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THEORIES OF ENTROPIES OF LIQUID METALS ; PHONONS VERSUS PACKING

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Abstract.- It is known that the entropy of a liquid metal can be largely explained in terms of atomic packing. We show that the Percus-Yevick phonon theory will also suffice and a connection between the two methods is established.

1. Introduction At the Bristol Conference, one of us gave a talk [1] in which the entropies of liquid metals were described in terms of the packing properties of the ions. Such an approach inevitably focusses primarily on the principal peak of the structure factor, $a(k)$. From this region of k -space, the packing and thereby the entropy was deduced.

Afterwards, the speaker was reminded by Prof. March of the PY (Percus and Yevick) phonon theory [2] which seemed capable of describing successfully such a property as the entropy. This is indeed the case, as we indicate below. But the phonon method would appear to be mainly concerned with much lower k -values than those around the first peak of $a(k)$. How then can the two methods be reconciled?

In an attempt to answer this question, Gray, Yokoyama and Young [3] calculated the entropy of liquid sodium using the PY description. They found that though the independent phonon contribution inevitably arises from the lower- k region, a contribution of order 5 - 10% arose from phonon-phonon interactions. The latter involve phonon pairs with quite large wavenumber differences and a description of them does indeed involve the principal peak of $a(k)$.

Nevertheless, the bulk of the entropy still arises from the independent phonons and the basic

problem remains of the connection between the two methods. The work below is addressed primarily to this matter.

2. The packing method We first briefly review the packing method. Suppose we are given a measured $a(k)$. Provided we avoid very low k 's [1, 4, 5] it is usually possible to describe it approximately by a hard sphere form [6, 7]. An effective diameter may thus be obtained, one method of unequivocally determining this being to match the heights of the first peaks. The entropy then follows from

$$S(\text{packing method}) = S_{\text{gas}} + S_{\eta} + S_{\text{elec}} \quad (1)$$

Here

$$S_{\text{gas}}/Nk_B = 2.5 + \ln[\Omega(Mk_B T/2\pi\hbar^2)^{3/2}] \quad (2)$$

which is the ideal gas expression and S_{η} is a well-understood [8] function of the packing fraction η . The term S_{elec} arises from thermal excitation of the conduction electrons, is small for simple metals, and is adequately approximated below by its Sommerfeld form.

If, as suggested above, matching takes place at the first peak, then the subsequent peak heights of the measured $a(k)$ are overestimated by the theory (fig. 3 of ref. [1]). In other words, the effective diameter obtained from the observed first peak alone is a little too big and the entropy is, therefore, correspondingly too small. Nevertheless, this simple procedure leads to lower

bounds which are reasonably accurate (fig. 7 of [1]).

3. The PY description Here we imagine the liquid to possess $3N$ normal modes of density-fluctuation form. We comment on this assumption in our concluding discussion but for the present accept it. Thus, the zeroth order picture is of longitudinal phonons with $\mathbf{k}$ -vectors occupying an enlarged Debye sphere of radius $k_0 = 3^{1/3}k_D$ where $k_D = (6\pi^2/\Omega)^{1/3}$ is the usual value.

The zeroth order phonon spectrum takes the form [9]

$$\omega(\mathbf{k}) = k\{k_B T/Ma(\mathbf{k})\}^{1/2} \quad (3)$$

and in terms of this one obtains an entropy contribution of

$$S_0 = Nk_B \sum_{\mathbf{k}} \left\{ \frac{x}{e^x - 1} - \ln(1 - e^{-x}) \right\}. \quad (4)$$

In this expression, $x = \hbar\omega(\mathbf{k})/k_B T$. When phonon interactions are introduced, a leading order correction S_1 is obtained (for details, see ref. [3]) and the total entropy from this point of view reads

$$S(\text{PY}) = S_0 + S_1 + S_{\text{elec}} \quad (5)$$

As Gray et al.'s fig. 3 shows, an Einstein description is reasonably appropriate for all except the lowest $\mathbf{k}$'s and the latter, of course, contribute with low weight. Because of this weighting, it is important that the size of $a(\mathbf{k})$ is adequately described for $k \sim k_0$.

We summarize, in table 1, some results obtained by the present authors using eq. (5) and measured structure factors [15]. The interested reader who refers to Gray et al. should note that we set their $S_1'' = 0$ and so $S_1 = S_1'$. It will be seen that the calculated values are accurate and that the method apparently leads to lower bounds. The numerical evidence (table 1 and

the concluding remarks of sec. 2) thus suggests that the PY method succeeds whenever the packing method succeeds. This proposition is now investigated.

Table 1

Entropies (in units of Nk_B) of some liquid metals

	T(K)	S_0	S_1	S_{elec}	$S(\text{PY})$	$S(\text{expt})$
Na	378	6.92	0.46	0.05	7.43	7.84
K	343	8.28	0.46	0.07	8.81	9.14
Rb	313	9.23	0.48	0.08	9.79	10.26
Cs	303	10.29	0.46	0.09	10.84	11.13
Mg	953	8.38	0.45	0.12	8.95	9.01
Al	943	8.05	0.47	0.11	8.63	8.62
In	433	8.20	0.43	0.07	8.70	9.13
Pb	613	10.50	0.48	0.12	11.10	11.19

4. Relationship between methods First, let us note that to high accuracy, the summand of eq. (4) can be expanded for small x to give $1 - \ln x$. It is then possible to write eq. (5) in the form

$$S(\text{PY}) = S_{\text{gas}} + S_{\text{pack}}^{\text{PY}} + S_{\text{elec}} \quad (6)$$

where

$$S_{\text{pack}}^{\text{PY}} = S_1 - 9Nk_B \int_0^1 \ln \left\{ \frac{1.90(k/k_0)}{\sqrt{a(k)}} \right\} \left(\frac{k}{k_0} \right)^2 d \left(\frac{k}{k_0} \right) \quad (7)$$

Eq. (7) depends on $a(k)$ and Ω but not

explicitly on T or M . In view of eqs. (1) and (6), the difference between the two methods of calculation hinges only on the difference between $S_{\text{pack}}^{\text{PY}}$ and S_n .

If we next specify $a(k)$ to be of hard sphere form, eq. (7) can be evaluated as a function of n only and comparison with S_n can be made (fig. 1). Under normal conditions the curves are close together; for example, for any given n in the range (0.32, 0.47), which encompasses a large majority of conceivable applications, the difference is less than $0.4 Nk_B$.

Fig. 1 Excess entropies (in units of Nk_B) versus packing fraction, η .

It follows from the above analysis that if a measured $a(k)$ is reasonably well represented by a single hard sphere form over the range of k between k_0^- and that of the principal peak, then the entropies obtained by the PY and packing methods will differ little. Such $a(k)$ behaviour is, in fact, the basis of the roughly equal qualities of the PY data of table 1 and the packing results of ref. [1].

Actually, the PY entropy for any given case is rather higher and, therefore, nearer to experiment than that obtained by the packing method. To see why, note that all systems of table 1 are near their melting points. It follows that (i) we are interested in the right part of fig. 1 and (ii) the measured $a(0)$ will be lower than that for hard spheres for any realistically chosen packing fraction [1, 4, 5]. Let us choose η , as in ref. [1], to yield the observed first peak height. By (i), we obtain a higher PY than packing entropy. But, by (ii), we expect (and find) that the hard sphere structure factor corresponding to η must be lowered a

little to match the observed $a(k)$ at $k \sim k_0$. A further increase in entropy is thereby obtained.

At higher temperatures, the left part of fig. 1 will apply and for this reason alone the PY entropy can be expected to be lower than the packing result. However, at sufficiently high T , the measured $a(k)$ rises above the hard sphere form at very low k so it is not possible to predict with certainty what happens at $k \sim k_0$. So far, we have not made any detailed calculations on real systems at elevated temperatures.

5. Discussion The packing method has achieved a measure of acceptance over the past decade and its value and usefulness seem to be established [1, 10]. On the other hand the ultimate validity of the PY method appears to be more uncertain.

The fundamental question is whether a given liquid can be adequately described by 3N normal vibrational models. The work of Bratby, Gaskell and March [11] suggests so for liquid metals but not for liquid argon. This is because of the rather different characters of the interatomic forces involved.

In this connection we emphasise that our calculation in section 4 was intended for hard spheres with, however, temperature and density dependent diameters. Such a prescription provides the same formal result for the entropy as one would obtain for absolutely invariant diameters [12], but the specific heats, for example, would differ by terms depending upon $3\eta/\partial T$.

Even if the basic hypothesis is accented, the choice of the 3N modes remains a problem. The PY selection, as we have seen, consists entirely of longitudinal phonons and indeed 3N well-defined density fluctuations appear to exist in Rb [13]. However, recently [14], the

presence of transverse vibrations has been established in a few liquid metal systems. Perhaps, in an improved theory, the phonons are of Einstein character and the polarization is unimportant. Under such circumstances the size but not the character of the higher frequencies would be important.

In the present work we have left such matters aside, however. Our aim has been to clarify the relationship between the PY method, in its unmodified form, and the packing method and this was achieved in sec. 4.

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