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Structural corrections to Stokes-Einstein relation for liquid metals near freezing

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Using recent progress relating the self-diffusion coefficient to excess entropy, structural corrections to the Stokes-Einstein relation are proposed for liquid metals near the melting temperature.

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In an earlier work [1,2] we have been concerned with a correlation between a transport property, namely the shear viscosity η of liquid metals and a thermodynamic quantity, the surface tension γ. If, as for the *s*-*p* liquid metals, a pair potential $\Phi(r)$ represents a useful approximation to the interionic force field (see Ref. [3] for monovalent Na and Ref. [4] for the divalent metal Be), then an early formula of Fowler [5] expresses γ in terms of $\Phi(r)$ and the pair correlation function $g(r)$ of the bulk liquid

$$\gamma = \frac{\pi}{8}\rho^2 \int_0^\infty r^4 g(r) \frac{\partial \Phi(r)}{\partial r} dr, \tag{1}$$

where ρ is the particle number density. But for Na and Be, knowledge of the experimental $g(r)$ for a given thermodynamic state is enough to determine $\Phi(r)$ for that state, as demonstrated explicitly by Reatto *et al.* [6] for the case of sodium, using x-ray measurements [7] of $g(r)$. Thus, Eq. (1) then shows that, at least approximately, γ is a functional of $g(r)$ and the number density ρ, for a specific thermodynamic state. While this should occasion no surprise for such a thermodynamic property, the correlation between γ and η we exhibited in an earlier work [1,2] leads us to conclude that the transport property η is also, to a useful approximation, a functional of number density ρ and pair correlation function $g(r)$, at least for simple *s*-*p* metals like Na.

It is our purpose here to invoke now the important study of Dzugutov [8], who proposed, on the basis of computer simulation using pair potentials of various types, a relation between a further transport property, namely the self-diffusion coefficient D, and the excess entropy, this later quantity being the total entropy minus the ideal gas contribution. The result of Dzugutov, followed up in later work [9,10], reads

$$D = 0.194 a^4 g(a) \rho \left[\frac{\pi k_B T}{M}\right]^{1/2} e^{S_2/k_B}, \tag{2}$$

where k_B is the Boltzmann constant, T the temperature, and M is the atomic mass. Here S_2 denotes the two particle approximation to the excess entropy [11,12], given in terms of the radial distribution function $g(r)$ by

$$\frac{S_2}{k_B} = -2\pi\rho \int_0^\infty \{g(r)\ln g(r) - [g(r)-1]\} r^2 dr \tag{3}$$

while a in Eq. (2) is the principal peak position of $g(r)$. For completeness we notice at this point that (a) some aspects of the Dzugutov result in Eq. (2) have appeared in the literature previously [13], and (b) corrections to the two-particle entropy approximation in Eq. (3) have been discussed by Laird and Haymet [14].

Since our main purpose here is to refine the Stokes-Einstein relation by introducing structural corrections via $g(r)$, we first stress that, to date, there is no direct analog of Eqs. (2) and (3) for the shear viscosity η. But fortunately, in a very early study, Brown and March [15] used physical arguments appropriate to liquid metals which were based fundamentally on the Green-Kubo transport theory, to evaluate η at the melting point T_m. They derived via this route the shear viscosity at the melting temperature as

$$\eta_{T_m} = c[(k_B T)^{1/2} M^{1/2} \rho^{2/3}]_{T=T_m}, \tag{4}$$

where c is a constant. Actually, in studies in the 1930s, Andrade [16] proposed a similar formula using kinetic theory but, as Faber [17] points out in his book, such a treatment is no longer adequate.

Evidently, then, by combining Eq. (4) with Eqs. (2) and (3), but now evaluated specifically at $T=T_m$, we can form the Stokes-Einstein combination, denoted x_m following March and Tosi [18]

$$x_m = \left[\frac{D\eta}{k_B T \rho^{1/3}}\right]_{T_m}. \tag{5}$$

The result for x_m then takes the form, after utilizing Eqs. (4) and (2)

$$x_m = c_1 [a^4 \rho^{4/3} g(a) e^{S_2/k_B}]_{T_m}, \tag{6}$$

where c_1 is a constant. This expression hence gives structural corrections to the Stokes-Einstein combination at the melting temperature, appearing on the right hand side of Eq. (5). While Eq. (6) constitutes the main result of the present study, we shall attempt in what follows to gain insight into likely reasons why x_m defined in Eq. (5) is rather constant for *s*-*p* electron liquid metals. To quantify this later statement, Table 1 in the paper of March and Tosi [18] shows that x_m^{-1} has an

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average value of 47 for five *s-p* metals, with a scatter of ±5.

Let us begin with the combination $a^4\rho^{4/3}g(a)$ appearing in Eq. (6) at the melting temperature T_m. We invoke then Eq. (6) of Bhatia and March [19] to write

$$a^2 g(a)\Delta r = \tfrac{1}{3}a^3 - \tfrac{1}{3}R_A^3[1 - S(0)] \tag{7}$$

to be utilized here at $T = T_m$. Δr in Eq. (7) is to be identified with the root mean square displacement of the ions, which in turn is a measure of the half width of the principal peak of $g(r)$, at position a. But Lindemann's law of melting, according to Faber [17], gives $(\Delta r/R_A)_{T_m} \approx 0.2$, where the mean interatomic separation R_A is related to the number density, $\rho = 3/4\pi R_A^3$. Since $a \approx 1.8R_A$, $\Delta r/a \approx 0.11$ at T_m, and hence from Eq. (7) it follows that

$$g(a) \approx 3.0 - 0.06[1 - S(0)]_{T_m}. \tag{8}$$

But the long wavelength limit $q \rightarrow 0$ of the structure factor $S(q)$ at T_m for *s-p* liquid metals is very much less than unity. Hence, since $a^3 \propto R_A^3 \propto \rho^{-1}$, it follows that $a^4\rho^{4/3}g(a)$ appearing in Eq. (6) at T_m is a constant from Eq. (8). It is worth remarking here that Eq. (8) is the counterpart in r space of the so-called Verlet rule that freezing occurs when the structure factor $S(q)$ has its principal maximum at a height of 2.8. No claim is made here that the r space criterion is (a) of comparable accuracy to the Verlet rule or (b) of easy access to experimental check (Reatto *et al.* [6] get $[g(a)]_{T_m} = 2.43$ for liquid metal Na, which is substantially lower than the "prediction" (8)).

But naturally, given the proposal of Eq. (6), the most likely variation of x_m through the *s-p* metals will arise from the factor e^{S_2/k_B}. To seek a little further insight here, it is natural enough to write Eq. (3) as the sum of two parts

$$\left(\frac{S_2}{k_B}\right)_{T_m} = \left(\frac{S_u}{k_B}\right)_{T_m} - \frac{1}{2}[1 - S(0)]_{T_m}. \tag{9}$$

Here, S_u denotes the contribution to S_2 from the product $g(r)U(r)$, where $U(r)$ denotes the potential of mean force defined by the Boltzmann-like relation

$$g(r) = e^{-U(r)/k_B T}. \tag{10}$$

While one form of Lindemann's law gives $[S(0)]_{T_m} = \text{const}$ for liquid metals, this is quite approximate. More importantly, at T_m it is known from the fluctuation theory result that $S(0) = \rho k_B T K_T$, where K_T is the isothermal compressibility, is such that $[S(0)]_{T_m} \ll 1$, and hence the second contribution on the right hand side of Eq. (9) is essentially constant.

To date, the only evaluation of S_u/k_B near to the melting point from diffraction experiments is that made by Wallace [20] for Na, who used Waseda's data to yield $(S_u/k_B) = -2.6(\pm 0.2)$. For Na, this is therefore the dominant contribution to S_2/k_B appearing in the basic Eq. (6). But why might this be rather constant among *s-p* electron metals? We conjecture, but of course, experiment will be needed eventually to allow confirmation or refinement, that $\int g(r)U(r)d^3r$ might correlate closely with $\int g(r)\Phi(r)d^3r$. Thus, Tankeshwar and March [21] have compared graphically $U(r)$ and $\Phi(r)$ for Na near freezing, using $U(r)$ given by Eq. (10) from $g(r)$ taken from x-ray diffraction studies [7]. It is then clear from Fig. 1 of Tankeshwar and March [21] that $|\int g(r)U(r)d^3r| < |\int g(r)\Phi(r)d^3r|$ but that they may well be related to one another via a numerical factor, as their overall shapes are quite similar. From the work of Bhatia and March [22], $[\int g(r)\Phi(r)d^3r]_{T_m}$ is related, for Na say, to the vacancy formation energy E_v in the hot solid near T_m, E_v being scaled with the thermal energy of melting $k_B T_m$. This ratio is ≈ 9 from experiment for close-packed *s-p* metals, as can be seen, for example, from Rashid and March [23], with again a scatter, however, $\approx \pm 2$. These considerations show how it may be possible still to understand using Eq. (6) the relative constancy of x_m^{-1} of around 50 for five *s-p* metals, with a scatter of ±10%. Of course, the true test of the practical utility of Eq. (6) must await further "experimental" data on the pair correlation function $g(r)$ near melting: we trust the present proposal (6) will stimulate further careful diffraction measurements near freezing on other *s-p* electron metals.

Our final comment concerns materials with force fields transcending pair potential representations, and in particular *d*-electron liquid metals such as Ni or W. It should not be assumed that the above arguments take over simply to such cases: appeal being made to pair potential simplifications frequently in the present study.

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