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Entropies and structure factors of liquid metals

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Abstract. Recent theory, relating the thermodynamics of a real liquid to that of a hard sphere reference system, suggests a correlation between the entropy and the structure factor. The extent to which this correlation exists in liquid metals is investigated by comparing, for each system and at various temperatures, the packing fractions deduced respectively from entropy and structure factor measurements. The quality of agreement is, overall, comparable with that obtained from previous comparisons of measured and hard sphere structure factors as functions of wave number.

The standard *ab initio* method of calculating interatomic forces in simple metals uses pseudopotential theory. The results of previous authors, together with the further calculations of the present paper, suggest that near the melting points, entropies for all valencies, and specific heats for lower ($\lesssim 3$) valencies, are adequately describable by the usual pseudopotential techniques (provided, for example, that sufficiently good model potentials and screening methods are used). For higher ($\gtrsim 3$) valencies, there is evidence that conventional calculations will lead to underestimated specific heats (typically by $\sim 30\%$) perhaps because of the inadequacy of second order perturbation theory for such cases.

1. Introduction

Within the past few years a new technique has arisen which seems capable of describing quantitatively many aspects of the thermodynamics of liquid metals. This development has been possible because of advances in a number of fields. First of all, second order pseudopotential theory enables us to describe a metal in terms of volume and pairwise forces (Harrison 1966, Heine and Weaire 1970). Second, the classical problem of the thermodynamics of hard sphere systems has been, for many practical purposes, solved (Thiele 1963, Wertheim 1963, 1964, Frisch and Lebowitz 1964, Carnahan and Starling 1969). Third, the Gibbs–Bogoloubov inequality (Isihara 1968, Lukes and Jones 1968) provides us with a variational principle for choosing a best hard sphere reference system in terms of which the real system can be described.

Jones (1971, 1973), Edwards and Jarzynski (1972) and Stroud and Ashcroft (1972), starting from specific pseudopotentials, have calculated various thermodynamic properties of liquid metals (including the entropy), while Umar and Young (1974) have investigated the structure factors. Practically no attention, however, has been given to the fundamental relationship between the entropy and the structure factor implicit in the above theory.

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This relationship does not depend on the details of the pseudopotentials and screening theory used and, indeed, as we will suggest, rests on such general foundations that it might persist even under conditions when the detailed formalism (§2) is no longer fully quantitative. In the first part of this work, therefore, we examine the experimental evidence relating to this matter. Our conclusion is that such a correlation does, in general, exist.

The further question is whether pseudopotential theory, as presently used, is capable of describing these effects fully and quantitatively. This is investigated in the final part of the paper.

2. Formalism

Let us begin with the formalism as it might be used in first principles applications to metals. Many aspects of what follows may be found in the papers cited in the second paragraph above. We also refer to the work of Umar *et al* (1974b) (see also Stroud 1973, Umar *et al* 1974a) which gives an explicit derivation for the binary alloy case. We will, therefore, not repeat the details but instead summarize the computational program which emerges.

Consider, first, a reference system of hard spheres of packing fraction η and with the same density n and temperature T as the real ionic system. Then, for this system, the free energy per atom is

$$F_{hs} = \tfrac{3}{2}k_B T - TS_{hs} \tag{1}$$

the entropy per atom being given by

$$S_{hs} = S_{gas} + S(\eta) \tag{2}$$

where

$$\frac{S_{gas}}{k_B} = \ln\left[\frac{e}{n}\left(\frac{emk_B T}{2\pi h^2}\right)^{3/2}\right] \tag{3}$$

and, for the moment, we leave $S(\eta)$ unspecified.

Then, a variational expression for the real system is

$$F = F_{hs} + F_{ps} \tag{4}$$

where

$$F_{ps} = F_{vol} + F_2 + F_M. \tag{5}$$

The latter arises from perturbation theory carried to second order in the pseudopotential (assumed to be local) and second order in T (to allow for nondegeneracy of the electron gas). The individual terms are (in Hartrees)

$$F_{vol} = E_{vol} - \tfrac{1}{2}z\gamma_{eg}T^2 \tag{6}$$

$$F_2 = (1/16\pi^3)\int_0^x v^2(\epsilon^{-1}-1)aq^4\,dq - \tfrac{1}{2}z\gamma_2(a)T^2 \tag{7}$$

$$F_M = (z^2/\pi)\int_0^x (a-1)\,dq. \tag{8}$$

In (6), E_{vol} is given by terms which are independent of η and T and need not be explicitly defined for the purpose of this paper, while the second term is the leading T dependent correction allowing for nondegeneracy of the electron gas. F_2 and F_M correspond respectively to the usual band structure and Madelung terms, though the former has been generalized (Appendix) to allow for nondegenerate electrons. The structure factor $a(q)$ depends on n and η but not explicitly on T. The dielectric screening function, the ϵ of equation (7), need not be specified in detail for the present.

The procedure next is to find (for a given metal, at fixed n and T) that packing fraction which minimizes F. Assuming the perturbation theory is good enough, then the Gibbs–Bogoliubov inequality assures us that, for the exact $S(\eta)$ and $a(q)$ for hard spheres, the F thus obtained should be an upper bound to the correct value. In practice, we use the Percus–Yevick approximation, for which relatively convenient exact closed form expressions are available (Thiele 1963, Wertheim 1963, 1964). Thereby, we arrive at a packing fraction to which we attribute physical significance.

Under the optimizing condition described above, we have

$$S = S_{hs} + S_{ps} \tag{9}$$

where

$$S_{ps} = z\gamma T \qquad \gamma = \gamma_{eg} + \gamma_2. \tag{10}$$

Much has been written on the calculation of γ_{eg}, but the conclusion seems to be (Faber 1972, p 296) that we can do rather well by taking the independent particle result $\gamma_{eg} = (\pi k_B/k_F)^2$. The term γ_2 is investigated in the Appendix and is shown to represent a small correction to γ_{eg}. Since, as we will see, S_{ps} is, itself, only a correction to S_{hs} (and, indeed, to $S(\eta)$, an object of more direct physical interest), the above choice of γ_{eg} is well justified, as is our decision to set $\gamma_2 = 0$, in general, below.

The procedure is now complete except for the specification of $S(\eta)$, a problem which has recently been discussed by Jones (1973). It is well known that different thermodynamic routes lead to different equations of state for a given approximate theory of the radial distribution function. Accordingly, integration of these equations of state (Mansoori and Canfield 1969) give different forms for F_{hs} and therefore $S(\eta)$. Using the exact Percus–Yevick solutions for the pressure of the hard sphere reference system†, derived respectively from the compressibility (Ornstein–Zernike) and pressure (virial) equations, leads to

$$\frac{S_{comp}}{k_B}(\eta) = \ln(1 - \eta) + \frac{3}{2}\left(1 - \frac{1}{(1 - \eta)^2}\right) \tag{11}$$

$$\frac{S_{press}}{k_B}(\eta) = -2\ln(1 - \eta) + 6\left(1 - \frac{1}{1 - \eta}\right). \tag{12}$$

But a better (though more empirical) equation for the pressure of a hard sphere system is known to result from averaging (in the ratio $\frac{2}{3}$ to $\frac{1}{3}$) the two Percus–Yevick pressures referred to above; the result is the Carnahan–Starling equation. Integration of this expression leads to

$$\frac{S_{CS}(\eta)}{k_B} = 3 - \frac{2}{1 - \eta} - \frac{1}{(1 - \eta)^2}. \tag{13}$$

The functions (11), (12) and (13) are plotted in figure 1.

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† We stress that this gives only one contribution to the total pressure of the actual liquid metal (see Umar *et al* 1974b, equation (28) and Watabe and Young 1974).
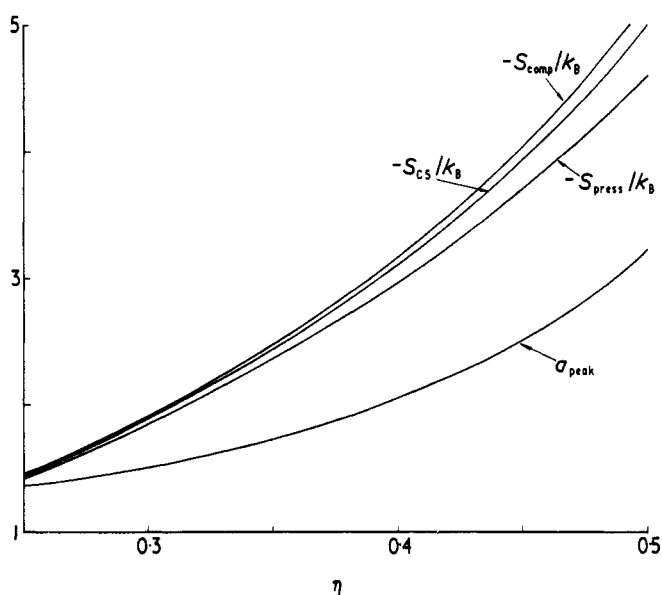
Figure 1. $S(\eta)$, in each of the approximations (11), (12) and (13), and the height of the first peak in the structure factor, all as functions of packing fraction, η.

Table 1. X ray and neutron data sources

Metal	Display points (figures 2, 3, 4)	Reference (Capitals, neutrons; lower case, x rays)	Comments
Li	●	A	
Na	●	A	
	×	a	
	∗	b	
K	●	A	No fine structure but some evidence of departures from
	×	a	hard sphere behaviour (Page *et al* 1969, Greenfield *et al*
	∗	b	1972, Waseda and Suzuki 1973)
Rb	●	A	
	○	B	
Cs	●	A	
	∗	b	
Cu	●	C	No fine structure
	×	c	
Ag	+	c	No fine structure
Au	+	c	No fine structure
Zn	●	D, E	Low angle side of first peak somewhat less steep than
	○	F	high angle side
	◉	G	
Cd	×	d	Low angle side of first peak less steep than high angle side. Persists to highest experimental temperature
Al	●	H	
	×	e	No fine structure
	+	f, g	

Table 1.—*Continued*

Metal	Display points (figures, 2, 3, 4)	Reference (Capitals, neutrons; lower case, x rays)	Comments
Ga	●	I	Shoulder on high angle side of principal peak around melting point; less pronounced at 423 K
	○	J	
	+	f	
	×	h	
In	×	i	No fine structure
	✳	j	
	+	f	
Tl	○	D	No fine structure
	×	k	
	+	f	
Sn	●	D	Low shoulder on high angle side of principal peak around melting point; absent at 873 K
	×	l	
	+	f, g	
Pb	●	D	No fine structure
	×	m	
	+	f, g	
Sb	○	K	Low shoulder on high angle side of principal peak at 933 K. Somewhat less pronounced at 1073 K
Bi	●	D	Low shoulder on high angle side of principal peak at lower temperatures; practically absent at 1223 K
	○	K	
	+	f, g	

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3. Entropies and structure factors

For given pseudopotential, v, and dielectric function, ϵ, it is possible, by the method outlined above, to calculate F and, thence, a variety of properties. However one result at least is practically independent of the specifics of v and ϵ (and, indeed, is more generally valid than the formalism of §2 would immediately suggest; we will return to this matter in the final discussion). We have seen that γ_2 does, in principle, depend on v and ϵ but that it has a negligible effect on S. Thus, for an assumed form of $S(\eta)$ (equations (11), (12) or (13)), the entropy specifies η and *vice versa*.

As we have seen, the structure factor is also specified by η. So, ideally, an experimentally determined structure factor will correspond to a unique η. In fact, this proves to be tolerably the case for many systems (Umar and Young 1974) as was first suggested by Ashcroft and Lekner (1966). In practice, therefore, we can obtain a definite η by fitting the first peak of a measured structure factor to the Percus–Yevick hard sphere form. Numerical computation leads to the relationship shown in figure 1.

We are now in the position to find, for a given system, η from two independent experimental sources. The entropies are relatively well known (Hultgren *et al* 1963), while x ray and neutron diffraction measurements of $a(q)$ are available for a variety of liquid metals.

Excepting mercury†, we have taken every simple metallic system of which we are aware, where diffraction data are available over a significant range of temperature (table 1), and obtained the corresponding packing fractions by the method indicated above. For the same systems, we have used the experimentally determined entropies also to evaluate $\eta(T)$. The density data employed were taken from Allen (1972) and $S(\eta)$ was specified via equation (13). The comparison between the results thus obtained are shown in figures 2, 3 and 4.

Typically, entropies are quoted by Hultgren *et al* to an accuracy of $\pm 0.02\ k_B$. As figure 1 shows, this has very little effect on the corresponding η's for any chosen form of $S(\eta)$. A much more significant variation is obtained by using either of equations (11) and (12) instead of (13). As figure 1 shows, the entropy which corresponds to $\eta = 0.46$, via (13), implies values of η of 0.454 and 0.475 on using (11) and (12) respectively. However, as we remarked in §2, equation (13) is known to be the most accurate expression of the three. Much more uncertainty probably lies in the radiation based points, a glance at figures 2–4 revealing considerable variations in η according to the experimental data chosen.

Bearing the above in mind, our conclusion (with certain exceptions to be discussed shortly) is that $\eta(T)$ data from the two types of sources do seem to agree quite well. The agreement between the absolute values at the melting points was inferred, in principle, by Faber (1972, pp 101–2), who demonstrated that the point (0.46, 4.15) on the Carnahan–Starling curve shown in figure 1 is consistent with the general features of the entropy and structure factor data. The main new feature, which arises from this study, is the good agreement, in general, in the temperature dependence.

For many of the systems studied in this paper, Umar and Young (1974) have compared as functions of wave number, measured structure factors with the corresponding Percus–Yevick hard sphere forms. Many details may be found in that

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† We avoided Hg because of experimental evidence (Orton and Street 1972, Umar and Young 1974) that $a(q)$ for this metal was badly represented by hard spheres. Recently, however, further experimental data have appeared (Waseda *et al* 1974) which leads to the opposite conclusion.
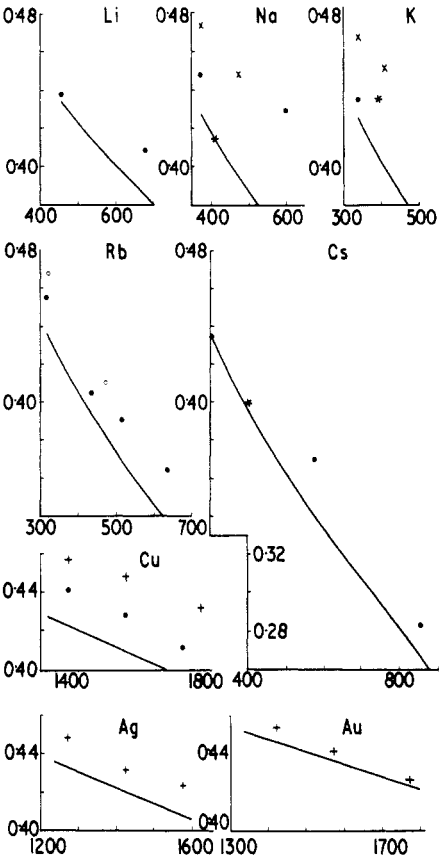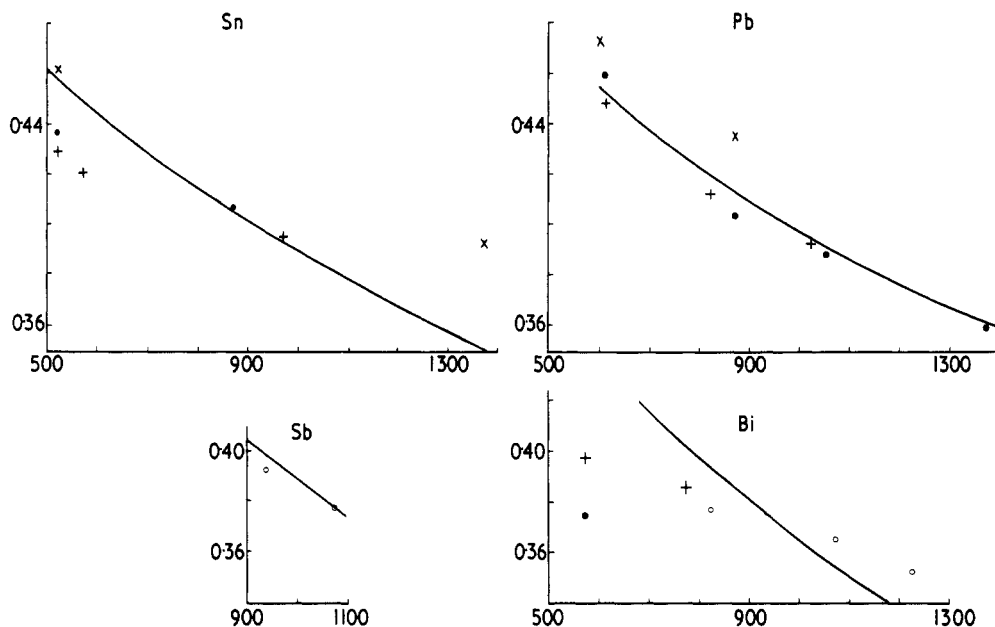
Figure 2. $\eta(T)$ derived from thermodynamic data (lines) and diffraction experiments (points) for univalent metals. References to and comments on the radiation data are given in table 1.
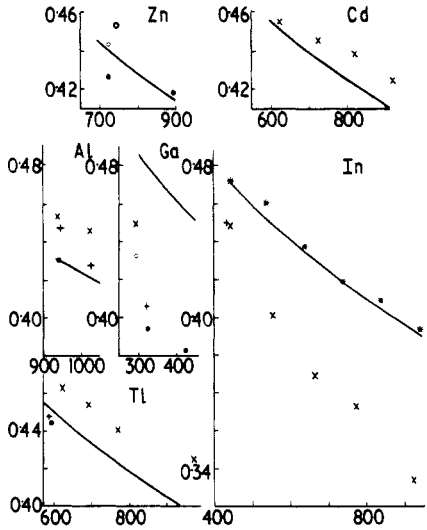
Figure 3. $\eta(T)$ derived from thermodynamic data (lines) and diffraction experiments (points) for divalent and trivalent metals. References to and comments on the radiation data are given in table 1.

Figure 4. $\eta(T)$ derived from thermodynamic data (lines) and diffraction experiments (points) for metals of valencies four and five. References to and comments on the radiation data are given in table 1.

work and for an excellent compilation of much of the available experimental information we recommend the work of Waseda and Suzuki (1973). For immediate reference, however, some of the main qualitative features are noted in table 1. Do those cases which exhibit the better (poorer) hard sphere behaviour in the wave number dependence of the structure factors give the more (less) satisfactory agreement in figures 2–4? The reader may judge for himself on the basis of table 1 and the figures. Our own feeling is that the overall quality of the structure factor data prevents us from drawing a definite conclusion in general, though in certain cases a positive answer to the question is suggested. For example, both methods indicate hard sphere behaviour for Pb; both indicate significant departures from this description for Bi.

In the case of the monovalent metals (figure 2), there is a distinct tendency for the radiation based data (for x rays especially) to exceed the corresponding values derived from the entropies, though the slopes seem to agree quite well. Egelstaff and March (1974) have sought to explain the differences between the results of x ray and neutron diffraction experiments on the basis that while x rays scatter from the ions and the valence electrons, neutrons scatter only from the former (or, more precisely, the nuclei). Thus, if a liquid metal behaves like a two component system, only the neutron studies measure the ion–ion structure factor properly. Egelstaff and March go on to point out that the effect should be largest in the alkalis, where the valence electron densities are lowest and the corresponding correlation effects are therefore strongest.

We have little directly to contribute to that problem, but it is of interest to note (figure 2) that the present theory calls for the identification of $a(q)$ with the ion–ion structure factor and that the thermodynamically derived $\eta(T)$ is (for the alkalis at least) closer to the neutron than the x ray based points.

There is, however, reason to believe that the present method might be at its poorest for the alkalis (Waseda and Suzuki 1973). Certainly Wehling *et al* (1972), for Na, and

Hasegawa and Watabe (1974), for Na and K, have obtained improved structure factors by taking account of departures from hard sphere behaviour. In the next section, we show that the experimental specific heats suggest that these metals may be somewhat less amenable than others to a hard sphere description. The method we use has some features similar to those of an analysis given by Hasegawa (1972).

4. Specific heats and interatomic forces

The formalism of §2 provides us, of course, with a means of examining specific heats. The latter are immediately given by the slopes of the curves plotted in figures 2–4, but it is more accurate and instructive, for the purposes of this section, to proceed via equation (9) which gives

$$\frac{C_p}{k_B} = \frac{3}{2} - T\left(\frac{\partial \ln n}{\partial T}\right)_p + \frac{S'(\eta)}{k_B} T\left(\frac{\partial \eta}{\partial T}\right)_p + \frac{zT}{k_B}\left[\gamma + T\left(\frac{\partial \gamma}{\partial T}\right)_p\right] \quad (14)$$

where, as before, γ_{eg} has its Sommerfeld value and γ_2 is (with complete justification) neglected. Using this equation and the experimental data, we have prepared table 2 (once again using equation (13) for $S(\eta)$), which shows melting point data for the liquid metals already studied.

The experimental data are displayed in the first four columns. The rather constant value for the excess entropies $S_E \equiv S - S_{gas}$ is responsible (recall §3) for the fact that η is also quite constant at the melting points. We now wish to examine the implication of the even smaller variations in C_p which are evident from table 2.

Since the final term of (14) is small and $S'(\eta)$ is approximately independent of the metal considered, it follows immediately (table 2) that $T(\partial \eta/\partial T)_p$ is also rather independent of system so that $(\partial \ln \eta/\partial T)_p$ is roughly inversely proportional to T.

This quantity is still not quite what we want, however, since we are really more interested in the variation in the diameter σ. Writing the volume of a hard sphere as $\omega = \frac{1}{6}\pi\sigma^3$, we have $\eta = \omega n$, so that

$$\left(\frac{\partial \ln \eta}{\partial T}\right)_p = \left(\frac{\partial \ln \omega}{\partial T}\right)_p + \left(\frac{\partial \ln n}{\partial T}\right)_p. \quad (15)$$

Table 2. Thermodynamic data (experimentally based) at the melting point

	T(K)	$-S_L/k_B$	C_p/k_B	$-(\partial \ln n/\partial T)_p \times 10^4$ K	$-T(\partial \eta/\partial T)_p$	$-(\partial \ln \eta/\partial T)_p \times 10^4$ K	$-(\partial \ln \omega/\partial T)_p \times 10^4$ K
Li	453	3·61	3·65	1·64	0·118	6·00	4·36
Na	371	3·45	3·83	2·37	0·132	8·34	5·97
K	337	3·45	3·87	2·68	0·132	9·17	6·49
Rb	312	3·63	3·78	2·72	0·120	8·80	6·08
Cs	302	3·56	3·84	2·83	0·125	9·57	6·74
Cu	1356	3·59	3·78	1·00	0·117	1·98	0·98
Zn	693	3·78	3·78	1·77	0·114	3·71	1·94
Cd	594	4·00	3·57	1·34	0·100	3·68	2·34
Al	933	3·49	3·52	1·14	0·105	2·62	1·48
Ga	303	4·62	3·35	1·00	0·080	5·44	4·44
In	429	4·34	3·55	1·15	0·093	4·56	3·41
Tl	576	3·93	3·62	1·15	0·103	3·93	2·78
Sn	505	4·08	3·57	0·88	0·101	4·31	3·43
Pb	600	3·91	3·68	1·23	0·105	3·83	2·60
Sb	904	3·04	3·77	0·85	0·118	3·25	2·40
Bi	544	3·76	3·83	1·25	0·117	4·80	3·55

The melting temperatures and densities were taken from Allen (1972) and S_E and C_p from Hultgren et al (1963). Then the remaining columns were deduced from equations (13), (14) and (15). The final column is a measure of the softness of the repulsive part of the interatomic potential.

Using this equation, we obtain the final column of table 2. The first term of (15) is (except marginally for Cu) bigger than the second, so ω has, very roughly, the same temperature dependence as η; the lower the melting point, the higher is $-(\partial \ln \omega/\partial T)_p$ and *vice versa*.

The point, of course, is that σ is a measure of the position of the repulsive edge of the interatomic potential (Ashcroft and Langreth 1967), so that $-(\partial \ln \omega/\partial T)_p$ measures the softness†. Indeed, if we were to ignore the volume variation with pressure† and follow a prescription used by Ashcroft and Langreth, we could draw sections of the repulsive parts of the interatomic forces using figures 2, 3 and 4, though we think that a better analysis might be forthcoming by using the formulation of §2. Be that as it may, the final column of table 2 shows that, at the respective melting points, the effective interatomic repulsions are softer for the metals with lower melting points and so a hard sphere description would appear to be least appropriate to these cases. (Note that, in reaching the latter conclusion, we are not saying that the repulsive parts of the potentials for high melting point metals are steeper *overall*—only that the parts of interest at the respective melting points are steeper.)

Having suggested that hard spheres are least applicable to alkalis, it should be remarked that, by way of contrast, second order pseudopotential perturbation theory (implicit in the above investigation; recall §2) becomes quantitatively less good at high valencies (Heine and Weaire 1970, Meyer *et al* 1971, Singh and Young 1972). Indeed, Hasegawa (1971 and private communication) has calculated the corrections to the pair forces defined by third order perturbation theory and found them to be significant. This possible deficiency of second order perturbation theory is a point to which we will return later.

5. Packing fractions from pseudopotentials

Finally, we ask how well the data shown in figures 2, 3 and 4 can be reproduced by specifying pseudopotentials and dielectric screening functions and carrying out the first principles calculations indicated in §2.

Partial answers are available from the various studies to date. In order to see a more complete picture, however, we felt it was necessary to investigate the absolute value and slope of $\eta(T)$, at the melting point, for a large number of metals. This, of course, amounts to computing the entropies and specific heats and the results of our calculations, together with all others of which we are aware, are shown in figure 5.

The results of Jones for Na and ourselves for Na, Mg, Al and Pb indicate the kind of spread obtainable, for a given pseudopotential and screening technique, when the hard sphere description is varied. The other theoretical results are obtained by a variety of pseudopotential and screening methods, the details of which are given in the figure caption.

The lesson which seems to follow from the entropy calculations is that, while the finer detail of the variations from element to element is difficult to reproduce, a good *average* value of $-S_E \sim 4k_B$ per ion is not. However, when we turn to the specific heats, we find that while for lower valency metals a correct average value of $\sim 3.6\ k_B$ per ion is

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† Actually, the potential itself will vary at constant pressure because of the small variation in volume. The difficulty would not arise at constant volume but, throughout this work, we have preferred to keep our analysis as close as possible to the usual experimental conditions. We do not expect the effect to be very large, at least in so far as the repulsive edge is concerned, since C_p/C_v is not too far from unity (being ~ 1.15; see Webber and Stephens 1968).
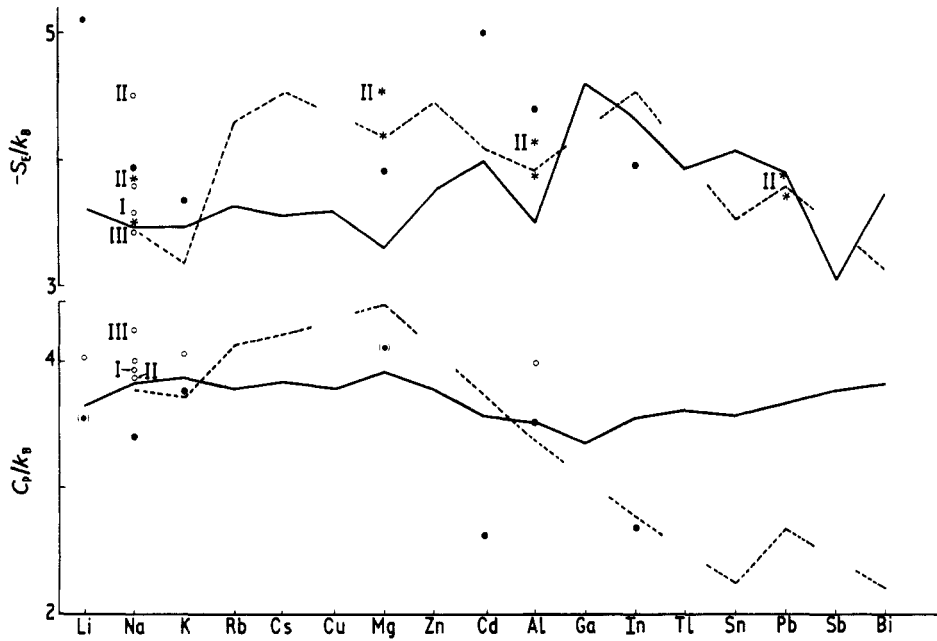
Figure 5. Excess entropies and specific heats (C_p) per atom at the melting points. The experimental points are joined by continuous lines. The key to the theoretical calculations is provided by the following table.

Authors	Figure 5 symbol	Pseudopotential	Screening	Hard sphere dynamics
Present	Broken lines	Empty core	Geldart–Vosko	equation (11)
	*	,,	,,	equation (13)
	II∗	,,	,,	equation (12)
Edwards and Jarzynski	●	Shaw (1969)	Shaw (1970)	equation (13)
	○	Modified point ion	Geldart–Vosko	equation (13)
Jones	I ○	,,	,,	equation (11)
	II ○	,,	,,	equation (12)
	III ○	,,	,,	equation (13) but using Verlet–Weis (1972) structure factor

Actually, Edwards and Jarzynski calculate their specific heats at constant volume. For comparison purposes we have obtained values of C_p from their results by using the experimental specific heat ratios of Webber and Stephens (1968). These ratios do not vary much from metal to metal so, in the cases of Li and Mg, where the data are not available, we felt justified in multiplying by the typical value of 1·15 to obtain the results indicated (●).

The empty core pseudopotential radii used in the present calculations were as in table 15 of Cohen and Heine (though in the case of Zn we followed Umar and Young by taking the adjusted value of 1·11 which fits the first Heine–Abarenkov node). For Rb, Cs and Pb, for each of which Cohen and Heine quote more than one value, we chose the alternatives 2·61, 2·93 and 1·47 respectively. For Cd, no radius is tabulated; we chose a value of 1·23 to fit the first Heine–Abarenkov node.
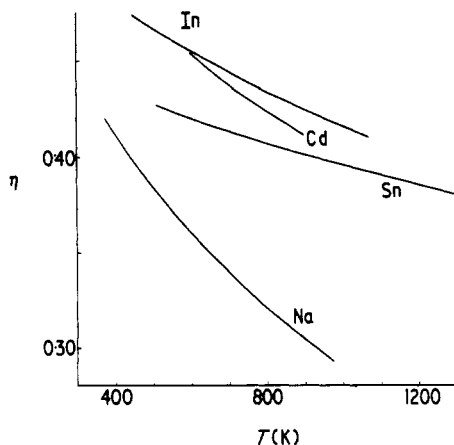
Figure 6. $\eta(T)$ calculated by the method of §2 (empty cores, Geldart–Vosko screening, equation (13)). Compare with the experimentally based results of figures 2, 3 and 4 and note that the *ab initio* curves are shallower than those obtained from the observed entropies in the higher valency cases (In and Sn). This behaviour is reflected in the underestimation of the specific heats for these metals (figure 5).

found, there is a distinct tendency to underestimate the experimental results at high valencies.

In relation to figures 2, 3 and 4, this means that calculated packing fractions start off with about the right magnitudes at the melting points, but for high valency cases the variation with temperature is too small, at least for obtaining agreement with the *thermodynamic* data. (For Sn, as it happens, the agreement with the radiation based points of figure 4 is good.) A selection of such theoretical $\eta(T)$ curves are shown in figure 6. The data for Na lead to a specific heat curve (Umar 1974) which is in good agreement with experiment, falling initially and rising as the temperature increases above $\sim 600°$C. Similar behaviour, with about the same quality of fit to experiment, has been calculated by Jones (1973) and, for this reason, we do not quote our result here.

At first sight, it might seem paradoxical that, in some higher valency systems, the first principles specific heat calculations lead to underestimates, whereas the entropy–structure factor correlations continue to be maintained. Such a situation occurs in the case of Pb, for example, as figures 4 and 5 demonstrate. The resolution of this apparent contradiction presumably is that the entropy–structure factor relationship is more general than §2 indicates. It is obvious that the volume and pairwise terms implicit in equations (5)–(8) need not be precisely as defined there in order that the correlation be established. In this connection, our remarks at the end of §4 are relevant. Pseudopotential perturbation theory beyond second order will lead to redefined volume and pairwise energies as well as many-ion contributions. As long as the latter are (in some sense) negligible or effectively subsumable into lower order terms and the pairwise interactions themselves are well approximated by those of hard spheres the entropy–structure factor correlation will emerge.

6. Discussion

In the above work, we have pointed to a relationship between entropies and structure factors of liquid metals which, as the remarks immediately above indicate, is rather

generally based. It does, however, presume that real liquid metals 'resemble' hard sphere systems (with temperature dependent diameters) in the Gibbs–Bogoliubov sense.

Figures 2–4 may be used to judge the degree to which this correlation holds in practice. Our conclusion is that the connection is established to about the same extent that structure factors against wave number are known to be describable by hard spheres. In some systems (eg Pb) a good description, in terms of hard spheres, of the structure factor against wave number is accompanied by a good correlation of structure factor and entropy. In other cases (eg Bi) both these pieces of evidence point to departures from hard sphere behaviour. In general, however, a rule is difficult to establish because of the variable overall quality of the radiation data.

In §5 we investigated the extent to which *ab initio* calculations, using the formalism of §2, are capable of describing, quantitatively, the experimentally based hard sphere diameters. Such calculations involve, of course, specific choices of pseudopotentials, dielectric screening functions and entropy expressions (equations (11), (12) and (13) in particular). The results of the present work, as well as those of previous authors, are summarized in figure 5, from which it would seem that near the melting points, entropies, for all valences, and specific heats, for lower ($\lesssim 3$) valencies, are adequately describable by techniques of the kind outlined in §2. As the spread of results obtained by various authors for Na, say, indicates, such discrepancies as exist between theory and experiment for these lower valency cases can probably all be explained in terms of the quality of the input data.

For higher ($\gtrsim 3$) valencies, there is evidence that such calculations are likely to underestimate specific heats somewhat (perhaps by $\sim 30\%$). Such underestimations are not necessarily at variance with the existence of a good experimentally based entropy-structure factor correlation, for, as we have seen, this correlation can be more general than the formalism of §2 would suggest.

Appendix. In this appendix we describe briefly the derivation of the expression for the correction term in the band structure energy F_2 due to the departure of the electron system from complete degeneracy.

The second order or band structure energy for a nonzero temperature Fermi distribution of conduction electrons is given by

$$F_2 = \frac{1}{16\pi^3} \int_0^\infty v^2(q) a(q) \left(\frac{1}{\epsilon_T(q)} - 1 \right) q^4 \, \mathrm{d}q. \tag{A1}$$

Here $\epsilon_T(q)$ is the dielectric function of the electron gas at temperature T and is conveniently expressed as

$$\epsilon_T(q) = 1 + \frac{4\pi}{q^2} \Pi_T^{(0)}(q) \left(1 - \frac{4\pi}{q_2} G(q) \Pi_T^{(0)}(q) \right)^{-1} \tag{A2}$$

in terms of the free electron polarization function (at temperature T)

$$\Pi_T^{(0)}(q) = \frac{1}{\pi^3} \int dk \; \frac{1}{(k+q)^2 - k^2} f_k \tag{A3}$$

f_k being the Fermi distribution function. $G(q)$ describes the correction to the random phase approximation dielectric function due to exchange and correlation. Here we neglect the temperature dependence of $G(q)$, which is very hard to estimate. Then the temperature dependence of F_2 arises simply from the temperature dependence of $\Pi_T^{(0)}(q)$, which can be calculated easily (up to T^2) as

$$\Pi_T^{(0)}(q) = \Pi_{T=0}^{(0)}(q) + \frac{k_F}{12} \frac{1}{x^2 - 1} f(x) \left(\frac{k_B T}{\epsilon_F} \right)^2 \tag{A4}$$

where

$$\Pi_{T=0}^{(0)}(q) = (k_F/\pi^2) f(x)$$

$$f(x) = \frac{1}{2} + \frac{x^2 - 1}{4x} \ln \left| \frac{1-x}{1+x} \right| \qquad x = q/2k_F.$$

k_F is the Fermi wave number and $\epsilon_F = \frac{1}{2} k_F^2$ is the Fermi energy. On substituting (A4) into (A1), F_2 can be calculated up to T^2 as

$$F_2 = (1/16\pi^3) \int_0^x v^2(q) \, a(q) [(1/\epsilon(q)) - 1] q^4 \, dq - \frac{1}{2} z \gamma_2 T^2. \tag{A5}$$

Here $\epsilon(q) \equiv \epsilon_{T=0}(q)$ is the usual zero temperature dielectric function and

$$\gamma_2 = \frac{2k_B^2}{3\pi^2 z} \int_0^x dx \, \frac{x^2}{x^2 - 1} f(x) \, v_{sc}^2(q) \, a(q) \tag{A6}$$

where

$$v_{sc}(q) = v(q)/\epsilon_e(q)$$

$$\epsilon_e(q) = 1 + (\mu^2/x^2)(1 - G(x)) f(x).$$

Detailed calculations, using (A6) for a variety of metals, revealed that in every case γ_2 was of order $10^{-2} \gamma_{eg}$ and therefore, in the context of this paper, negligible (§2).

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