Generalized Stokes-Einstein relation for liquid metals near freezing

N. H. March[1] and M. P. Tosi[2]

[1]Oxford University, Oxford, England, and Department of Physics, University of Antwerp, RUCA, Antwerp, Belgium
[2]Istituto Nazionale di Fisica della Materia and Classe di Scienze, Scuola Normale Superiore, I-56126 Pisa, Italy

Deviations from a Stokes-Einstein relation between the self-diffusion coefficient D and shear viscosity η for liquid metals near freezing are shown to correlate with a net transit parameter ξ introduced recently by Wallace [Phys. Rev. E **58**, 538 (1998)] in a two-parameter model of D. Brief comments are made on the single exception of In, for the seven liquid metals for which suitable experimental data are available. [S1063-651X(99)07108-1]

Wallace [1] has recently analyzed self-diffusion data for some ten liquid metals using a two-parameter model. One of his parameters, a frequency, is related directly to crystal properties. The second and dimensionless parameter, which Wallace terms a net transit parameter, is then extracted from experiments measuring the self-diffusion coefficient D, and his finding is that this parameter, termed ξ [see Eq. (2) below], varies between 1/2 and 1 for the liquid metals he considers.

The purpose of this Brief Report is to relate this variation of ξ, entering Wallace's independent ion model of self-diffusion to deviations from the Stokes-Einstein relation for liquid metals near freezing.

In this context, it is relevant to note that Zwanzig [2] has already proposed a generalization of the Stokes-Einstein result for dense liquids, having the form

$$D \eta / k_B T \rho^{1/3} = 0.0658(2 + \eta / \eta_l) = C'. \qquad (1)$$

In Eq. (1), η and η_l are, respectively, the shear and longitudinal viscosities, while ρ is the atomic number density. One of the problems in using Eq. (1) for liquid metals near freezing is that experimental data on η_l are not currently available. A second point, noted by March and Alonso [3], is that, while C' as defined by Zwanzig through Eq. (1) has bounds that can vary between 0.13 and 0.18 in accord with data on a variety of organic liquids, these bounds are violated for some liquid metals at the melting temperature T_m.

With this background, we return to the analysis of experimental data for the self-diffusion coefficient for ten liquid metals by Wallace. As he points out, the model he uses seems at first sight closely related to that of Zwanzig, which led that author to propose Eq. (1). Zwanzig supposed that the atoms in a subvolume of the liquid perform oscillations about equilibrium positions, before jumping to new equilibrium sites. He assumes that the net effect of jumping is to destroy coherence of the oscillations within the subvolume. Zwanzig then describes the atomic motion by a sum over harmonic modes about a fixed equilibrium configuration, multiplied by a factor $\exp(-t/\tau)$, where τ is the waiting time.

However, Wallace stresses that, whereas in the model of Zwanzig the diffusive jump itself is an essentially instantaneous part of the atomic motion, in the Wallace model, within a volume consisting of an ion plus its near neighbors, diffusive jumps can occur several times within a Debye period. Second, in his independent-ion model, the transits that represent the diffusive jumps are incorporated within the description of the atomic motion. The model leads to a two-parameter formula for D at temperature T that reads

$$D = \frac{4 k_B T}{\pi M \omega} \left(\frac{\xi}{2 - \xi} \right). \qquad (2)$$

The frequency ω, within this model is linked with a well-defined rms frequency related to a Brillouin-zone average of the square of quasiharmonic phonon frequencies. Wallace then uses experimental data for D at T_m (also away from $T = T_m$, but we use here only the melting point analysis) to extract ξ at T_m, say ξ_m. For reasons that will emerge below, we take the inverse ξ_m^{-1} of his extracted values in Table I for ten liquid metals at T_m. The values of ξ_m^{-1} are seen to range from 1 to 2. Our aim below is to supply an interpretation of these results in terms of the Stokes-Einstein approach.

One of us [2] used the early work of Brown and March [4], which estimated $D_{BM} \approx k_B T / M \omega_d$, with ω_d a suitable Debye frequency, to write at T_m,

$$D_{T_m} = \text{const} \times \frac{T_m^{1/2}}{M^{1/2} \rho^{1/3}}. \qquad (3)$$

Hence we rewrite Eq. (1) in the approximate form

TABLE I. Transport data on liquid metals at the freezing point.

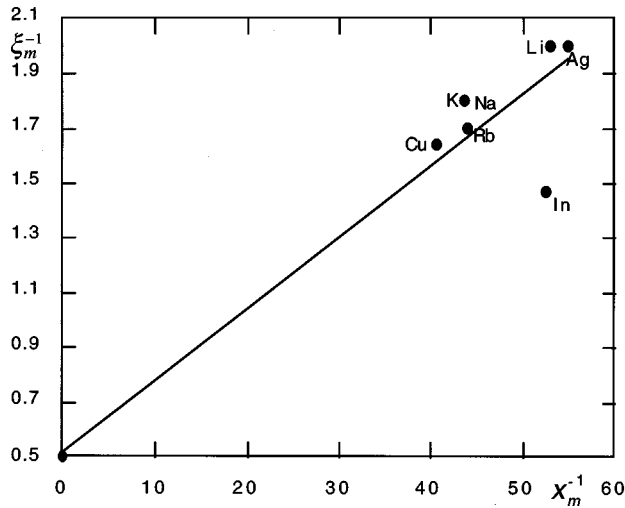| Metal	ξ_m^{-1}	D_{T_m} (10^{-5} cm²/s)	η_{T_m} (cp)	T_m (K)	ρ_m (g/cm³)	x_m^{-1}
Li	2.0	5.96	0.60	453.7	0.515	53.(0)
Na	1.8	4.23	0.69	371.0	0.925	43.(7)
K	1.8	3.70	0.54	336.4	0.829	43.(5)
Rb	1.7	2.72	0.67	312.6	1.479	44.(0)
Cu	1.6(4)	3.98	4.1	1357.	8.000	41.(7)
Ag	2.0	2.55	3.9	1234.	9.346	54.(9)
Pb	1.6(7)	1.74		600.6	10.68	
Zn	1.9(2)	2.03		692.7	6.58	
In	1.4(7)	1.68	1.9	429.8	7.02	52.6
Hg	1.0(9)	0.97		234.3	13.7	

FIG. 1. A plot for ξ_m^{-1} against x_m^{-1} (in arbitrary units) for seven liquid metals near freezing.

$$D_{T_m} = \text{const} \times \frac{T_m^{1/2}}{M^{1/2}\rho^{1/3}} \left(\frac{\xi_m}{2-\xi_m} \right). \qquad (4)$$

But Brown and March also obtained the shear viscosity from Green-Kubo-type arguments as

$$\eta_{T_m} = \text{const} \times T_m^{1/2} M^{1/2} \rho^{1/3}, \qquad (5)$$

a formula that goes back to Andrade [5], who however used kinetic theory arguments that would no longer seem adequate, as mentioned by Faber [6].

Multiplying Eqs. (4) and (5) to lead to a Stokes-Einstein form immediately yields

$$x_m \equiv (D\eta/k_B T\rho^{1/3})_{T_m} = \text{const} \times \left(\frac{\xi_m}{2-\xi_m} \right), \qquad (6)$$

this Eq. (6) defining the quantity x_m. Rewriting Eq. (6), one is led to the result

$$\xi_m^{-1} = \frac{1}{2} + \text{const} \times x_m^{-1}, \qquad (7)$$

and thus the variation of ξ_m^{-1} shown in Table I from Wallace's two-parameter model is linked with the variation of $D\eta/k_B T\rho^{1/3}$ at the melting temperature T_m.

Figure 1 shows a plot of Eq. (7), the ordinate ξ_m^{-1} going from 1/2, the predicted intercept in Eq. (7), to the maximum value 2.0 appearing in Table I. As the constant in Eq. (7) is not predicted by the preceding analysis, x_m^{-1} is in arbitrary units in Table I and Fig. 1. Though these is scatter around the straight line prediction, for all but liquid metal In the results are quite compatible with Eq. (7).

It will be of obvious interest for the future, when suitable experimental data become available, to add other liquid metals to the plot in Fig. 1. It is relevant, however, to note from Wallace's data, reflected directly in the second column of Table I, that In and Hg are the ''exceptional'' cases of the ten liquid metals listed there. Apart from possible error bars on the experimental data used, one might ask whether other methods of estimating the frequency ω in Wallace's model might have to be considered. Notwithstanding these questions, the main proposal of the present study is that Eq. (7) constitutes a step forward in representing deviations from a Stokes-Einstein relation in liquid metals near freezing.

[1] D. C. Wallace, Phys. Rev. E 58, 538 (1998).

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[4] R. C. Brown and N. H. March, Phys. Chem. Liq. 1, 141 (1968).

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[6] T. E. Faber, An Introduction to the Theory of Liquid Metals (Cambridge University Press, Cambridge, England, 1972).