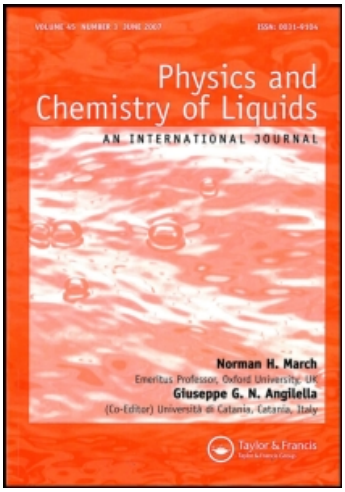

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Letter

On the Validity of Liboff's Approximate Theory of Liquid Structure for Metals near Freezing

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An approximate liquid structure theory due to Liboff is employed at the melting point of close-packed metals to calculate the vacancy formation energy in the hot crystal. Numerical calculations are proposed, from computer simulation experiments, to test this theory rather directly.

Bernasconi *et al.*[1] have used the so-called modified hypernetted chain (MHNC) theory as a basis for calculating the vacancy formation energy in hot close-packed crystals from knowledge of the liquid structure just above the melting temperature T_m. These workers have demonstrated that the bridge function of the MHNC theory, outside the core diameter, is of major importance within this framework.

Very recently, Liboff[2,3] has developed an alternative structural theory, derived from a kinetic equation for the time-dependent phase space distribution function $g(\mathbf{r}, \mathbf{p}, t)$. In the time-independent limit of this equation, one obtains[3] the approximate structure theory:

$$\frac{\partial h(r)}{\partial r} + \frac{1}{k_B T} \frac{\partial \phi(r)}{\partial r} g(r) + \frac{\rho}{k_B T} \frac{\partial F(r)}{\partial r} = 0 \tag{1}$$

where $h(r) = g(r) - 1$ is the total correlation function, $\phi(r)$ is the pair potential, while $F(r)$ is defined by

$$F(r) = \int \mathrm{d}\mathbf{r}' \phi(|\mathbf{r} + \mathbf{r}'|) g(r') \tag{2}$$

in terms of $\phi(r)$ and the pair function $g(r)$.

Using Faber's formula[4] for the vacancy formation energy E_v, in the **r**-space formulation of Minchin *et al.*[5], one finds

$$E_v = -\frac{\rho}{2}\int g(r)\phi(r)\,\mathrm{d}\mathbf{r} \tag{3}$$

which is readily seen from Eq. (2) to be given by

$$E_v = -\frac{\rho}{2}F(r=0). \tag{4}$$

This Eq. (4) links, therefore, rather directly, the Liboff Eq. (1) for the radial distribution function $g(r)$ with the vacancy formation energy E_v. This is the point we press in the development below.

Returning to Eq. (1), let us integrate this 'first order' equation to yield

$$h(r) + \frac{\rho}{k_B T}F(r) = \frac{1}{k_B T}\int_r^\infty \frac{\partial\phi(s)}{\partial s}g(s)\,\mathrm{d}s \tag{5}$$

where we have used the 'boundary condition' that the left-hand-side of Eq. (5) must tend to zero at infinity in integrating Eq. (1). It is worth noting at this point that the function on the right-hand-side of Eq. (5) appears in the approximate theory of liquid structure due to Born and Green,[6] and as there we shall denote it by $E(r)$:

$$E(r) = \frac{1}{k_B T}\int_r^\infty g(s)\phi'(s)\,\mathrm{d}s. \tag{6}$$

Putting $r = 0$ in Eq. (5), and using the condition $g(r=0) = 0$ in dense liquid metals, we obtain at the melting temperature T_m:

$$\frac{E_v}{k_B T_m} = -\tfrac{1}{2}(1 + E(r=0))_{T_m}. \tag{7}$$

Empirically, for close-packed metals,[1] $E_v/k_B T_m \sim 10$ and we can expect to be able to neglect unity relative to $2E_v/k_B T_m$ in Eq. (7).

Of course, it can properly be asked why Eq. (7) has any merit relative to the original formula (3). The first point to be made is that the approximation (7) to Eq. (3) will be good if Liboff's Eq. (1) is useful for liquid metals near freezing. Secondly, since $E(r=0)$ involves the force $-\phi'$ from Eq. (6), we expect it to depend less on the long-range behaviour of $\phi(r)$ than the Faber formula (3).

In summary, formula (7) follows directly from (i) the Faber formula (3) for close-packed metals plus (ii) the approximate Eq. (1) of Liboff. Given a consistent pair, $g(r)$ and $\phi(r)$, from computer simulation experiments, it would be of interest to evaluate both Eqs (3) and (7) for

some close-packed metals, using such liquid structural information at the melting temperature T_m. The possible relation between the shape and size of $E(r)$ and the Ornstein–Zernike direct correlation function $c(r)$ would also be of interest for such metals, in view of the study of Bhatia and March[7] on condensed phases of rare gases. In that work, it was shown that in these materials the vacancy formation energy, in units of the thermal energy $k_B T_m$, is determined solely by properties of $c(r)$ at T_m.

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