Electrical Conductivity, Self-Diffusion, and Volume Expansion of Alkali Halides at the Melting Point[1]

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In an earlier paper, Heisenberg's uncertainty principle was invoked at the melting point T_m of crystalline solids to provide fundamental justification for Lindemann's melting law and to compute diffusion coefficients of several alkali halides. The uncertainty principle defines breakdown of Debye zone boundary (ZB) phonons as valid collective excitations when phonon energies and line widths due to anharmonicity become comparable at T_m. Upon breakdown, random, high-frequency single-particle motion or "partial decoupling" of crystal ions sets in. Lifetimes of these single-particle ZB motions are determined from the "minimum-uncertainty product" inequality by assuming that it becomes an equality at T_m for ZB phonons. The present paper addresses improved formulation of that work and extended application to ionic electrical conductivities of 18 molten alkali halides at T_m. It is shown that use of the Debye model produces an approximate lower bound to the mean free time, not the unconstrained direct estimate previouslu implied. This feature is generally reflected in results for ionic conductivities and alkali halide diffusion coefficients for which comparison experimental data were found. However, in spite of this lower-bound formulation and the simple nature of the computation, the results compare favorably with experiment. A model of random single-particle harmonic motion superimposed on the lower-frequency collective motion is proposed to account for volume expansion accompanying the partial decoupling for hard-sphere ions. Experimental comparisons for 15 alkali halides show the decoupling volume change to account largely for the total volume change of melting (in the hard-sphere approximation), yielding a closer agreement with experiment than recent calculations aimed explicitly at the total volume change.

KEY WORDS: alkali halides; diffusion; electrical conductivity; melting; zone boundary phonons; volume expansion.

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1. INTRODUCTION

It was pointed out earlier [1] that the Heisenberg uncertainty principle (HUP) could be invoked at the melting temperature T_m of crystalline solids to provide fundamental justification of the Lindemann melting law [2, 3] This justification was based on the observation that, for maximum-lattice frequency phonons, phonon line widths due to anharmonicities become comparable to phonon energies at T_m [3, 4, 5]. The high-temperature three-phonon transition rate given by Roufosse and Klemens [6] was used in conjunction with the HUP to derive Lindemann's law in the context of the Debye approximation. The approach of Ref. 1 is reviewed and clarified herein and applied to self-diffusion and electrical conductivity of molten alkali metal halides at the melting point. Additional results for monatomic melt self-diffusion coefficients are discussed briefly to indicate generality for the theory. A "partial decoupling" of maximum-frequency lattice modes at T_m is postulated wherein single-particle motion replaces collective motion on the time scale of these modes. Heuristic arguments are presented to account for this effect. A model is presented which associates a volume increase with the partial decoupling for hard-sphere atoms (ions), since they will take up more volume while in random relative motion than when moving synchronously. This volume increase turns out to approximate the total increase in fusion for alkali halides, which are known to display hard-sphere behavior. Thus, partial decoupling may account for the transition from the solid to the liquid phase, since the volume increase associated with fusion is sufficient to allow the atoms to slip past each other, engage in free diffusion, and break down the long-range crystalline order.

2. USE OF THE UNCERTAINTY PRINCIPLE AT THE MELTING POINT

We start with the HUP for energy and lifetime uncertainties [7, 8] associated with a phonon of angular frequency ω_q (here q is meant to imply wave vector and polarization) reduced to the form

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

where $\tau(T, \omega_q)$ is the lifetime due to all anharmonic interactions. An ideal crystal is assumed and T is absolute temperature in kelvins (K). The transition rate $1/\tau(T, \omega_q)$ increases linearly with T above the Debye temperature T_D [3, 6]. Hence, the line width must similarly increase according to Eq. (1). This inequality is the "minimum-uncertainty product" form of the HUP (for which the equality is attained only for Gaussian distributions of

the values of the uncertainties [7, 8]). We let Ω_q represent the maximum frequency of the branch associated with q, so that $\Delta\omega_q \leqslant \Omega_q$. Equation (1) then yields

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

Expressed in terms of the transition rate, this expression,

$$1/\tau(T, \omega_q) \leqslant 2\Omega_q \tag{3}$$

establishes an upper limit to the total anharmonic transition rate. Since anharmonic phonon transition rate expressions generally increase monotonically with ω_q, we assume that the maximum transition rate is achieved for $\omega_q = \Omega_q$. Our model of melting is therefore based on the assumption that

$$1/\tau(T_m, \Omega_q) \cong 2\Omega_q \tag{4}$$

for longitudinal branches. This is, of course, the condition referred to above that expresses the loss of validity of phonons in the mode q as collective excitations. (If it should happen that $1/\tau \to A\Omega_q$ as Ω_q approaches its maximum value, where A is independent of q, then this mode failure condition will be met simultaneously for all relevant modes. Although such behavior would explain the suddenness of the melting transition and is possible [9], it would be difficult to establish in general even if true.) We further assume that single-particle motion sets in for time intervals of the order of $1/(2\Omega_q)$ when Eq. (4) is satisfied, since such intervals are no longer included in the spectrum of collective excitations.

　　To obtain a mean lifetime for the proposed single-particle motion, we need to average $\tau(T_m, \Omega_q)$ of Eq. (4) over all longitudinal Ω_q of the Brillouin zone. Calling this mean τ_M, Eq. (4) yields

$$\tau_M = \langle 1/(2\Omega_q) \rangle \tag{5}$$

where the angle braces signify the appropriate average. Because of the complexity of phonon spectra and of the Brillouin zone geometry, we must now resort to the Debye approximation [2] for further progress. We then have only to deal with a spherical zone with the maximum frequency and wave number on its surface, the Debye zone boundary (ZB). In this approximation, and by appeal to the fact that a harmonic average is less that a direct average (Schwartz's inequality), Eq. (5) may be written

$$\tau_M \geqslant 1/(2\langle \Omega_q \rangle) \cong 1/(2\omega_D) \tag{6}$$

where ω_D is the Debye angular frequency. Thus, the inverse of twice the Debye frequency provides an approximate lower bound for the mean free

time of the postulated single-particle motion. The distance λ_{ZB} which a Debye ZB phonon can travel in time $(2\omega_D)^{-1}$ is

$$\lambda_{ZB} = v/(2\omega_D) = a/[2(6\pi^2)^{1/3}] \tag{7}$$

where a^3 is the volume per atom and v is the Debye mean velocity [10]. Thus, at high temperatures, ZB phonons are highly localized [6, 11]. Although the precise numerical value of the Debye result in Eq. (7) cannot be taken seriously, the order of magnitude of localization to an interatomic distance is important.

It is interesting to compare the distance traveled by an ion and by a ZB phonon at high temperatures. Consider a Na$^+$ ion moving with thermal velocity $(3k_B T)^{1/2}/M = 1.15 \times 10^5$ cm·s^{-1} at the melting temperature of NaCl. In the time $(2\omega_D)^{-1} = 1.26 \times 10^{-14}$ s given by the NaCl Debye frequency, it would move a distance $d = 1.49 \times 10^{-9}$ cm. The mean free path λ_{ZB} of the Debye ZB phonon has the value $0.13a$, which is 3.7×10^{-9} cm for $a = 2.87$ Å computed from the NaCl lattice constant extrapolated to the melting point [18]. Distances of this order of magnitude are insufficient, on the average, to permit escape of the Na$^+$ ion from its cage of nearest neighbors, as the radius of its nearest-neighbor shell is about 2.8 Å.

High-frequency diffusive motion has been discussed theoretically by Egelstaff [13] in terms of an "effective mass" which accounts for the impeding effect of neighbors. However, we assume that the atoms remain trapped within their nearest-neighbor cages until there is sufficient high-frequency, single-particle motion of all the atoms to expand the lattice so that each can escape, *viz.*, there is sufficient room such that each can slip past the other, at which point the liquid state has been achieved. Thus, we assume that free diffusion occurs without interference from neighbors because of the short time and distance intervals involved. This permits use of the true mass and allows us to avoid ambiguous or adjustable parameters.

We close this section with a heuristic description of the breakdown of maximum-frequency mode validity. Recall that phonon theory starts from specification of the motion of an atom in a crystal relative to a lattice point i, where

$$\vec{r}_i = \vec{l}_i + \vec{u}_i \tag{8}$$

is the position vector to the atom from some coordinate origin fixed in the crystal [2]. The vector to the lattice point i is denoted by $\vec{l}_i$, so that $\vec{u}_i$ is the vector displacement of the atom relative to the lattice point. Quantization of the relative displacements $\vec{u}_i$ lead to phonon theory. The normal

modes of cooperative oscillation are traveling-wave Fourier components of the vectors $\vec{u}_i$. For a time average taken over $\vec{r}_i$, denoted by $\langle \vec{r}_i \rangle$, including any number of complete periods of oscillation, the result will always be $\langle \vec{r}_i \rangle = \vec{l}_i$, since $\vec{l}$ is the equilibrium position or center of oscillation, and the periodic $\vec{u}_i$ obey $\langle \vec{u}_i \rangle = 0$. However, as T is increased, the highest-frequency modes will ultimately fail to sustain propagating periodic motion because of the increasing anharmonicity. As indicated above, we assume that this occurs at the melting point. The Fourier amplitudes of the highest-frequency traveling waves must die out, or become "overdamped" [5]. However, it will still be possible to perform a localized Fourier expansion of the motion of the $\vec{r}_i$ which will include (in general) all frequencies. The atom at i will not stop moving with high-frequency components. But the high-frequency components will no longer be normal modes of the phonon field. The expansion of the $\vec{u}_i$ in terms of traveling waves will now be incomplete. A complete description of the motion must contain some localized terms comprising single-particle motion, which, in general, will not be periodic. The time average $\langle \vec{r}_i \rangle$ mentioned above will no longer produce a constant value of $\vec{l}_i$ independent of the averaging period. Non-zero contributions will appear from the aperiodic motion which will add incrementally to the $\vec{l}_i$ and thus represent irreversible changes in atomic positions, *viz.*, diffusion. We assume that smaller-q, lower-ω_q motion continues to exist as valid collective (phonon) excitations since the anharmonic transition rate decreases strongly with decreasing ω_q [6].

3. A HARD-SPHERE MODEL FOR THE MELTING TRANSITION

We have proposed above that longitudinal ZB phonons lose validity as collective excitations and that single-particle motion sets in on their time scale at T_m. We now discuss the nature of the single-particle motion. The motion of an atom trapped in a cage of nearest neighbors, while participating in single-particle motion at a high frequency, suggests that the transition to the liquid state may occur through an intermediate stage of independent Einstein oscillator behavior at or near the frequency of the no-longer-valid ZB phonons. In this picture, ZB collective oscillations first decouple into individual, localized oscillators vibrating independently of each other. Such independent vibrations sweep out more volume than the previous synchronous vibrations. So in this step, the lattice must expand. We can estimate the expansion for hard spheres, and if it turns out to approximate the fusion volume expansion, atoms can slip past each other, lose their long-range order, and arrive at the liquid state. This model is frankly heuristic; we are unable to produce a mathematical description for a transition from collective phonon modes to independent oscillator modes

[14] even though it is universally accepted that collective behavior loses importance toward high temperatures and the independent Einstein oscillator description becomes valid.

We conjecture the following scenario for breakdown of the highest-frequency phonon modes as $T \to T_m$, $\tau^{-1}(\omega_D) \to 2\omega_D$, and the ZB phonon line width becomes equal to the frequency $2\omega_D$. (We refer, for simplicity, to these highest-frequency modes as ZB modes because of our use of the Debye approximation.) The mean free path of the ZB phonons decreases to an atomic distance so that the phonon "coalesces" onto an atom as the mode breaks down. The energy $\hbar\omega_D$ of the coalescing phonon sets the atom into local harmonic oscillation in its ground state with energy of the order of $\hbar\omega_D$, the energy of the "dying" phonon. This oscillation is superimposed upon the collective modes of motion below the ZB which retain their validity. The localized high-frequency independent oscillations, as mentioned above, will expand the lattice due to their random, asynchronous character. (We assume only simple crystal structures.) When the expansion of the lattice reaches the point that atoms have sufficient space to slip past each other, they will do so due to their random "thermal" motion. Thermal is placed in quotes, because the high-frequency single-particle motion involves only a small portion of the total degrees of freedom of the assembly, so it is not thermal in the sense of being able to attach a value $k_B T/2$ to this energy for each spatial dimension. However, this motion must be driven by the underlying reservoir of thermal energy present in the assembly of particles. Once the particles are able to slip past each other, the liquid state has been reached, a meaningful distinction between oscillations and "jumps" of single-particle motion on the time scale of ω_D is probably lost [13], and we can think of the atoms as moving as free particles on this time scale, as will be discussed more fully in the sequel.

Let us now focus on a single atom in its cage of neighbors on the solid side of the melting transition. To describe its motion we employ an isotropic oscillator model [15]. The ground-state energy of such an oscillator is $(3/2)\hbar\omega$, where ω is its fundamental frequency, which we take to be the Debye frequency. The rms amplitude r_0 of this oscillator is given by

$$r_0 = [3\hbar\omega_D/(2K)]^{1/2} = [3\hbar/(2M\omega_D)]^{1/2} \qquad (9)$$

where the spring constant $K = M\omega_D^2$ and M is the atomic mass. As an example of magnitude, r_0 for the Na^+ ion in NaCl turns out to 3.22×10^{-10} cm. We superimpose the oscillator motion on the normal lattice structure by adding this rms amplitude to each of the "hard-sphere" atomic radii along the "direction of contact" of the unit cell. The hard-

sphere approximation is relatively good for the alkali metal halides [14]. Adding an increment r_0 for each of the positive and negative ion radii along the cube edge of the fcc NaCl cell will increase the lattice constant a_0 by the amount δa_{dc}, where

$$\delta a_{dc} \cong 2[r_0(+) + r_0(-)] = 2\hbar[M_+^{-1/2} + M_-^{-1/2}]/(k_B T_D)^{1/2} \qquad (10)$$

and $(+)$ and $(-)$ refer to the positive and negative ions. With an increase in lattice constant of δa_{dc}, the relative change in volume of the unit cell is

$$\delta V_{dc}/V = (a_0 + \delta a_{dc})^3/a_0^3 - 1 \qquad (11)$$

The "decoupling volume effect" we wish to describe is obtained by inserting δa_{dc} from Eq. (10) into Eq. (11). The results of this calculation for 15 alkali metal halides are shown in Table I. For comparison, experimental values of $(\delta V_f/V)$, the volume change of fusion are also shown [16, 17]. The lattice constants and Debye temperatures used in the calculation are also given. Nine of the lattice constants (indicated by citations) are values

Table I. Comparison of Volume Change $\delta V_{dc}/V$, Due to Independent Oscillations Superimposed on the Lattice, with Experimental Volume Change upon Fusion $(\delta V_f/V)$ exp.[a]

Species	a_0(Å)	T_D(K)	δa_{dc}(Å)	$(\delta V_{dc}/V)$	$(\delta V_f/V)$ exp
LiF	4.078[b]	700	0.393	0.318	0.294[d]
LiCl	5.13[c]	390	0.473	0.316	0.262[d]
LiBr	5.49[c]	247	0.534	0.321	0.243[d]
LiI	6.00[c]	175	0.604	0.333	0.202[e]
NaF	4.711[b]	473	0.344	0.344	0.274[d]
NaCl	5.729[b]	303	0.369	0.206	0.250[d]
NaBr	5.96[c]	209	0.378	0.203	0.224[d]
NaI	6.46[c]	153	0.410	0.203	0.186[d]
KF	5.33[c]	317	0.373	0.225	0.172[d]
KCl	6.395[b]	226	0.372	0.185	0.173[d]
KBr	6.696[b]	166	0.360	0.170	0.166[d]
KI	7.166[b]	126	0.378	0.167	0.159[d]
RbCl	6.723[b]	162	0.370	0.174	0.143[d]
RbBr	7.036[b]	130	0.329	0.147	0.135[d]
RbI	7.460[b]	102	0.333	0.140	0.123[e]

[a] The lattice constant is denoted a_0, T_D is the Debye temperature in kelvins, and δa_{dc} is the change in the lattice constant according to Eq. (10) in the text.
[b] Extrapolated from the formula of Srivastava and Merchant [18].
[c] Busch and Schade [12].
[d] Ubbelohde [16].
[e] Rubcic and Rubcic [17].

extrapolated to the melting point from the formulas of Srivastava and Merchant [18]; the remainder are room-temperature values [12]. Little error is introduced thereby due to partial cancellation of the thermal expansion correction to $\delta V_{dc}/V$. The Debye temperatures are room-temperature, elastic-constant values [19]. Equation (11) has an average (absolute) error of 18% compared to the listed experimental values, whereas the direct calculation of $(\delta V_f/V)$ by Agrawal et al. [20] has a corresponding average error of 36%.

4. SELF-DIFFUSION ON THE LIQUID SIDE OF THE MELTING POINT

Since breakdown of ZB modes into superimposed single-particle oscillations leads to a consistent description of the melting transition, we now apply these concepts to diffusion in the liquid at T_m. Once the liquid state has been achieved, there is no longer a barrier to free diffusion on a short time/distance scale because there is sufficient space for the atoms to slide past each other [17, 20]. Egelstaff discusses the concept of effective mass noting that the true mass is used in computations of Brownian motion, but for a liquid, a larger mass is required because the diffusing atom must displace its neighbors. However, comparing diffusion mean free times of the present approach with those of Egelstaff, we find ours to be about two orders of magnitude smaller. For example, $\tau_M \gtrsim 1/(2\omega_D)$ is about 3×10^{-14} s for metallic Na, compared to Egelstaff's [13] diffusive time step of $1.0–1.6 \times 10^{-12}$ s. Similarly, for Ar, his other example, our value (based on a Debye temperature of 105 K [22]) is 3.6×10^{-14} s, compared to Egelstaff's reported 10^{-12} s. Thus, we feel justified in using the true mass, as in the Brownian motion case, rather than a larger effective mass. In any event, it is well established that for high-frequency, short-distance motion in liquids, the atoms move as in a perfect gas [13, 21]. Accordingly, we use the perfect-gas diffusion equation $D_{pg} = k_B T\tau/M$ to determine the self-diffusion coefficient. With $\tau = \tau_M \gtrsim 1/(2\omega_D)$ as in Eq. (6), we obtain the result

$$D \lesssim \frac{\hbar}{2M}\left(\frac{T_m}{T_D}\right) \tag{12}$$

Table II compares the results of this formula with experiment for four alkali halides for which experimental data were found [24]. The Debye temperatures used are the same as those in Table I for the three halides common to both tables. For CsCl, the value $T_D = 170$ was used [25]. The individual ionic coefficients show a factor-of-two type of agreement, while

Table II. Comparison of Theory and Experiment for the Ion Self-Diffusion Coefficients of Four Alkali Halides at the Melting Point[a]

Species	D_+(th)	D_-(th)	D_+(exp)	D_-(exp)
NaCl	4.9	3.2	8.76	6.32
RbCl	2.3	5.5	4.65	4.07
CsCl	1.3	4.8	3.33	3.69
NaI	8.4	1.5	6.50	3.66

[a] The units are $cm^2 \cdot s^{-1} \times 10^5$. $D_\pm$(th) is from Eq. (12) in the text, and $D_\pm$(exp) from Young and O'Connell [24].

the interdiffusion sums $(D_+ + D_-)$, except for NaCl, are in much closer agreement [1]. This is not surprising since both T_D and T_m are joint properties of the ions in combination. It is more surprising that the agreement is as close as it is, since diffusion coefficients typically change by several orders of magnitude across T_m. In view of the magnitude of this discontinuity, prediction of a diffusion coefficient at the melting point is a particularly sensitive test. Cotterill et al. [26, p. 413] discuss in detail the orders of magnitude change in D across the fusion transition.

Since there are not many experimental data on alkali metal halide diffusion coefficients, we present in Table III some comparisons for mon-

Table III. A Comparison of Theory and Experiment for Some Monatomic Liquid Self-Diffusion Coefficients at the Melting Point[a]

Species	T_m(K)	T_D(K)	D(th)	D(exp)
Ar	83.8	105[b]	0.63	1.8[d]
				1.6[e]
Cu	1358	332[c]	2.0	4.0[f]
Zn	693	231[c]	1.5	2.0[d]
Ga	303	89[c]	1.6	1.6[d]
Ag	1235	213[c]	1.7	2.6[f]
Sn (white)	505	184[c]	0.74	2.0[d]
Hg	234	37[c]	1.0	0.93[d]
Pb	601	81[c]	1.1	2.2[d]

[a] The units of D are $cm^2 s^{-1} \times 10^5$. D (th) was obtained from Eq. (12) in the text. The melting and Debye temperatures T_m and T_D, respectively, are given in kelvins.
[b] Keeler and Batchelder [22].
[c] Gschneidner [27].
[d] Faber [28].
[e] Egelstaff [13].
[f] Nachtrieb [21].

atomic liquid elements. Elastic-constant values of T_D from Gschneidner [27] were used where available. For Ar, Keeler and Batchelder's value [22] was used, and for Hg the electrical resistivity value given by Gschneidner was employed. The experimental values of D cited in Table III are from Faber [28], Nachtrieb [21], and Egelstaff [13] and are all quoted as being measured at or very near to the melting point.

In this comparison of eight monatomic cases, four show more-or-less factor-of-two-type agreement as is the case for the alkali halide ions in Table II. The others are in relatively close agreement. In all cases, the theoretical values are less than or equal to the experimental values (subject to the effect of round-off), as befits the formulation of Eq. (12) as an approximate lower bound. Results for Li, Na, K, and In were given previously [1], with a 10–20% difference between experiment and theory.

Although Eq. (12) is derived to be valid strictly at the melting point, it is interesting that Nachtrieb [21] identified several liquid metals (Sn, In, Hg) for which D continues to increase linearly with T above T_m for a wide span of temperatures. Hence, Eq. (12) may have more general validity than our derivation implies. There is another interesting aspect to this result. The ratio T_m/T_D does not vary greatly for solids, usually being less than 10. Hence the order of magnitude of D at the melting point is principally established by the factor $\hbar/(2M)$. The numerical magnitude of the self-diffusion of liquids is well known to be of the order of 10^{-5} cm$^2 \cdot$ s^{-1} [13, 26, 29], rising typically from about 10^{-9} cm$^2 \cdot$ s^{-1} just below T_m to 10^{-5} just above [13]. Nachtrieb [21] states that liquid metals, "like all normal unassociated liquids, have diffusion coefficients that lie in the narrow range 10^{-4} to 10^{-5} cm$^2 \cdot$ s^{-1}." Egelstaff [13] discusses this order of magnitude at length (phenomenologically) and states that the physical reasons why this magnitude is characteristic of liquids are not clear. Taking his two main examples of Na and Ar, we find that $\hbar/(2M)$ is equal to 1.38×10^{-5} and 0.79×10^{-5} respectively, compared to 4.3×10^{-5} and 1.6×10^{-5}, respectively, for D. Thus, we see that a quantum scale factor provides the physical basis of the observed order of magnitude.

A more precise statement can be made in the case of a perfect gas. We write the energy-time HUP for a free particle of energy $E = Mv^2/2$, and lifetime between collisions Δt as

$$E \geqslant \Delta E \geqslant \hbar/(2\Delta t) \tag{13}$$

where ΔE is the uncertainty in E. This can be taken as less than the total energy E under classical conditions (*viz.*, a sufficiently large container for not too many atoms). If we now take a long-term time average ($\langle \ \rangle$) over the particle motion, we get

$$3k_B T \geqslant \langle \hbar/\Delta t \rangle \geqslant \hbar/\langle \Delta t \rangle \tag{14}$$

where the second step follows from Schwartz's inequality. Labeling $\langle \Delta t \rangle \equiv \tau$, the mean free collision time, relation (14) can be written as

$$D_{pg} = \frac{k_B T \tau}{M} \geqslant \hbar/(3M) \tag{15}$$

in terms of the perfect-gas diffusion coefficient D_{pg} introduced earlier. Thus, a fundamental basis exists in the context of perfect-gas theory for the order of magnitude of D for liquids. However, it makes sense only if the diffusive motion in liquids is of a sufficiently high frequency to obey the perfect-gas relation. Real gases tend to have self-diffusion constants several orders of magnitude greater than the lower limit of inequality (15). It is interesting that this limit is reached at the liquid state where the atomic potential energy, neglected for the perfect gas, becomes comparable to its kinetic energy. Furthermore, the limit is violated for crystals, where potential energy dominates the motion. The reason for this behavior is that $\Delta E \ll E$ generally, for gases, but is of the order of E for diffusive motion in liquids, as we have shown above. For solids, diffusive motion occurs for individual atoms trapped in relatively deep potential wells with energies well above the average atom energy, so that the uncertainty in E for such a particle is very large and one cannot form an inequality such as (13). These results for free diffusion on the short time scale dictated by the HUP may provide a way out of the dilemma posed by Egelstaff [13]. He presents a thorough, fundamental discussion of the two approaches to diffusion, the "jump" model and free diffusion, and points out that neither approach is satisfactory. But he argues (somewhat curiously) that these approaches span the totality of diffusion phenomenology because, although representing opposite extremes, they predict approximately the same unrealistic and somewhat inconsistent results [13, p. 131].

5. ALKALI HALIDE CONDUCTIVITY AT THE MELTING POINT

The classical kinetic formula for electrical conductivity σ is [14]

$$\sigma = Ne^2\tau/M \tag{16}$$

where N represents concentration of charge carriers—ions in the present case, e is the electric charge on the carriers, and M is the carrier mass. This kinetic conductivity σ is not independent of the diffusion constant D. Their connection, known as the Nernst–Einstein relation, is given by Lidiard [30] as

$$\sigma = \frac{Ne^2}{k_B T}(D_+ + D_-) \tag{17}$$

Because of this connection, one expects a good prediction of D to imply a similar result for σ, and vice versa. Considerably more experimental data exist for ionic conductivities than for self-diffusion coefficients for alkali halides at the melting point. Thus, it is worthwhile to evaluate σ in order to obtain broader comparison with experiment. If we sum Eq. (16) over the $(+)$ and $(-)$ ions, set $\tau = (2\omega_D)^{-1} \cong \tau_M$, and evaluate the fundamental constants, the result can be expressed as

$$\sigma \gtrsim \frac{5.896 \times 10^{-19}}{V_M T_D \bar{M}} \tag{18}$$

in $\text{mho} \cdot \text{cm}^{-1}$. The molar volume of the liquid at T_m in cm^3 is denoted V_M, and $\bar{M}$ is the reduced mass of the ion pair in gms. Table IV shows a comparison of the prediction of Eq. (18) with experiment for 18 alkali halides. The values of V_M as well as the experimental values of σ were obtained from Young and O'Connell [24]. The average (absolute) difference between theory and experiment for these cases is 18%. Four percent of this average difference is due to the worst case alone, LiI. This

Table IV. Comparison of Theory and Experiment for Ionic Conductivities in $\text{mho} \cdot \text{cm}^{-1a}$

Species	V_M	$\sigma(\text{th})$	$\sigma(\text{exp})$
LiF	14.33	6.97	8.27
LiCl	28.24	5.56	5.72
LiBr	34.35	6.56	4.91
LiI	42.81	7.21	3.97
NaF	21.49	3.36	4.76
NaCl	37.52	2.24	3.48
NaBr	44.00	2.16	2.76
NaI	54.70	2.18	2.30
KF	30.41	2.88	3.51
KCl	48.79	1.73	2.15
KBr	55.95	1.46	1.65
KI	67.91	1.39	1.33
RbCl	53.78	1.63	1.56
RbBr	60.85	1.09	1.14
RbI	73.08	0.93	0.91
CsF	41.33	2.26	2.47
CsCl	60.31	1.24	1.15
CsI	81.62	0.58	0.72

[a] The theoretical values $\sigma(\text{th})$ have been calculated from Eq. (18) in the text. The experimental values $\sigma(\text{exp})$ along with the liquid molar volumes V_M (in cm^3) are from Young and O'Connell [24].

case and LiBr are also the only ones for which $\sigma(\text{th})$ is significantly larger than $\sigma(\text{exp})$, again showing consistency with the formulation of $(2\omega_D)^{-1}$ as an approximate lower bound to the mean free collision time τ_M. The fact that asymmetry of the ion masses affects diffusive motion in alkali halides, particularly those of Li^+, has been noted by Hansen and McDonald [23].

6. CONCLUSION

We have presented herein a combination of fundamental statements based on the Heisenberg uncertainty principle and heuristic scenarios. The justification and outcome of the diffusion and electrical conductivity discussions are the strongest. The substantial range and quality of these predictions make them difficult to challenge. The Einstein oscillator melting transition model is perhaps the weakest part, depending particularly upon a vivid imagination, although involving only conventional ideas when taken one at a time. It is hard, however, to dismiss the alkali halide volume expansion results as accidental in view of the range and quality of the experimental comparison. It is important to note that the melting-point diffusion and electrical conductivity theory advanced is independent of the Einstein oscillator approach to the melting transition. Those portions of the present work do not appear to depend at all upon how the liquid-state transition is achieved.

However, the difficulty of formulating a complete fundamental theoretical justification of the suggestions advanced in this article is substantial. The mixture of single-particle and collective description required for such a justification requires new theory of a formidable nature. It is hoped that the approach presented herein will stimulate this difficult undertaking.

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