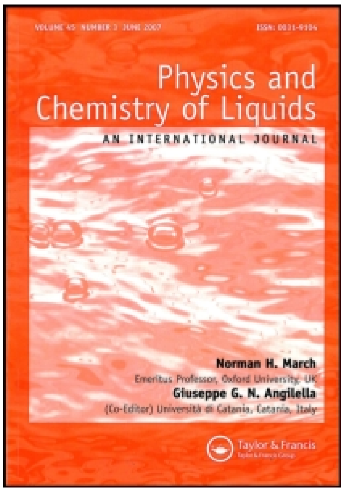

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EXCESS ENTROPY-DENSITY FLUCTUATION CORRELATION IN LIQUID METALS

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A plot of measured excess entropy ΔS against measured density fluctuation function $S(0)$ for each of the simple liquid metals at its melting temperature yields, very roughly, a single curve. This curve extrapolates to coincide, again very roughly, with one defined by the expanded alkali liquids in coexistence with their vapours. We use the melting temperature data to confirm qualitatively a recent picture of *ab initio* calculated interatomic potential trends throughout the Periodic Table.

KEY WORDS: Excess entropy, density fluctuation, liquid metals.

1 INTRODUCTION

Consider a monatomic liquid[1] of N particles of mass M at temperature T in a total volume Ω. Then, if its absolute entropy is S, its excess entropy ΔS is defined relative to that of an ideal gas at the same temperature and volume and containing particles of the same mass. Specifically,

$$\Delta S = S - S_{\text{ideal}} \tag{1}$$

where

$$S_{\text{ideal}}/Nk_B = \tfrac{5}{2} + \ln[(\Omega/N)(Mk_BT/2\pi\hbar^2)^{3/2}] \tag{2}$$

For the same liquid, let us introduce the density-density correlation function $S(0)$ as follows. If, at any time, $\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N$ are the positions of the particles, then the microscopic density is

$$\rho(\mathbf{r}) = \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{R}_j) \tag{3}$$

of which the $\mathbf{q}$-th Fourier component is

$$\rho(\mathbf{q}) = \sum_{j=1}^{N} e^{i\mathbf{q}\cdot\mathbf{R}_j} \tag{4}$$

Then the structure factor is defined by

$$S(q) = \frac{1}{N} \langle |\rho(\mathbf{q})|^2 \rangle \tag{5}$$

where the angular brackets denote a thermodynamic average. $S(0)$ is the $q \to 0$ limit of the above and it is also given, alternatively, by the well-known formula

$$S(0) = (N/\Omega)k_B \mathrm{T} \kappa_T \tag{6}$$

Here κ_T is the isothermal compressibility.

The above formalism most directly describes atomic disorder in liquid insulators. To describe such disorder in liquid metals, a modification is needed because of the presence of free electrons. The latter provide an entropy contribution which, in Sommerfeld approximation, can be written

$$S_{\mathrm{elec}}/Nk_B = 3.266 \times 10^{-6} z^{1/3} (\Omega/N)^{2/3} \mathrm{T} \tag{7}$$

The excess entropy due to ionic disorder alone is then given by

$$\Delta S = S - S_{\mathrm{ideal}} - S_{\mathrm{elec}} \tag{8}$$

rather than by Eq. (1). S_{elec} is small near melting point but contributes substantially at higher temperatures.

The formalism for $S(0)$ remains unaltered for metals. Moreover, within the long wave approximation[2], we can regard Eqs. (5) and (6) as decided by pairwise density-independent forces between the ions.

It is clear that ΔS and$S(0)$ are both measures of atomic disorder in a liquid but is there any simple direct relationship between them? In a one-parameter system, this is so. For example, for a hard sphere fluid, the excess entropy is

$$\Delta S_{\mathrm{hs}}(\eta)/Nk_B = -\eta(4 - 3\eta)/(1 - \eta)^2 \tag{9}$$

and the density fluctuation function is

$$S_{\mathrm{hs}}(0, \eta) = (1 - \eta)^4/[(1 + 2\eta)^2 - 4\eta^3 + \eta^4] \tag{10}$$

Here, the packing fraction η provides a connecting parameter.

The $\Delta S - S(0)$ curve defined by Eqs. (9) and (10) does not fit the data for real liquids. This is not surprising, considering the variety of interatomic potentials involved. It was, however, surprising to uncover[2] a different single curve that described, albeit rather roughly, the available measured data for simple liquid metals. We elaborate on this below.

2 CORRELATION EXPLORATION

In the present work, we use the experimentally derived absolute entropies S from the compilation of Hultgren *et al.*[3] and the measured densities of Allen[4] (for all cases at the melting temperatures) and of Hornung[5] (for the expended alkalis). In this way we find ΔS values from Eq. (8). Eq. (6) is used to find $S(0)$ from the measured data of Hornung[5] for the alkalis. In the other cases (all at the melting temperature) we rely on the compilation of Young.[2]

The results for the simple liquid metals at melting are shown in Figure 1 and it will be seen that, with at most one or two exceptions, these define, very roughly, a

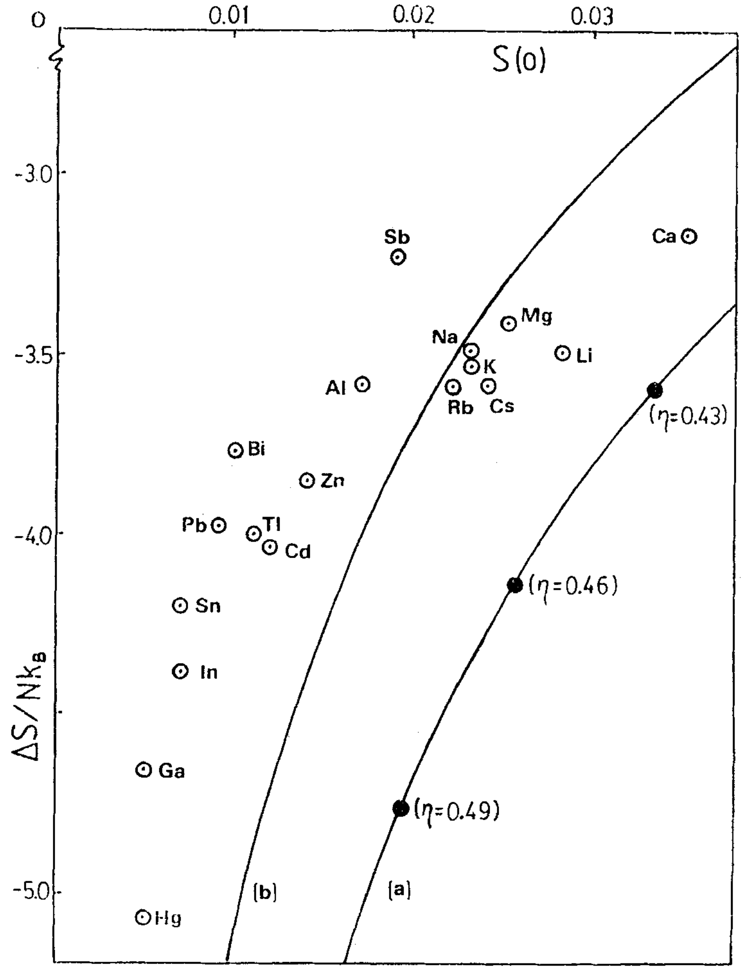

Figure 1 ΔS versus $S(0)$ for the simple liquid metals at their melting temperatures. The points shown rely on data from a variety of sources; for details, see text. Curve (a) shows the hard sphere result based on Eqs. (9) and (10), while curve (b) corresponds to Eq. (11)

single curve. A similar story emerges for the expanded liquid metal results shown in Figure 2 and, in fact, the resulting curve can be viewed as an extrapolation of that in Figure 1. This is made clear in Figure 3. We have tried to perform a similar study for expanded mercury but the necessary accuracy was difficult to obtain with the data[3,6,7] available to us. As far as we can judge, however, the mercury curve follows the common metallic trajectory.

We have also calculated the curve for expanded Ar using the entropy data of Angus and Armstrong[8], the compressibilities quoted by Rowlinson[9] and the densities provided by both sets of authors. The result, as Figure 2 indicates, is quite different from that of the expanded liquid metals.

It will be seen that the hard sphere description provided by Eqs. (9) and (10) fails to satisfy the data. However, it can help in analysing the latter and, with this end in view, we introduce a second related curve, in Figures 1 and 3, that we will find useful later. This is obtained by retaining Eq. (9) unchanged but replacing η by $\eta + 0.05$ in Eq. (10). It is, therefore, described by

$$\Delta S = \Delta S_{\mathrm{hs}}(\eta), \qquad S(0) = S_{\mathrm{hs}}(0, \eta + 0.05) \tag{11}$$

This curve is shown in Figures 1 and 3.

DISCUSSION

The following qualitative explanation of the above curves is a development of the one used by Young[2,10] earlier. We follow van der Waals by assuming that the interactions between particles are binary and that these can be considered to consist of strongly repulsive cores combined with weak tails. The latter are usually thought of as attractive but need not be so.

The entropy is decided only by the cores and, if we use the Gibbs-Bogoliubov (GB) method to find the effective diameters of these, it emerges[11] that Eq. (9) applies with a suitably chosen effective diameter or, equivalently, packing fraction η. The latter is determined by a weighted average over all collisions (through the so called GB condition).

On the other hand compressibilities, and so the $S(0)$, are decided by both cores and tails. This is recognised by the Weeks–Chandler–Anderson (WCA) procedure[12], which separates out core from tail and allocates a diameter to the former. This diameter determines a hard sphere fluctuation function of the form (10) which can then be corrected, in a random phase approximation[13], to include a tail effect.

An important point to note is that the criterion deciding the WCA diameter (the vanishing of the so-called blip function) involves only the weak collisions describing phonon-like modes. It follows, therefore, that the effective packing fraction is larger in this case than in the GB description, which involves more, as well as less, energetic collisions. *Ab initio* calculations[14] suggest a difference in the packings of about 0.05 and this effect alone (ignoring tails) would give rise to Eq. (11).

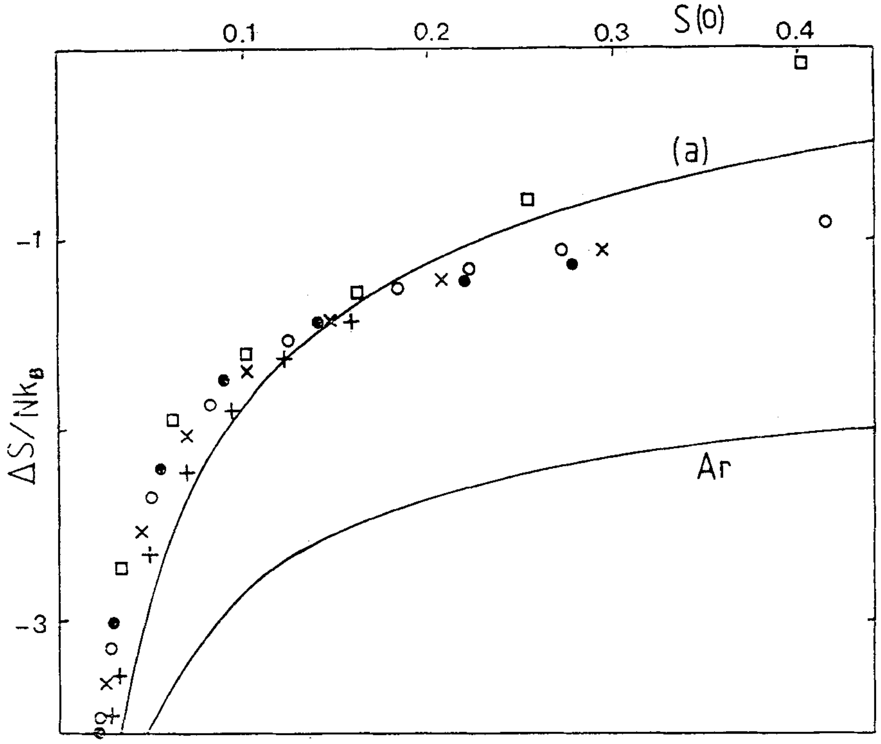

Figure 2 ΔS versus $S(0)$ for some expanded monatomic liquids (in coexistence with their vapours). References to the data used are provided in the text. The liquid metal results are indicated as follows: + + + (Li), × × × (Na), ○ ○ ○ (K), ● ● ● (Rb), □ □ □ (Cs). These form a family*, the behaviour of which resembles neither that for hard spheres (curve (a)) nor that for Ar. *We view the anomalous high T results for Cs with some suspicion. They lie on the "wrong" side of the hard sphere curve.

Tails are incorporated, in the random phase approximation, using an average tail strength parameter, $\bar{v}_{\text{tail}}$, in such a way that the final curve, that attempts to explain the observations, is obtained by replacing (11) by

$$\Delta S = \Delta S_{\text{hs}}(\eta), \qquad S^{-1}(0) = S_{\text{hs}}^{-1}(0, \eta + 0.05) + \bar{v}_{\text{tail}}/k_B T \tag{12}$$

For a repulsive (on average) tail, $\bar{v}_{\text{tail}} > 0$, thus suppressing density fluctuations, while for the attractive (on average) case, $\bar{v}_{\text{tail}} < 0$, which enhances such fluctuations.

A glance at the measured data in relation to curve (b) now reveals the influence of tails. The alkalis (normal and expanded), Mg and Ca are seen to require net attractive tails while the others need net repulsive ones. This is, in fact, the message that emerges from the *ab initio* calculations of Hafner and Heine[15] and we regard the present analysis as providing qualitative support for their results.

Finally we remark that while the above analysis is satisfactory as far as it goes, it is still unclear to us why the measured data lie (very roughly, to be sure) on a single line and, to the extent this is true, are characterised by a single parameter.

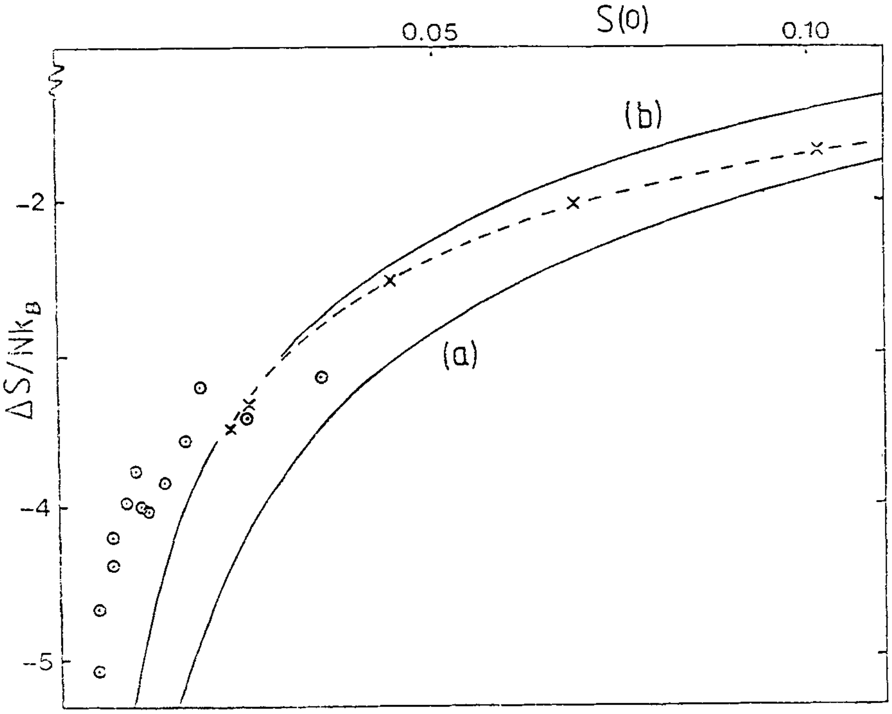

Figure 3 ΔS versus $S(0)$ to show how the data of Figures 1 and 2 match. The points ⊙ are from Figure 1 and the connected crosses × are from Figure 2 for Na. (For the sake of clarity, the latter are the only alkali data shown in this figure). Curves (a) and (b) are as in the earlier figures. It is of some interest to note that a good fit to the data for $S(0) \lesssim 0.1$ can be obtained by displacing curve (a) by 0.015 to the left.

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