.** The long-wavelength limit of the structure factor extracted from the WCA theory.  $a_{hs}(0)$  was calculated from equation (38) while  $a(0)$  was obtained from experiment via equation (36). The compressibility data are the same as those quoted in table 3.

Metal	$\eta$	$a_{hs}(0)$	$a(0)$
Na (ECM)	0.455	0.026	
Na (No dep. hole)	0.499	0.028	
Na ( $\delta$ -fn, dep. hole)	0.461	0.025	0.024
Na (Uniform dep. hole)	0.483	0.021	
Cs	0.483	0.021	0.023
Rb	0.488	0.020	0.022
K	0.487	0.020	0.024
Cd	0.393	0.046	0.011
Mg	0.473	0.023	0.025
Zn	0.494	0.019	0.016
Ga	0.492	0.019	0.005
Al	0.457	0.026	0.017
Sn	0.425	0.035	0.007

In order to reproduce the results from the method of homogeneous deformation (double differentiation of the free energy) one should include terms which are of third and fourth order in the pseudopotential in the method of long waves (equation 36). The difference between compressibilities calculated by the two methods is not expected to be serious for the alkalis but may be large for a polyvalent metal such as Al. The analogous problem for crystalline metals has been discussed by several authors (eg Lloyd and Sholl 1968, Wallace 1969, Price *et al* 1970, Pynn 1972 and Finnis 1974) and they have reached a similar conclusion. The method of long waves is expected to yield a value of  $\chi_T$  for Al which is considerably larger than the experimental result (see also Bertoni *et al* 1974). This is in agreement with our present result for liquid Al.

## 6. Discussion

We can summarize the main results of this work as follows:

(i) The pairwise potentials calculated from Shaw's *ab initio* OMP and the Vashista and Singwi dielectric function give rise to realistic packing fractions and reasonable values for the excess entropy in liquid Na, K, Rb, Cs, Cd, Mg, Zn, Ga, Al and Sn but lead to non-physical values for these quantities in liquid Li, In, Tl and Pb.

(ii) The excess entropies calculated from the WCA perturbation theory are, in general, closer to the experimental values than those obtained from the variational calculations.

- (iii) The specific heats from the WCA theory are in fair agreement with experiment.
- (iv) Polyvalent liquid metals have repulsive forces which are harsher than those in the alkali metals and this is reflected in the liquid structure factors.
- (v) The isothermal compressibility of liquid Na, K, Rb, Cs and Mg can be reasonably well described by the effective hard-sphere model but this is inadequate for the other simple liquid metals considered here.

In this paper we have only considered pairwise potentials calculated from second-order perturbation theory (equation 2). If one works to third order in the pseudopotential an additional pairwise potential  $\phi_2^{(3)}(R; n_0)$  and a three-body potential  $\phi_3^{(2)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3; n_0)$  arise. Approximate calculations of  $\phi_2^{(3)}$  for Na and K by Hasegawa (1976) indicate that this potential is short-ranged and attractive. Its effect is to move the repulsive part of  $\phi(R; n_0)$  to smaller distances  $R$ . Hasegawa argues that even in Na and K, where one might have expected the expansion in powers of the pseudopotential to be rapidly convergent, the inclusion of  $\phi_2^{(3)}$  changes the packing fraction of the WCA effective hard spheres from his calculated value of 0.52 to 0.42 i.e. from a non-physical value in second-order theory to a reasonable value in third order. We find, on the contrary, that the pairwise potentials  $\phi(R; n_0)$  calculated from second-order theory give adequate packing fractions in Na and K (see table 2). Our calculations differ from those of Hasegawa in that we have used the Vashista and Singwi form of  $f(q)$ . This tends to shift the repulsive part of  $\phi$  to smaller distances (figures 2 and 3). Furthermore we have included effective-mass corrections which have a similar effect (figures 5, 6 and 7). Consequently, we are not convinced that third or higher order perturbation contributions are necessary for describing the structure or entropy of liquid Na and K. In many of the polyvalent metals, where the pseudopotentials are much stronger than those in Na and K, higher order contributions may well play an important role so that second-order theory becomes inadequate for quantitative purposes. We believe this is the case in In, Tl, Pb and perhaps Li. Some indications of the failings of the present model are also evident in the evaluation of the compressibility which is probably more sensitive to the higher order contributions than say the entropy. We should also note that the structure factors of Ga and Sn show pronounced 'shoulders' on the high-angle side of their first peaks. It is hard to see how such large asymmetries could arise from the simple repulsive-pair forces which we have calculated here. Multi-ion interactions are probably necessary to explain such behaviour.

We wish to comment on the recent analysis of experimental structure factor and entropy data of many liquid metals published by Silbert *et al* (1975). These authors insert the measured entropies into the variational expression (equation 26) and invert this to get an empirical packing fraction,  $\eta_e$ . Another empirical packing fraction  $\eta_s$  is obtained by fitting the first peak of the measured structure factor to the Percus-Yevick hard-sphere form of  $a(q)$ . For almost all the metals which they consider they find  $\eta_e < \eta_s$  i.e. they require smaller hard-sphere diameters to fit the entropies than those required to fit the structure factors. We believe that this inconsistency results from the crudeness of the variational method. Since one is forced directly to a hard-sphere model *all* the excess entropy is accounted for by an effective hard-sphere contribution. In the more sophisticated WCA treatment, the potential is first divided into repulsive and attractive forces and only the former enter the hard-sphere modelling procedure with the result that the excess entropy consists of the hard-sphere part plus two further contributions (equation 27). As we discussed in § 4 these reduce the hard-sphere contribution to  $-S_E$ . Consequently, it is possible that a *single* empirical value of  $\eta$  can give a reasonable fit to both the first peak in  $a(q)$  and to the entropy for many metals.

Finally we stress that all the calculations reported here are based on the approxi-

mate WCA† or variational schemes. It would be valuable to compare the present results with those of Monte Carlo or molecular dynamics calculations based on the same input data. We have only been able to do this for the pair distribution function of liquid Rb. Further work would allow us to assess the reliability of these schemes for other liquid metals where the interatomic potentials are much softer than those usually employed for classical liquids.

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† Recently we have extended the WCA model to the case of an inhomogeneous liquid i.e. one with a surface. This allowed us to construct an approximate theory for the ion density profile and surface tension of liquid simple metals (Evans and Kumaravadivel 1976).

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