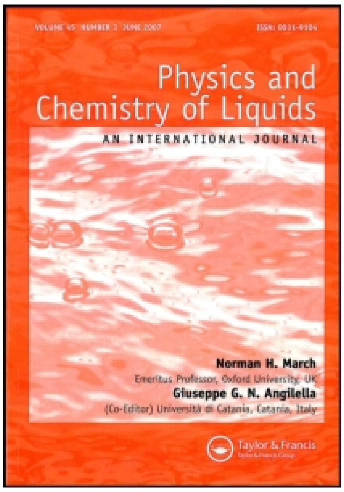

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Review Article

Liquid Structure at the Melting Temperature Related to Surface Energy and to Vacancy Formation Energy in the Hot Crystal

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A review is first given of the theoretical basis for the relation, valid near the triple point,

$$\sigma K_T = l$$

where σ is the liquid surface energy, K_T is the bulk isothermal compressibility while l measures the thickness of the liquid–vapour interface.

Attention is then focussed on the work of Alonso and March in which, for liquid metals, it is shown that $l = \alpha\{S_{T_m}(0)/k_B T_m\}^{1/2}$ where $S_{T_m}(0)$ is the long wavelength limit of the bulk liquid structure at the melting temperature T_m, while α is a constant so far determined only empirically.

A modified free electron argument is then given to relate surface energy to vacancy formation energy, for simple metals like the alkalis. Again, the argument does not take account of ionic structure. Finally therefore, a pair potential theory of the vacancy formation energy, worked out in argon to avoid the complication of density dependent pair potentials in metals, is shown to relate vacancy formation energy E_v, now in the hot solid, to bulk liquid structure at the melting point.

1 INTRODUCTION

Empirical correlations between the vacancy formation energy E_v, melting temperature T_m and isothermal compressibility K_T have been known for a long time. Such correlations are useful, but are not to be expected, from the data, to have an exact basis. In this paper, we shall summarize arguments, usually based on rather simple models that can be developed analytically, that throw light on the above correlations, plus further correlations involving liquid surface energy σ at T_m.

The outline of the review is as follows. In section 2 below, we summarize a simple density functional calculation[1] of the surface energy of a liquid metal. This leads to the result

$$\sigma K_T = \text{constant } l, \tag{1.1}$$

where l measures the thickness of the liquid-vapour interface, while the constant is a pure number of order unity. Equation (1.1) was already known to Frenkel[2] to express a strong empirical correlation between surface energy and bulk compressibility for liquids near the triple point, and the relation was rediscovered by Egelstaff and Widom.[3]

However, the density functional model used to derive (1.1) neglects ionic structure, which is probably justified only for Na and K, and thus the result $l \propto \mu^{-1/2}$ (see section 2, below eqn (2.5)) where μ is the electron chemical potential, cannot be expected to apply to a wide range of liquid metals.

Therefore, following Alonso and the writer,[4] appeal is made to the semi-empirical arguments of Miedema et al[5], which hitherto were applied principally to correlate solid-state properties. These arguments lead then, when appropriately applied to liquids, to the conclusion that the width l of the liquid–vapour interface at the melting temperature T_m involves the bulk liquid structure factor $S_{T_m}(0)$ in the long wavelength limit, which reflects, in turn, the marked short-range ionic ordering in the liquid. Thus, it will be demonstrated that

$$l = \alpha\{S_{T_m}(0)/k_B T_m\}^{1/2} \tag{1.2}$$

where the constant α, so far, is known from empirical considerations only.

Then, in section 3, a nearly free electron argument, motivated by the remarkable similarity between numerically calculated electron density profiles through a solid Al surface and round a vacancy in the same metal, is shown to correlate surface energy of simple s–p solid metals with vacancy formulation energy. This then leads naturally, following work of Bhatia and the writer,[6] to a theory of vacancy formation energy E_v, now in a hot crystal such as, say, argon near its melting point, based on a pair potential formulation due to Faber[7]: see also Minchin *et al.*[8] This theory is shown to relate $E_v/k_B T_m$ directly to bulk liquid structure. Section 4 constitutes a summary, plus some remarks on prospects for further work in the areas covered here.

2 SURFACE ENERGY OF LIQUID METALS AT THE MELTING TEMPERATURE RELATED TO BULK COMPRESSIBILITY AND THICKNESS OF LIQUID–VAPOUR INTERFACE

We shall summarize first a simple density functional calculation of the surface energy of a liquid metal, given by Brown and March.[1] This is based on three, admittedly somewhat oversimplified, assumptions, but given these it has the merit that then the entire calculation of electron density profile and liquid surface energy can be carried through analytically. The assumptions are:

i) That because ions and electrons both spill out from the liquid metal surface, electrical neutrality will make the electrostatic contribution to the potential energy V in the Schrödinger equation for the conduction electron wave functions through the liquid–vapour interface substantially smaller than it would be for a corresponding solid-state situation where the ionic density cuts off abruptly.

ii) Because of (i), the electrons move, largely independently, in their own exchange potential, taken to be the usual Dirac–Slater $\rho^{1/3}$ form[9], ρ being the electron density through the interface.

iii) The inhomogeneity in ρ through the surface can be usefully treated by adding to the bulk electron gas energy density function[al] $\varepsilon(\rho)$ a von-Weizsäcker–Kirzhnits kinetic energy correction $\lambda\hbar^2/8m \int (\nabla\rho)^2/\rho \, d\mathbf{r}$.

Thus, Brown and March[1] write for the total energy of the liquid metal in the presence of the surface:

$$E = \int \left[\varepsilon(\rho) + \frac{\lambda\hbar^2}{8m}\frac{(\nabla\rho)^2}{\rho}\right] \mathrm{d}\mathbf{r}. \tag{2.1}$$

They then employ the usual variation principle,

$$\delta[E - \mu N] = 0, \tag{2.2}$$

N being the total number of electrons, with the Lagrange multiplier μ having its usual significance as the chemical potential of the electronic charge distribution. Putting $\psi = \rho^{1/2}$, the Euler equation is found to be:

$$-\frac{\lambda\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}z^2} + \left(\frac{\partial\varepsilon}{\partial\rho} - \mu\right)\psi = 0 \tag{2.3}$$

z being measured perpendicular to the planar metal surface.

The surface energy, following Brown and March[1] is

$$\sigma = \frac{\lambda \hbar^2}{m} \int_{-\infty}^{\infty} (\psi')^2 \, dz \tag{2.4}$$

With the free electron choice $\varepsilon(\rho) = \varepsilon_{\text{kinetic}} + \varepsilon_{\text{exchange}}$, these workers integrated Eq. (2.3) to find

$$\rho(z) = \frac{\rho_0}{[1 + B \exp(z/l)]^3} \tag{2.5}$$

where ρ_0 is the (constant) density deep in the bulk liquid metal, while B is a constant of order unity, chosen to ensure neutrality. l in Eq. (2.5) evidently measures the extent of the electron spill-out into the vapour, and using Eq. (2.5) in (2.4) Brown and March regain Eq. (1.1), with $l \propto \mu^{-1/2}$, as already mentioned above.

Though this last result is too simple to work for, say, the s–p polyvalent liquid metals, or more obviously, d-electron metals, where the influence of

TABLE I

Data on surface tension, compressibility and structure at melting temperature T_m (after Ref. 4)

Metal	σ (dyn cm^{-1})		$l = \sigma K_{T_m}$	$S_{T_m}(0)$	$l \Big/ \left(\frac{S_{T_m}(0)}{N k_B T_m}\right)^{1/2}$ 10^{-3} dyn$^{1/2}$ cm$^{1/2}$
Li	410	(11)	0.45	0.031	5.0
Na	200	18.6	0.37	0.023	4.3
K	110	38.2	0.42	0.023	4.7
Rb	85	49.3	0.42	0.022	4.6
Cs	70	68.8	0.48	0.024	4.9
Be	(1350)	(1.94)	0.26	0.047	4.3
Mg	570	5.06	0.29	0.025	5.0
Ca	350	11.0	0.38	0.035	6.2
Sr	295	13.1	0.39	0.031	6.4
Ba	255	17.8	0.45	0.036	6.9
Cu	1310	1.49	0.19	0.021	4.5
Ag	910	2.11	0.19	0.019	4.5
Zn	770	2.50	0.19	0.015	3.8
Cd	590	3.24	0.19	0.011	4.0
Hg	485	3.75	0.18	0.005	3.6
Al	865	2.42	0.21	0.017	4.5
Ga	715	2.19	0.16	0.005	3.6
In	560	2.96	0.17	0.007	3.9
Tl	465	3.83	0.18	0.010	3.9
Sn	570	2.71	0.15	0.007	3.9
Pb	460	3.49	0.16	0.009	3.8
Sb	390	4.90	0.19	0.019	3.8
Bi	380	4.21	0.16	0.009	3.6
Fe	1830	1.43	0.26	0.027	6.2

ionic structure must be incorporated explicitly, the above density functional argument leads, naturally enough, to the relation (1.1), based originally on empirical correlations.

Subsequent work of Alonso and March[4] has therefore focussed all attention on understanding the way the values of l, found empirically from Eq. (1.1) by putting the constant equal to unity, vary though the entire range of liquid metals at the melting temperature T_m. These values of l are collected in Table I, where l can be seen to vary by a factor between 2 and 3, whereas the separate variations in σ and K_T over the range of liquid metals are an order of magnitude greater.

2.1 Miedema's empirical correlations extended to liquid metals at the melting point

Following Miedema and co-workers,[5] Alonso and March[4] have demonstrated, using boundary density data n_b as in the solid, and experimental values of liquid surface energy σ at T_m that

$$\sigma = \text{constant } n_b$$

is well obeyed in the liquid at T_m. Furthermore, these workers show that

$$n_b = \text{const}\left\{\frac{1}{K_T\Omega}\right\}^{1/2} \tag{2.7}$$

where K_T is the bulk liquid compressibility at T_m while Ω is the atomic volume. Using finally the well-known result of fluctuation theory that the long-wavelength limit $S(0)$ of the liquid structure factor $S(k)$ is related to K_T by

$$S_{T_m}(0) = n_i k_B T_m K_T, \tag{2.8}$$

the melting temperature having been explicitly inserted in Eq. (2.8), Eqs (1.1), plus Eqs (2.6)–(2.8), readily yield Eq. (1.2). This formula nicely accounts for the variation of l found empirically and recorded in Table I through the entire range of liquid metals.

3 VACANCY FORMATION ENERGY IN HOT CRYSTAL RELATED TO SURFACE ENERGY AND TO BULK LIQUID STRUCTURE

Having established the basis for Eqs (1.1) and (1.2), let us return to the correlations referred to in the Introduction involving E_v, T_m and K_T. That E_v and surface energy ought to be related was emphasized by the present writer,[10] by comparison of the numerically calculated electron density profile of Kohn and Lang[11, 12] for the semi-infinite jellium model of a solid

Al surface and that for a vacancy in Al determined by Stott *et al.*[13] These are indistinguishable to graphical accuracy (see Figure of Ref. 10) and motivated the nearly free electron argument outlined below. First, one writes Eq. (2.8) in terms of ionic mass M and velocity of sounds V_s, to obtain

$$S_{T_m}(0) = \frac{\gamma k_B T_m}{M v_s^2} \tag{3.1}$$

where $\gamma = C_p/C_v$ is the ratio of the specific heats.

From a linear theory of the vacancy energy E_v for a free electron metal of valency Z, one finds, with $E_f = \frac{1}{2}mV_f^2$ being the Fermi energy,

$$E_v = \tfrac{4}{15} Z E_f \tag{3.2}$$

and if this is combined with the Bohm–Staver formula[14] for the velocity of sound

$$V_s = \sqrt{\frac{Zm}{3M}}\, V_f \tag{3.3}$$

one obtains, ρ_0 being the ionic density,

$$E_v = \frac{2}{5} \frac{\gamma}{\rho_0 K_T} \tag{3.4}$$

Using Eq. (1.1), now with constant 3/4, this yields[10]

$$E_v = \frac{8}{15} \frac{\gamma\sigma}{\rho_0 l}. \tag{3.5}$$

Since l and γ, at the melting point, vary respectively by a factor between 2 and 3, and a factor $\sim\frac{3}{2}$ over the entire range of liquid metals at the melting point, a strong correlation between E_v and σ emerges according to Eq. (3.5); σ here referring to the solid.

However, since σ just above the melting point is correlated with bulk structure, from the arguments of section 2, it is clearly implied that E_v in the hot crystal near T_m should relate approximately to bulk liquid structure.

3.1 Pair potential theory of E_v in a hot, close-packed argon crystal

That this is indeed so has been demonstrated by Bhatia and March (1984) whose work, based on a pair potential approach, we shall therefore summarize below. That $E_v/k_B T_m$ for metals is a number ~ 10 emerges from the empirical correlations referred to in the Introduction. We shall see below that a number of this order can be definitely identified with well defined quantities obtainable from the bulk liquid structure factor $S(k)$ at the melting point.

To avoid the not inconsiderable complications of density dependent pair potentials appropriate to metals, we shall consider, following Bhatia and March,[6] the case of solid argon near the melting temperature. In this close-packed crystal, it is a reasonable first approximation to neglect atomic relaxation round the vacant lattice site. Then Faber[7] has given a formulation of pair potential theory in wave vector **q** space, in the language of liquid state theory. His formula for the vacancy formation energy has been expressed in **r** space by Minchin *et al.*[8] and their formulation was the starting point of the work of Bhatia and March,[6] discussed in some detail below.

Minchin *et al.* give

$$E_v + p\Omega = -\frac{n}{2}\int g\phi \, d\mathbf{r} - \frac{n}{6}\int r\frac{\partial\phi}{\partial r} g \, d\mathbf{r} \tag{3.6}$$

where $g(r)$ is the usual pair correlation function, ϕ is the pair potential, n is the atomic number density, $n = \Omega^{-1}$ while p is the pressure. Since the local coordination changes but little on melting solid argon; we assume E_v in the hot crystal can be evaluated from the liquid $g(r)$ at melting. That the term involving $\partial\phi/\partial r$ makes only a small contribution to E_v in Eq. (3.6) is clear if we invoke the virial equation of state, namely

$$p = nk_BT - \frac{n^2}{6}\int r\frac{\partial\phi}{\partial r} g(r) \, d\mathbf{r}. \tag{3.7}$$

Putting $p = 0$ yields the second term on the right-hand-side of Eq. (3.6) as $-k_BT_m$ and since $E_v \gg k_BT_m$ the $\int g\phi \, d\mathbf{r}$ is plainly the dominant term in determining E_v from Eq. (3.6).

Bhatia and March[6] now invoke the Ornstein–Zernike direct correlation function $c(r)$, related to the total correlation function $h(r) \equiv g(r) - 1$ by

$$h(r) = c(r) + n\int c(\mathbf{r} - \mathbf{r}')h(\mathbf{r}') \, d\mathbf{r}' \tag{3.8}$$

Next Woodhead-Galloway *et al.*[15] have approximated the liquid direct correlation function $c(r)$ for argon by

$$c(r) \simeq c_{\text{hard-sphere}}(r) - \frac{\phi_{\text{long-range}}(r)}{k_BT}, \tag{3.9}$$

where $\phi_{\text{long-range}}(r) \equiv \phi(r)$ outside the hard core of diameter σ. Using the Percus-Yevick solution of Wertheim[16] and Thiele[17] for $c_{\text{hard-sphere}}(r)$ and noting that this yields $c = 0$ outside $r = \sigma$, we can evidently write

$$c(r) \simeq \frac{-\phi(r)}{k_BT}, \; r > \sigma. \tag{3.10}$$

In the term involving $\int g\phi \, d\mathbf{r}$ in Eq. (3.6), $g \simeq 0$ for $r < \sigma$ and hence, putting the term in $\partial\phi/\partial r$ equal to $-k_B T_m$ as argued above, we find

$$E_v \simeq \frac{1}{2}\left[nk_B T\left\{\int g(r)c(r)\,d\mathbf{r} - \frac{2}{n}\right\}\right]_{T=T_m}, \tag{3.11}$$

or

$$\frac{E_v}{k_B T_m} = \frac{1}{2}\left(n\int c(\mathbf{r})\,d\mathbf{r} + n\int h(\mathbf{r})c(\mathbf{r})\,d\mathbf{r} - 2\right)_{T_m}. \tag{3.12}$$

Defining the Fourier transform $\tilde{c}(q)$ by

$$\tilde{c}(q) = n\int c(r)\exp(i\mathbf{q}\cdot\mathbf{r})\,d\mathbf{r}, \tag{3.13}$$

and using $h(r = 0) = -1$, we obtain

$$n\int h(r)c(r)\,d\mathbf{r} = -[1 + c(r = 0)] \tag{3.14}$$

which inserted into Eq. (3.12) yields

$$\frac{E_v}{k_B T_m} \simeq \tfrac{1}{2}\{\tilde{c}(0) - c(r = 0) - 3\}_{T_m}; \tag{3.15}$$

the principal result of the work of Bhatia and March.[6] It clearly relates $E_v/k_B T_m$ to the bulk liquid structure factor at the melting temperature T_m.

3.2 Estimates based on hard sphere approximation for direct correlation function

Using the Percus-Yevick hard sphere solution to estimate $c(r = 0)$ in Eq. (3.15) one finds

$$c(r = 0) \simeq c_{hs}^{PY}(r = 0) = -(1 + 2\eta)^2/(1 - \eta)^4 \tag{3.16}$$

where $\eta = (\pi/6)n\sigma^3$ is the packing fraction. For many simple liquids near T_m, $\eta \simeq 0.45$ and Eq. (3.15) becomes, using $\tilde{c}(0) = 1 - 1/S(0)$, $K_T = B^{-1}$ with B the bulk modulus, and Eq. (2.8),

$$\frac{E_v}{k_B T_m} + \frac{1}{2}\frac{B\Omega}{k_B T_m} \simeq 20. \tag{3.17}$$

Invoking dimensional arguments of the type involved in deriving Lindemann's melting law, $B\Omega \sim$ constant $k_B T_m$ and it turns out that $E_v/k_B T_m \simeq 10$ for argon, for which $T_m \simeq 85$ K. While agreement with experiment is somewhat better than semi-quantitative, the large number ~ 20 on the right-hand-side of Eq. (3.17) clearly has its origin in the large negative value of $c(r = 0)$ in liquid argon at T_m.

4 SUMMARY AND PROSPECTS

Insight is now possible into the basic origin of an empirical relation of type (1.1) between liquid values of surface energy and bulk compressibility at the melting temperature T_m. Furthermore, the width l of the liquid–vapour interface at T_m has been shown by Alonso and March[4] to correlate with bulk liquid structure $S_{T_m}(0)$, and thermal energy $k_B T_m$ through Eq. (1.2). The discussion in Ref. 4 outlines some basis for the Miedema correlations invoked to obtain Eq. (1.2), as well as possibilities for an eventual first principles calculation of the constant α in this relation. Plainly, however, the direct correlation function in the presence of the surface will have to be decoupled in terms of the bulk direct correlation function and the density profile to permit such a calculation to be carried through.

Further work, following up that of Minchin *et al.*[8] on the evaluation of E_v for metals will be fruitful, as will work on the relation between σ and E_v for d-electron metals. This will, no doubt, relate to the work of Lannoo and Allen,[18] who correlate E_v for transition metals to the occupancy of the d-band, and to the study of σ in these metals in the liquid state by Cyrot-Lackmann,[19] who relates σ again to the d-band occupancy.

References

1. R. C. Brown and N. H. March, *J. Phys.* **C5**, L363 (1973).
2. J. Frenkel, *Kinetic Theory of Liquids*, University Press, Oxford (1942).
3. P. A. Egelstaff and B. Widom, *J. Chem. Phys.* **53**, 2667 (1970).
4. J. A. Alonso and N. H. March, *Surface Science*, in press.
5. A. R. Miedema, P. F. de Châtel and F. R. de Boer, *Physica* **100B**, 1 (1980) and other references given there.
6. A. B. Bhatia and N. H. March, *J. Chem. Phys.* **80**, 2076 (1984).
7. T. E. Faber, *Introduction to the Theory of Liquid Metals*, Cambridge, University Press (1972).
8. P. Minchin, A. Meyer and W. H. Young, *J. Phys.* **F4**, 2117 (1974).
9. See, for example, *Theory of the Inhomogeneous Electron Gas*, Plenum, New York. Eds. S. Lundqvist and N. H. March, (1983).
10. N. H. March, in Atomic Structure and Mechanical Properties of Metals: *Proc. Int. School of Physics 'Enrico Fermi'*: Course LXI, 1976 (North-Holland, Amsterdam) p. 120.
11. N. D. Lang and W. Kohn, *Phys. Rev.* **B1**, 4555 (1970).
12. N. D. Lang, Chapter 5 in ref. 9.
13. M. J. Stott, S. Baranovsky and N. H. March, *Proc. Roy. Soc.* **A316**, 201 (1970).
14. D. Bohm and T. Staver, *Phys. Rev.* **84**, 836 (1952).
15. J. Woodhead-Galloway, T. Gaskell and N. H. March, *J. Phys.* **C1**, 271 (1968).
16. M. S. Wertheim, *Phys. Rev. Lett.* **10**, 321 (1963).
17. E. J. Thiele, *J. Chem. Phys.* **38**, 1959 (1963).
18. M. Lannoo and G. Allan, *J. Phys. Chem. Sol.* **32**, 637 (1971).
19. F. Cyrot-Lackmann, *J. Phys. Chem. Sol.* **29**, 1235 (1968).