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Vacancy Formation Energy of Close-packed Metals Related to Liquid Structure at the Melting Point

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Data on the long wavelength limit $S(0)$ of the liquid structure factor $S(k)$ near the melting temperature T_m are examined for about twenty liquid metals. $S_{T_m}(0)/T_m$ is sensibly constant within families of chemically similar liquid metals, or equivalently $B\Omega = \text{constant}$ with B the bulk modulus and Ω the atomic volume.

Pair potential theory of the vacancy formation energy E_v , in units of $k_B T_m$ is then developed using a generalization of the hypernetted chain theory of liquid structure at T_m . This leads to the conclusion that in close-packed low melting point metals typified by Pb, the empirical value $E_v/k_B T_m \sim 10$ arises from a strong cancellation between a negative term depending on $S_{T_m}(0)$ and a positive contribution from the so-called bridge diagrams outside the core. The relation between E_v and $B\Omega$ is also briefly discussed.

1 INTRODUCTION

Present analytic theories which relate liquid structure factor $S(k)$ to a pair potential $\phi(r)$ remain at best semi-quantitative. The present paper is in this general area, but specifically for liquid metals. Our aims are first to expose substantial regularities among a whole class of liquid metals by focussing on the long wavelength limit $S(0)$ of the structure factor at the melting temperature T_m . Secondly by invoking one of the integral equation theories of liquid structure, namely the modified hypernetted chain (HNC) method,¹ we

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re-express the pair potential formula of Faber² for the vacancy formation energy E_v in close-packed metals in such a form that we can throw light on the importance, and the nature, of the so-called bridge term in the modified HNC equation. This bridge term will be shown to be quite essential for the calculation of E_v for the low melting point close-packed metals typified by Pb.

The outline of the paper is as follows. In Section 2 immediately below we present the experimental data and emphasize the regularities to be accounted for. Then in Section 3 we discuss $E_v/k_B T_m$ in terms of liquid structure theory.

2 EMPIRICAL REGULARITIES OF LONG WAVELENGTH STRUCTURE FACTOR

Table I collects experimental data for $S(0)$ and the isothermal compressibility K_T near the melting temperature T_m of some twenty liquid metals.³

TABLE I
Thermodynamic properties of liquid metals

Liquid metal	$S_{T_m}(0)$	$K_T(10^{-12}\text{cm}^2\text{dyn}^{-1})$	$B\Omega(\text{eV}/\text{atom})$
Li	0.031	(11)	1.3
Na	0.023	18.6	1.3
K	0.023	38.2	1.2
Rb	0.022	49.3	1.2
Cs	0.024	68.8	1.1
Be	0.047	(1.9)	2.6
Mg	0.025	5.06	2.9
Ca	0.035	11.0	2.8
Sr	0.031	13.1	2.9
Ba	0.036	17.8	2.4
Cu	0.021	1.49	5.0
Ag	0.019	2.11	5.3
Zn	0.015	2.50	3.6
Cd	0.011	3.24	4.1
Hg	0.005	3.75	3.8
Al	0.017	2.42	4.5
Ga	0.005	2.19	5.0
In	0.007	2.96	5.3
Tl	0.010	3.83	4.5
Sn	0.007	2.71	5.9
Pb	0.009	3.49	5.3
Sb	0.019	4.90	3.6
Bi	0.009	4.21	4.7
Fe	0.027	1.43	5.8

From the Table, the alkali metals are seen to have a low value of $B\Omega$ where $B = K_T^{-1}$ is the isothermal bulk modulus and Ω is the atomic volume, compared with all the rest. Excluding these, together with the alkaline earth metals, it will be seen that the rest of the liquids have rather constant $B\Omega$ reflected by an average value

$$B\Omega = 4.7 \pm 1.0 \text{ eV/atom.} \quad (2.1)$$

From the fluctuation theory result

$$S(0) = k_B T/B\Omega \quad (2.2)$$

we have the equivalent average statement

$$S_{T_m}(0)/k_B T_m \simeq \text{constant.} \quad (2.3)$$

We stress that, for the exceptional cases, the statements that $B\Omega$ and $S_{T_m}(0)/k_B T_m$ are constants are also true for (i) the alkali metals and (ii) the alkaline earth metals, but with substantially different constants.

3 RELATION BETWEEN VACANCY FORMATION ENERGY IN HOT METAL CRYSTAL AND LIQUID STRUCTURE AT MELTING POINT

Having exposed regularities in $B\Omega$ or equivalently $S_{T_m}(0)/T_m$, we turn now to relate liquid structure theory to vacancy formation energy. This problem was examined by Bhatia and March⁴ for rare gas crystals: here we are solely concerned with metals.

The starting point is the formula of Faber, which assumed (i) a pair potential $\phi(r)$ and (ii) that relaxation round the vacancy can be neglected. The convenient form for our purposes is that in \mathbf{r} space as given by Minchin *et al.*,⁵ namely

$$E_v + p\Omega = -\frac{1}{2}\rho \int g(r)\phi(r) \, \mathbf{dr} - \frac{1}{6}\rho \int g(r)r \frac{\partial\phi}{\partial r} \, \mathbf{dr}. \quad (3.1)$$

Using the virial expression for the pressure yields⁴

$$E_v = -\frac{1}{2}\rho \int g(r)\phi(r) \, \mathbf{dr} - k_B T_m. \quad (3.2)$$

To gain confidence in the application of Eq. (3.2) to hot close-packed metals we have taken computer simulation data⁶ for Al, and find from Eq. (3.2) that $E_v = 0.58$ eV compared with an experimental value⁷ of 0.66 eV. This agreement demonstrates the usefulness of Eq. (3.2) for close-packed metals.† For comparison, Eq. (3.2) applied to Ar yields $E_v = 0.06$ eV in good agreement with the experimental value⁹ of 0.05 eV.

To examine a series of metals such as discussed in Section 2, we shall use the form of current liquid structure theory¹ by writing, at the melting temperature T_m

$$\phi(r)/k_B T = h(r) - \ln g(r) - c(r) - b(r), \quad (3.3)$$

$c(r)$ being the Ornstein-Zernike function and $h(r) = g(r) - 1$. If the so-called bridge term, denoted by $b(r)$, is put to zero, then Eq. (3.3) reduces to the so-called hypernetted chain (HNC) theory of structure. While $b(r)$ as formally introduced in Eq. (3.3) constitutes the exact correction to that theory, in practice, of course, as will be discussed further below, it will have to be approximated for the present purposes by truncating a diagrammatic expansion at low order.

However, we proceed by inserting Eq. (3.3) into Eq. (3.2) to find

$$\begin{aligned} E_v/k_B T_m = & -\frac{1}{2} \rho \int g(r)[h(r) - \ln g(r)] dr + \frac{1}{2} \rho \int g(r)c(r) dr \\ & + \frac{1}{2} \rho \int g(r)b(r) dr - 1. \end{aligned} \quad (3.4)$$

Considering the first term on the right-hand side of Eq. (3.4), we have numerically evaluated it using experimental structure data, for Na, K, Cs, Fe, and Ar. Though ρ varies by a factor of 10 over this range of liquids, we find the result

$$-\frac{1}{2} \rho \int g(r)[h(r) - \ln g(r)] dr = -2.5 \pm 0.2. \quad (3.5)$$

To fix ideas on magnitudes, $E_v/k_B T_m$ is recorded, from experiment,^{7,10} in Table II. Typically it is seen to be ~ 10 , and hence Eq. (3.5) is only a modest

† The Faber formula will be inappropriate for vacancies in body-centred-cubic alkali metals, where Flores and March⁸ have demonstrated that ionic relaxation round the vacant site contributes a major part of the formation energy in Na and K.

TABLE II
Contributions to vacancy formation energies

Metal	$E_v(\text{eV})$	$E_v/k_B T_m$	$-\frac{1}{2}[1 + c(r=0) - \bar{c}(k=0)]$	$\bar{b} = \frac{1}{2} \rho \int g(r)b(r) dr$
Cu	1.31	11.2	6.0	9
Ag	1.11	10.5	-1.5	16
Au	0.94	8.2	-2.0	14
Zn	0.54	9.1	-14 ^a	27
Cd	0.39	7.6	-26 ^a	37
Al	0.66	8.3	-5.0	17
In	0.55	14.9	-52 ^a	70
Pb	0.50	9.7	-33	46

^a In these cases, we have used the Percus-Yevick hard sphere value for $c(r=0)$ in the absence of calculations from diffraction data. This is generally consistent with Table I of Ref. 11: namely $c(r=0)$ is approximately constant for all liquid metals studied to date, and close to the Percus-Yevick value.

contribution. Turning to the second term in Eq. (3.4), the work of Bhatia and March⁴ allows one to write

$$\frac{1}{2} \rho \int g(r)c(r) dr = -\frac{1}{2} [1 + c(r=0) - \bar{c}(k=0)] \quad (3.6)$$

From the work of Bernasconi and March,¹¹ $c(r=0)$ is available from experimental structure data, while $\bar{c}(k=0)$ is, essentially, recorded in Table I from thermodynamic measurements ($\bar{c}(k) = 1 - 1/S(k)$). Using these data the quantity (3.6) is given in Table II. The main point to note, at this stage, is the variation in sign and magnitude of this contribution.

At this point, it is easy to demonstrate that setting $b(r) = 0$ in Eq. (3.3) leads to unphysical results in that it yields negative values of E_v in most metals. An alternative might be to insert the Percus-Yevick approximation for $\phi(r)$ in Eq. (3.2). Then the work of Johnson *et al.*¹² shows in at least one example that the correct sign of E_v is obtained but that the magnitude is much too small.

In the absence of first principles calculation of $b(r)$ for metals outside the core, the region clearly involved in the term $\frac{1}{2} \rho \int g(r)b(r) dr \equiv \bar{b}$ in Eq. (3.4), we have chosen to estimate this empirically from Eq. (3.4) and the entries in Table II. The values of \bar{b} thereby obtained are recorded in the final column of Table II.

3.1 Role of bridge term as an effective repulsive potential

While we noted the variation in sign and magnitude of the second contribution on the right-hand side of Eq. (3.4), Table II shows that the corresponding contribution from the bridge term is always positive. The simplest interpretation of this result is to argue that in Eq. (3.4), $b(r)$ is playing the role of an effective repulsive potential arising from many-particle correlations. While the quantity $b(r)$ has been studied by earlier workers, and in particular by Rosenfeld and Ashcroft,¹³ their studies focussed mainly on the form of $b(r)$ inside the core. This region is eliminated in Eq. (3.4) by the presence of $g(r)$ multiplying $b(r)$.

More appropriate for our purposes is a formula valid asymptotically at large r . This has been studied in the work of Iyetomi and Ichimaru¹⁴ in connection with the classical one-component plasma and by Ballone, Pastore and Tosi¹⁵ in molten salts. This contribution to $b(r)$ can be written as

$$b^{(4)}(r) = -\frac{1}{2} \rho^2 \iint d\mathbf{r}' d\mathbf{r}'' h(r') h(r'') h(|\mathbf{r}' - \mathbf{r}''|) h(|\mathbf{r} - \mathbf{r}''|). \quad (3.7)$$

These calculations strongly suggest that $b^{(4)}(r)$, besides being repulsive, may have a non-monotonic behaviour, before decaying away to zero at sufficiently large r faster than either $\phi(r)$ or $c(r)$. Such structure in $b(r)$ from the available calculations is plainly a manifestation of indirect pair correlations due to many-particle structures.

The conclusion that there is a likelihood of such structure in $b(r)$ in some cases outside the core seems to be supported by the large contribution that \bar{b} makes to $E_v/k_B T_m$, especially in Pb, In and Cd, namely metals for which $S_{T_m}(0)$ is unusually low.

3.2 Form of direct correlation function outside core

Related to this, Bernasconi and March¹¹ in their Figure 4.1 depict schematically the form of $c(r)$ outside the core in three metals Pb, Sn and Ga with small $S_{T_m}(0)$. The negative region they exhibit is clearly related to the bridge term $b(r)$ discussed above in terms of an effective repulsive potential. Returning to Eq. (3.3), when $h(r) = g(r) - 1$ is less than 1 then $h(r) - \ln g(r)$ is $O(h^2)$ and this suggests

$$c(r) = -\phi(r)/k_B T_m - b(r) + O(h^2) \quad (3.8)$$

well outside the core. Thus $b(r)$, from the above reasoning, can be expected to make an additional contribution to $c(r)$ at intermediate r . From Table II, this contribution will be particularly large in Pb, in agreement with the deduction of Bernasconi and March.

4 SUMMARY AND CONCLUSION

Liquid metals show marked regularities just above the melting temperature T_m , exemplified by $S_{T_m}(0)/T_m \simeq$ constant within families of chemically similar metals. An equivalent statement is that $B\Omega$ is approximately constant within such families.

Then the rest of the paper has been concerned with the relation between vacancy formation energy E_v in hot close-packed metals in units of $k_B T_m$ and liquid structure theory. It is relevant to note here that proposals to relate E_v and $B\Omega$, both however in the low temperature solid, have been frequently made in the past. The present work demonstrates that E_v does not correlate closely with $B\Omega$ evaluated in the liquid state at T_m . Rather $E_v/k_B T_m \simeq$ constant is the significant correlation. From Eq. (2.2) at the melting temperature this yields $E_v/S_{T_m}(0)B\Omega \simeq$ constant. That $S_{T_m}(0)$ is not at all constant is plain from Table I.

Returning to the relation to liquid structure theory, in the low melting point close-packed metals exemplified by Pb, a large negative contribution to the ratio $E_v/k_B T_m$ as given by the Faber formula is demonstrated to arise from essentially the long wavelength structure factor $S_{T_m}(0)$. We infer therefore that a larger positive contribution must come from the bridge term $b(r)$ outside the core.

It is important to emphasize that while a first principles theory will have to start from a force field, usually described by a pair potential $\phi(r)$, structural properties are less simply related to this quantity than in simple insulating liquids like Ar. Specifically, in Ar, the direct correlation function $c(r)$ outside the core is already usefully approximated by $-\phi(r)/k_B T$, while a characterization of the depth of $\phi(r)$ is given by a constant times $k_B T_m$. In liquid metals, as we have demonstrated, neither of these correlations is close. What does emerge, in common with rare-gas systems, is that $E_v/k_B T_m$ is rather accurately constant at a value of about 10.

The final comments we want to make concern the relation of all this to the modern statistical mechanical theory of freezing.^{16,17} In this theory, the essential structural input information is the height of the principal peak of $S(k)$, which in the low melting point metals of Pb, Cd and Zn say does not take an anomalous value near freezing. This in turn suggests that the main microscopic order parameter, i.e. the first Fourier component of the crystal-line density, is not anomalous near melting, this being compatible with the constancy of $E_v/k_B T_m$.

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References

1. See, for example, E. Meeron, *J. Math. Phys.*, **1**, 192 (1960).
2. T. E. Faber, Introduction to the theory of liquid metals (Cambridge: University Press) 1972.
3. J. A. Alonso and N. H. March, *Surf. Sci.*, **160**, 509 (1985).
4. A. B. Bhatia and N. H. March, *J. Chem. Phys.*, **80**, 2076 (1984).
5. P. Minchin, A. Meyer and W. H. Young, *J. Phys.*, **F4**, 2117 (1974).
6. D. Levesque, J. J. Weis and L. Reatto, *Phys. Rev. Lett.*, **54**, 451 (1985).
7. R. W. Siegel, in Points defects and defect interactions in metals: Eds: J. I. Takamura, M. Doyama and M. Kiritani, University of Tokyo Press, 1982, p. 533.
8. F. Flores and N. H. March, *J. Phys. Chem. Solids*, **42**, 439 (1981).
9. P. Varotsos and K. Alexopoulos, *Phys. Rev.*, **B15**, 4111 (1977).
10. A. Seeger, *J. Phys.*, **F3**, 248 (1973).
11. J. M. Bernasconi and N. H. March, *Phys. Chem. Liquids*, **15**, 169 (1986).
12. M. W. Johnson, N. H. March, D. I. Page, M. Parrinello and M. P. Tosi, *J. Phys.*, **C8**, 751 (1974).
13. Y. Rosenfeld and N. W. Ashcroft, *Phys. Rev.*, **A20**, 1208 (1979).
14. H. Iyetomi and S. Ichimaru, *Phys. Rev.*, **A25**, 2434 (1982).
15. P. Ballone, G. Pastore and M. P. Tosi, *J. Chem. Phys.*, **81**, 3174 (1984).
16. T. V. Ramakrishnan and M. Yussouff, *Solid State Commun.*, **21**, 389 (1977); *Phys. Rev.*, **B19**, 2775 (1979).
17. See also N. H. March and M. P. Tosi, Coulomb liquids (Academic: London) 1984.