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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 $q(r, p, t)$. In the time-independent limit of this equation, one obtains³ 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

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

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

Using Faber's formula⁴ for the vacancy formation energy E_n , in the r-space formulation of Minchin *et a[.',* one finds

$$
E_v = -\frac{\rho}{2} \int g(r)\phi(r) dr \qquad (3)
$$

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

$$
E_v = -\frac{\rho}{2} F(r = 0).
$$
 (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,.* This is the point we press in the development below.

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

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

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 $E(r)$:

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

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 :

$$
\frac{E_v}{k_B T_m} = -\frac{1}{2} (1 + E(r = 0))_{T_m}.
$$
\n(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 Liboffs 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 March⁷ 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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