Self-Diffusion at the Melting Point: From H_2 and N_2 to Liquid Metals

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A nominal lower bound to the mean free diffusion time at the melting point T_m was obtained earlier which provided a factor-two type estimate for self-diffusion coefficients of the alkali halides, alkali metals, eight other metals, and Ar. The argument was based on the classical Uncertainty Principle applied to the solid crystal, whereby maximum-frequency phonons lose validity as collective excitations and degenerate into aperiodic, single-particle diffusive motion at the melting point. Because of the short time scale of this motion, the perfect-gas diffusion equation and true mass can be used to obtain the self-diffusion coefficient in the Debye approximation to the phonon spectrum. This result for the self-diffusion coefficient also yields the scale factor that determines the order of magnitude of liquid self-diffusion coefficients, which has long been an open question. The earlier theory is summarized and clarified, and the results extended to the more complex molecular liquids H_2 and N_2. It is also demonstrated that combining Lindemann's melting law with the perfect-gas diffusion equation estimate yields a well-known empirical expression for liquid-metal self-diffusion at T_m. Validity of the self-diffusion estimate over a melting temperature range from 14 to more than 1300 K and over a wide variety of crystals provides strong confirmation for the existence of the specialized diffusive motion at the melting point, as well as confirmation of a relation between the phonon spectrum of the solid crystal and diffusive motion in the melt.

KEY WORDS: melting; melting point; phonons; self-diffusion; uncertainty principle.

1. INTRODUCTION

It was proposed earlier that the frequency–time Uncertainty Principle (UP) could be applied to zone-boundary phonons at the melting point in the

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Debye approximation to phonon theory. The outcome of this application was a derivation of Lindemann's law of melting, as well as putative lower bounds on self-diffusion coefficients and ionic conductivities [1–4]. Estimates were obtained in the earlier work for self-diffusion coefficients of metals (Li, Na, K, In, Cu, Zn, Ga, Ag, Sn, Hg, and Pb) which, on average, were in better than factor-two agreement with experiment. Closer agreement was obtained for the interdiffusion sum for several of the alkali halises. Consistent agreement at this level is significant because prediction of a diffusion coefficient at the melting point is a particularly sensitive test; diffusion coefficients typically change by several orders of magnitude across the melting point [5]. The only low-temperature case studied in the earlier work was Ar, for which the lower bound self-diffusion coefficient, at about one-third the experimental value, was the poorest estimate found. Thus, it is interesting to compare the UP estimate for other low-temperature cases as well as more complex molecular structures. It is also of interest to know how the UP estimate relates to other formulas for the self-diffusion coefficient. The present article addresses both these issues by application to the molecular liquids H_2 and N_2 and by derivation of the relation of the UP estimate to a well-known empirical formula for the self-diffusion coefficient of liquid metals discussed by Iida and Guthrie [6]. Toward this end, a summary and clarification of the theory are given in the next section, followed by a discussion of the Iida-Guthrie empirical formula and application to H_2 and N_2.

2. ZONE-BOUNDARY MODE FAILURE AND SELF-DIFFUSION AT THE MELTING POINT IN THE DEBYE APPROXIMATION

We make use the classical UP in the form [7, 8]

$$\Delta\omega_q \tau(T, \omega_q) \geqslant 1/2 \tag{1}$$

where $\tau(T, \omega_q)$ is the lifetime of a phonon of angular frequency ω_q at temperature T due to anharmonic interactions, and $\Delta\omega_q$ is the frequency uncertainty associated with a phonon of angular frequency ω with polarization and wave vector denoted q. The uncertainty of a phonon's frequency must be bounded in the Debye approximation by the Debye (angular) frequency ω_D. Because of this it follows from Eq. (1) that

$$\omega_D \tau(\omega_D, T) \geqslant 1/2 \tag{2}$$

An analytic estimate of the high-temperature three-phonon U-process

transition rate which dominates the lifetime of high-temperature phonons was given by Roufosse and Klemens (RK) [9]:

$$\tau_{\text{pp}}(\omega, T)^{-1} = \frac{2\sqrt{2}\,(6\pi^2)^{1/3}\,\gamma^2 k_{\text{B}} T \omega^2}{M v^2 \omega_{\text{D}}} \tag{3}$$

In this expression, calculated for sc crystals, M is atomic mass, v is the Debye mean velocity (determined by the elastic constants of the crystal), and γ is the Grüneisen constant.

This formula shows $1/\tau(\omega, T)$ to increase monotonically with both ω and T. Thus, τ of Eq. (2) reaches its minimum value on both independent variables at the Debye zone boundary (zb) ω_{D}, and the melting temperature T_{m}, the maximum values that both these variables can have in a Debye solid. The frequency uncertainty cannot vanish. On the liquid side of the melting transition (zb) phonons are not valid excitations so we expect that Eq. (1) cannot be satisfied on the liquid side for zb phonons. It is suggested, therefore, that Eq. (1) passes through equality near or at the melting point for zb phonons. That is, we assert that, in the Debye approximation,

$$\frac{1}{\tau(\omega_{\text{D}}, T_{\text{m}})} \cong 2\omega_{\text{D}} \tag{4}$$

There is some experimental evidence [10–12] that phonon line widths due to anharmonicities become comparable to phonon frequencies for maximum lattice frequency phonons. Substituting the RK transition rate from Eq. (3) into Eq. (4) yields Lindemann's melting law:

$$k_{\text{B}} T_{\text{m}} \cong \frac{T_{\text{D}}^2 V_0^{2/3} A}{C^2} \tag{5}$$

where V_0 is atomic volume, T_{D} is Debye temperature, A is atomic weight, and

$$C^2 \equiv (72)^{1/2}\,\pi^3 \hbar^2 \gamma^2 L k_{\text{B}}^{-2} \tag{6}$$

where L is Avagadro's number. As used herein, C differs from the conventional Lindemann constant [13] by a factor $(k_{\text{B}}^{1/2} L^{1/3})$ which simplifies its units and makes it, in cgs units, 1.0078 times the conventional value. The numerical values of C were shown [1] to be in reasonable agreement with those inferred experimentally for a set of bcc crystals, using thermal expansion values of the Grüneisen gammas and a modest adjustment to account

for the difference between the bcc crystal structure and the sc structure used in the RK calculation. It should be noted that, although the coefficient of the RK transition rate is the result of strong approximations, an accurate value is obtainable in principle. It follows that a more accurate value of the Lindemann constant C can also be obtained in principle from the above arguments.

The Bloch electron–phonon interaction relaxation time, subjected to the Heisenberg UP in the Debye approximation, leads to analogous results [3]. In particular, the electron–phonon relaxation time inferred from the high-temperature Bloch resistivity formula [13] by means of the classical kinetic conductivity expression can also be used in Eq. (4) to derive Lindemann's law. The coefficient C^2 is, of course, made up of different parameters (including the Fermi velocity). However, upon evaluation it is numerically similar to the coefficient given above as determined by the RK formula. The accuracy of the Bloch formula is limited by the spherical Fermi surface, Debye approximation, and Bloch electron–phonon interaction approximations, just as the RK result is limited by the use of spherical wave vector surfaces, the Debye approximation, and the approximation of an average Grüneisen constant. It should be noted that Eq. (4) does not require the Lindemann hypothesis of a maximum vibrational amplitude, yet yields the same result.

The interpretation posed earlier for the validity of Eq. (4) involves the transformation of collective phonon motion into single-particle motion at the melting point. That is, it is assumed that atom, ion, or molecule single-particle motion on the time scale $(2\omega_D)^{-1}$, determined by Eq. (4), replaces motion previously described by phonon normal modes, which are no longer valid excitations. This single-particle motion must be localized since it can no longer be represented by traveling-wave normal modes and is no longer periodic. Thus, it can be expected to lead to or accompany loss of long-range order and the melting transition. Modes of lower frequency do not violate the UP because of the strong frequency dependence of the relaxation time. Hence, it is assumed that they retain their integrity until the melting transition is completed (and even then, some modes may exist in the liquid state). However, the single-particle, aperiodic motion of time scale $(2\omega_D)^{-1}$ is now superimposed on the lower-frequency motion for which the phonon model retains some validity. On the basis of this heuristic model, $\tau(\omega_D, T_m)$ of Eq. (4) is identified with the mean free collision time for the aperiodic "partially decoupled" motion that appears at T_m and leads to self-diffusion and (usually) expansion of the lattice. This mean free collision time is sufficiently short that the perfect-gas scattering law applies [14].

Upon identifying τ of Eq. (4) with single-particle random (diffusive)

motion of ions at the melting point, it can be inserted into the perfect-gas diffusion law $D_m = k_B T \tau / M$ to obtain

$$D_m \cong \frac{\hbar}{2M} \left(\frac{T_m}{T_D} \right) \tag{7}$$

Because of Eq. (2), the result given in Eq. (7) above was stated as an inequality[2] in the earlier work. This is not strictly correct, however, because the association of the high-frequency phonon motion with single-particle motion at the melting point is a heuristic rather than an exact step. The numerical results obtained earlier as well as those obtained herein nevertheless bear out the fulfillment of an inequality in almost all cases. Therefore, we will sometimes refer to Eq. (7) as a "nominal lower bound," as well as an approximation. It was noted earlier [2] that $\hbar/(2M)$ has the order of magnitude of liquid self-diffusion coefficients because T_m and T_D usually have the same order of magnitude. This is not a quantum effect; $\hbar$ appears because of the use of the Debye temperature. If the Debye frequency were used instead, $\hbar$ would not appear. However, this convenient coefficient with numerical magnitude of liquid self-diffusion coefficients would also not appear. The use of the true mass in Eq. (7) as opposed to an effective mass [14] is discussed in Ref. 2 and is based on the short time scale involved as is the justification for use of the perfect-gas formula, noted above.

It was found [1, 2] that Eq. (7) predicts self-diffusion coefficients consistently close to, but somewhat less than, experiment (about a factor two or better) for the 11 metals listed above in Section 1 and Ar. These results utilized room-temperature values of T_D. Since diffusion coefficients vary by several orders of magnitude across the melting point, this accuracy is not unfavorable. For alkali halides, the interdiffusion sum of the positive and negative ion contributions to diffusion is given by Eq. (7) with the mass M replaced by the reduced mass $\bar{M}$. With this replacement, Eq. (7) predicts results for NaCl, RbCl, CsCl, and NaI comparable to those for metals cited above [1, 2]. Because interdiffusion leads to electrical conductivity in molten salts, the ionic conductivity σ of 18 alkali halides at T_m was also computed according to the above method with average accuracy of about 18% below the experimental values [2]. That is, σ was evaluated according to

$$\sigma = \frac{Ne^2}{k_B T} (D_+ + D_-)$$

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[2] The sense of the inequality of Eq. (12) of Ref. 2 was erroneously reversed; the expression should read that D is greater than or equal to the rhs.

The fact that these values tend to be below the experimental values is consistent with the statement given above that the numerical results of Eq. (7) typically display a lower-bound behavior.

The Debye approximation to the phonon spectrum of solids is used exclusively in the present article. Lifting of this approximation by use of the true phonon spectrum and discrimination between different phonon polarizations is discussed in the prior work [2–4]. It is expected to be a formidable task requiring large-scale numerical computation on crystal models.

3. EMPIRICAL FORMULA FOR LIQUID METALS

In a recent book [6], Iida and Guthrie (IG) quote an empirical expression for D_m of liquid metals at the melting point. Their expression is equivalent to

$$D_m = f \left(\frac{k_B T_m}{A} \right)^{1/2} V^{1/3} \text{ cm}^2 \cdot \text{s}^{-1} \tag{8}$$

where f has the value 3.0×10^2. In this expression, A is atomic weight, V is the liquid molar volume at the melting point T_m, and the explicit Boltzmann constant k_B is inserted in Eq. (8) to render f dimensionless. According to IG, this relationship has been known for some time. Although their discussion (Sect. 7.6.2 of Ref. 6) leaves the impression that no theoretical basis exists for this formula, the authors have already quoted (Eq. 7.16 of Ref. 6) a hard-sphere theory formula due to Faber [15] which has this identical form for an appropriate choice of hard-sphere packing fraction. However, it is true that Faber's formula is partly based on molecular dynamics calculations (cf. Eq. 3.12 of Ref. 15) and, thus, may be considered quasiempirical. In their Eq. 7.17, IG evaluate Faber's formula at the melting point with packing fraction equal to 0.45 to obtain the equivalent of $f = 340$. Now, Faber recommended the packing fraction 0.46, which yields $f = 310$, whereas the choice of 0.465 yields the precise $f = 300$ as selected by IG in their empirical expression (Eq. 7.26 of Ref. 6). The difference between the latter two values is not significant.

As we now proceed to demonstrate, a theoretical basis can be identified for Eq. (8), which is unrelated to hard-sphere theory or molecular dynamics. By elimination of T_D between Eq. (5) and Eq. (7), one obtains Eq. (8) with f determined as

$$f = \frac{\hbar L^{2/3}}{2k_B C} = 2.7236 \times 10^4 C^{-1} \tag{9}$$

Since Lindemann C's usually exceed 100 (typically 100–140), the coefficient f given by Eq. (9) generally underestimates the IG value of 300, again showing consistency with the nominal lower-bound behavior noted above. Using Eq. (6) for C as obtained in the derivation of Lindemann's law, the formula for f can be reduced further to

$$f = \frac{L^{1/6}}{72^{1/4}\pi^{3/2}\gamma} \tag{10}$$

In this form, the IG coefficient f is seen to depend only on Avagadro's and Grüneisen's constants. Equation (10) yields the value $f = 283.25/\gamma$, which agrees with the IG value of 300 for a γ of 0.94. It is interesting that this is the gamma value for Li and is close to the values for other bcc metals, for which the present theory gives reasonably good agreement. It must be kept in mind that Eq. (3) does not account for differences in crystal structure. If such differences were accounted for, one would obtain different coefficients f for each crystal structure. Most gamma values are larger than 0.94; such larger values of gamma lead to smaller values of f, which again is consistent with the lower-bound nature of the theory.

Table I shows four numerical examples for three liquid metals and H_2, where f is computed from Eq. (9). Debye temperatures of Na and K, and of Ga, are room-temperature values from Martin [16] and Gschneidner [17], respectively, while that for ortho-H_2 is from Egelstaff et al. [18]. The molar volume used for hydrogen was calculated from the solid density at 13 K given in Ref. 19. This will introduce a modest error due to the difference between the solid molar volume and the liquid volume required by the IG formula. The true value of f will be smaller than the value given in Table I. The Lindemann C values were computed from Eq. (5) using the Debye and observed melting temperatures shown in Table I, and thus these

Table I. Examples of the Liquid-Metal Empirical Self-Diffusion Equation Coefficient f Computed from Eq. (9) Based on the Perfect-Gas Self-Diffusion Formula and Lindemann's Melting Law[a]

Species	T_D (K)	T_m (K)	C (s × K)	$10^{-2}f$
Na	149	371	109	2.5
Ga	89	303	97	2.8
K	87	336	108	2.5
H_2	80	14	91	3.0

[a] T_D and T_m are the Debye and melting temperatures, respectively, and C is the experimentally determined Lindemann constant.

values of C may be considered experimental values. The values of f are all close to 300, and smaller, continuing the lower-bound behavior of the theory (recalling that the value for H_2 is greater than it should be due to the use of the solid molar volume).

4. SELF-DIFFUSION OF H_2 AND N_2

The objective of this section is to extend application of UP-phonon breakdown theory plus onset of single-particle diffusive motion at T_m beyond the species and temperature ranges considered in Refs. 1 and 2. Toward this end, self-diffusion coefficients at the melting point for H_2 and N_2 as given by Eq. (7) are compared with experiment in Table II. The experimental self-diffusion coefficient and Debye temperature for ortho-H_2 (at 15 K) are from Egelstaff et al. [18], the self-diffusion coefficient for N_2 at the triple point is from Hansen and McDonald [20], and its Debye temperature was obtained from Busch and Schade [21]. The results for RbCl and Cu, repeated from Ref. 1, are also shown in Table II for comparison. (The sources of T_D and the experimental D_m for RbCl and Cu are given in Ref. 1.) Again, reasonable accuracy is demonstrated and the nominal lower-bound behavior of the theory is confirmed for these cases.

The factor two or better agreement between the UP estimate and experiment is seen to extend across a remarkable range of temperature as well as types of crystals. It demonstrates a strong connection between the phonon spectrum of the solid crystal and the diffusive particle motion in the liquid at the melting point. Because the UP estimate for D_m is inversely proportional to the Debye frequency and usually up to a factor two too small, it follows that the use of a frequency up to a factor two smaller than the Debye frequency in Eq. (7) would yield agreement between theory and

Table II. Comparison Between Theory and Experiment for Self-Diffusion Coefficients of Two Molecular Liquids, One Alkali Halide, and Cu Near the Melting Point[a]

Species	T_m (K)	T_D (K)	D_m(th)	D_m(exp)
H_2	14	80	2.8	4.7
N_2	63	70	1.0	1.0
RbCl	995	162	7.7	8.7
Cu	1358	332	2.0	4.0

[a] Self-diffusion coefficients D_m(th) are nominal lower bounds, while D_m(exp) are experimental values. The units are $10^5 \, cm^2 \cdot s^{-1}$.

experiment. It is interesting that this is the range of frequency of the transverse zb modes in most crystals, and failure of transverse modes is often believed to be associated with melting.

5. CONCLUSION

Earlier theory of breakdown of zone-boundary phonons at the melting point and onset of single particle motion is revisited and shown to apply to the molecular liquids H_2 and N_2 and to yield a well-known empirical law connecting self-diffusion of liquid metals to the melting temperature. It provides factor two or better agreement between experiment and theory for self-diffusion coefficients and related quantities over an exceptionally wide range of melting temperature and crystal species and type. This wide range of agreement supports the proposed partial model of microscopic particle dynamics at the melting point. It also confirms a strong relation between the crystal phonon spectrum on the solid side of the melting point and diffusive particle motion on the liquid side of the melting point. In addition, the theory yields the scale factor $\hbar/(2M)$ that determines the order of magnitude of liquid self-diffusion coefficients, which has long been an open question [14].

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