Ionic diffusion in superionic-conductor melts

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Abstract. The self-diffusion coefficients D_+ and D_- of the two ionic species in molten AgI, CuCl, CuBr and CuI are evaluated and contrasted with those calculated for molten NaCl. The evaluation adopts a simple model for liquid-state dynamics, earlier proposed by Zwanzig to justify the Stokes–Einstein formula for monatomic fluids, and by suitable approximations relates the self-diffusion coefficients to pair potentials and to the pair structure of the melt. The results offer an interpretation for molecular dynamics data showing that, whereas for a 'normal' system such as NaCl the ratio D_+/D_- in the melt is of order unity, a sizeable difference between D_+ and D_- persists in salts melting from a fast-cation conducting solid. This difference is explicitly related to liquid structure through differences in the structural backscattering of cations by cations and of halogens by halogens. The calculated magnitudes of D_+/D_- are quite satisfactory, while the absolute magnitudes of D_+ and D_- are in good agreement with the data only for those salts (AgI, CuBr and NaCl) in which the masses of the two ionic species are not greatly different.

1. Introduction

The melts of copper halides and silver iodide, which show fast-ion conduction by cations in the high-temperature solid phase, have recently been modelled by suitable effective pair potentials [1]. The main features of the liquid pair structure in the model agree with those observed in molten CuCl in neutron diffraction experiments [2, 3], i.e. (i) the cation–cation distribution function is almost structureless except for excluded volume, and (ii) the cation–anion and anion–anion distribution functions qualitatively resemble those of 'normal' ionic melts such as NaCl. The model has also been applied in computer simulation studies of ionic mobilities and ionic conductivity in the liquid state [4]. The self-diffusion coefficients of cations and anions in the melt are found to differ by large amounts. For instance, on comparing the results for CuCl with those of a similar study [5] on NaCl near their respective freezing temperatures, one finds (in units of $\times 10^{-5}$ cm^2 s^{-1}) $D_{Cu} = 10.0$ and $D_{Cl} = 2.5$ in molten CuCl at 773 K against $D_{Na} = 9.77$ and $D_{Cl} = 8.55$ in molten NaCl at 1164.5 K. Thus, both structurally and dynamically it appears that traces of the cationic disorder and superionic behaviour of the high-temperature solid persist in the melt near freezing. The aim of this work is to examine theoretically the relationship between the mass transport coefficients and the nature of the liquid structure.

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As is well known, the self-diffusion coefficient is a macroscopic manifestation of the autocorrelations of the single-particle velocity in time. Much progress in understanding the dynamics of dense gases and liquids has been based on the Mori–Zwanzig formalism, using phenomenological ansatzes and mode-coupling approximations for the memory functions. The approach is extensively discussed by Boon and Yip [6] and by Hansen and McDonald [7]. This line of approach has also been followed in theoretical work [8–12] on the collective and single-particle dynamics of molten salts such as NaCl, KCl and RbCl, with satisfactory results as judged by comparison with computer simulation data. In particular, the velocity autocorrelation functions (VACF) in such ionic melts have been evaluated within the framework of mode-coupling theories [11] and related to collective motions by a configuration dependent velocity field approach [12]. However, no similar studies have as yet been reported on superionic-conductor melts, and the reasons for the large difference in mobilities of the two ionic species are not understood in detail.

From computer simulation runs in solid CaF_2 [13] and α–AgI [14] at high temperature, the diffusion of the fast ions has been analysed in terms of discrete jumps between sets of preferred locations in the crystal. Models of liquid-state diffusion through jumping processes have also been developed for simple liquids [15]. The model that we adopt to calculate diffusion in molten copper halides and AgI, and that we test also by calculations on molten NaCl, belongs to this class, since it invokes a combination of vibrational and jumping motions of the ions. It derives from an idea of Stillinger and Weber [16], as developed and exploited by Zwanzig [17] and Mohanty [18] to derive transport coefficients in cold dense fluids directly from the Green–Kubo time correlation formulae. The general picture has been clearly stated in the work of Zwanzig [17]. The model assumes that the configuration space of the many-body system is divided into 'cells', each cell being associated with a local minimum on the potential-energy hypersurface. Some of these minima correspond to almost crystalline configurations, while others correspond to liquid-like configurations. The configuration of the melt remains in one of these minima, performing approximate harmonic vibrations about it, until it finds a saddle point in the potential energy surface and jumps to another cell. The effects of a cell jump are (i) to rearrange the equilibrium positions of the particles in some subvolume V^*, and (ii) to interrupt the oscillations within it, so that the motions in V^* before and after the jump are uncorrelated. Similar ideas have been used by one of us [19] to evaluate diffusion in a monatomic fluid, with results in good agreement with simulation results.

The main result of our application of the above model to superionic-conductor melts is to explicitly relate the difference in self-diffusion coefficients of the two ionic species to the nature of the liquid structure through the different backscattering imposed on each ion species by the shell of second-neighbour-like ions. Our numerical calculations involve the use of pair potentials and of pair distribution functions obtained from them, so that the pair potentials are in fact the essential input. The calculations are successful in predicting the ratio of self-diffusion coefficients for the two ionic species in all the melts that we have considered, as well their individual magnitudes in AgI, CuBr and NaCl. The absolute magnitudes are instead overestimated in CuCl and CuI.

The layout of the paper is briefly as follows. In section 2 we develop the model to be used in the calculation of self-diffusion coefficients. The results are presented and discussed in section 3, where we also comment on the memory function approach in connection with the present problem. Section 4 gives a short summary and some concluding remarks.

2. Theory

We consider an ionic melt consisting of N cations with mass m_+ and N anions with mass m_-. The self-diffusion coefficients D_+ and D_- are given by the Green–Kubo formulae

$$D_+ = \frac{k_B T}{m_+} \int_0^\infty C_+(t)\,dt \tag{1a}$$

and

$$D_- = \frac{k_B T}{m_-} \int_0^\infty C_-(t)\,dt \tag{1b}$$

where $C_+(t)$ and $C_-(t)$ are the VACFs of cations and anions. These are, respectively, given by

$$C_+(t) = \frac{1}{N} \sum_{i=1}^N \langle v_i^+(t) v_i^+(0)\rangle / \langle (v_i^+)^2\rangle \tag{2a}$$

and

$$C_-(t) = \frac{1}{N} \sum_{i=1}^N \langle v_i^-(t) v_i^-(0)\rangle / \langle (v_i^-)^2\rangle \tag{2b}$$

where $v_i^+(t)$ and $v_i^-(t)$ are the velocities of the ith cation and anion at time t, respectively. The angular brackets in equations (2) represent the ensemble average.

The realization of Zwanzig's model recalled in section 1 introduces a spectrum of oscillation frequencies to reduce the sum over coordinates in (2) to a sum over normal modes localized in the various subvolumes V^* and having a time dependence of the form $\cos(\omega t)$. One also introduces a waiting time distribution for cell jumps destroying coherence in any V^*, we take that to be of the form $\mathrm{sech}(t/\tau)$ [19]. Considering that optic-like rattling motions of an ion in the structural cage of its neighbours should be important for its diffusion, we approximate the frequency spectrum by Einstein frequencies ω_+ and ω_- for cations and anions, respectively, and correspondingly introduce jumping frequencies τ_+^{-1} and τ_-^{-1}. With these approximations (1) gives

$$D_+ = \frac{k_B T}{m_+} \int_0^\infty dt \cos(\omega_+ t)\,\mathrm{sech}(t/\tau_+)$$

$$= \frac{k_B T}{m_+} \tfrac{1}{2}\pi\tau_+ \,\mathrm{sech}(\tfrac{1}{2}\pi\omega_+\tau_+) \tag{3}$$

and

$$D_- = \frac{k_B T}{m_-} \int_0^\infty dt \cos(\omega_- t)\,\mathrm{sech}(t/\tau_-)$$

$$= \frac{k_B T}{m_-} \tfrac{1}{2}\pi\tau_- \,\mathrm{sech}(\tfrac{1}{2}\pi\omega_-\tau_-). \tag{4}$$

An advantage of using the same frequencies for all the cations or anions is that the parameters $\omega_{+,-}$ and $\tau_{+,-}$ can be estimated from the microscopic sum rules satisfied by

the VACF. On comparing the short-time expansion of the integrals in (3) and (4) with the exact short-time expansion of the VACF, which is

$$C(t) = 1 - C_2(t^2/2!) + C_4(t^4/4!) + \ldots \tag{5}$$

we obtain

$$\tau_+^{-2} = (C_4^+ - (C_2^+)^2)/4C_2^+ \tag{6}$$

and

$$\omega_+^2 = (5(C_2^+)^2 - C_4^+)/4C_2^+. \tag{7}$$

Similar expressions relate ω_- and τ_- to the coefficients C_2^- and C_4^- in the short-time expansion of $C_-(t)$. As can be seen from equations (3)–(7), if $C_4 = C_2^2$ then $D = 0$, implying perfect crystalline behaviour. On the other hand, for $C_4 > 5C_2^2$ diffusion is gas-like and no backscattering process is present.

In order to calculate the self-diffusion constants from (3) and (4) we need the sum rule expressions for C_2 and C_4. After simple algebra we obtain

$$C_2^+ = \frac{n}{2m_+} \int drg_{++}(r)U_{xx}^{++} + \frac{n}{2m_+} \int drg_{+-}(r)U_{xx}^{+-} \tag{8}$$

and

$$C_{4(2)}^+ = \frac{n}{m_+^2} \int drg_{++}(r)(U_{x\alpha}^{++})^2 + \frac{n}{2m_+}\left(\frac{1}{m_+} + \frac{1}{m_-}\right) \int drg_{+-}(r)(U_{x\alpha}^{+-})^2 \tag{9}$$

where $C_{4(2)}$ represents the two-body contribution to the fourth sum rule. The derivation of the triplet contribution to this sum rule is given in the appendix. In (8) and (9) n is the ionic number density, $g_{++}(r)$ and $g_{+-}(r)$ are the partial cation–cation and cation–anion radial distribution functions, $U^{++}(r)$ and $U^{+-}(r)$ are the corresponding pair potentials and the notation

$$U_{\alpha\beta} = d^2 U(r)/(dr_\beta \, dr_\alpha) \tag{10}$$

has been used, with the convention of summation over the repeated Cartesian index α. The second and fourth sum rules for the anion, C_2^- and C_4^-, follow by interchanging the indices $+$ and $-$ in (8) and (9). Clearly, each sum rule contains a contribution from like ions and a contribution from unlike ions. We shall separately consider these two contributions below, giving them with the notation $C_2^+ = C_2^{+(+)} + C_2^{+(-)}$ etc. Obviously, $C_2^{+(+)} = m_- C_2^{+(-)}/m_+$. In the next section we proceed to evaluate these sum rules and hence the self-diffusion coefficients.

3. Calculation and results

The inputs for the numerical calculation of the frequency sum rules of the VACF are the interatomic potentials and the partial radial distribution functions. For the copper halides and AgI, we have used the potentials adopted by Stafford *et al* [1] in their molecular dynamics (MD) work, together with the structure factors that they obtained

Table 1. Contributions to the sum rules C_2 (in units of $\times 10^{26}$ s^{-2}) and C_4 (in units of $\times 10^{52}$ s^{-4})[a].

Salt	$C_2^{+(+)}$	$C_2^{+(-)}$	$C_{4(2)}^{+(+)}$	$C_{4(2)}^{+(-)}$	$C_2^{-(-)}$	$C_2^{-(+)}$	$C_{4(2)}^{-(-)}$	$C_{4(2)}^{-(+)}$
AgI	4.5×10^{-6}	2.86	0.22	25	1.92	2.43	6.4	21
CuCl	1.7×10^{-4}	2.02	0.59	45	3.25	3.62	31	81
CuBr	1.3×10^{-4}	1.27	0.34	6.6	1.05	1.01	3.0	5.2
CuI	1.3×10^{-4}	0.69	0.51	1.4	0.61	0.34	0.72	0.69
NaCl	0.57	7.72	44	137	1.03	5.01	31	89

[a] The thermodynamic state of each melt is as listed in table 2. The values of C_2^+ and C_2^- do not contain the electrostatic contributions, which cancel out as discussed in the text.

Table 2. Values of the self-diffusion coefficients D_+ and D_- (in units of $\times 10^{-5}$ cm^2 s^{-1}) obtained from (3) and (4), compared with molecular dynamics (MD) results. The results in round brackets are obtained from (11) and (12) within a memory-function approach.

Salt	T (K)	n (Å^{-3})	D_+	$(D_+)_{MD}$	D_-	$(D_-)_{MD}$	D_+/D_-	$(D_+/D_-)_{MD}$
AgI	873	0.0286	3.65	3.8[a]	0.34	0.3[a]	10.7	12.7[a]
			(3.66)		(1.19)		(3.07)	
CuCl	773	0.0410	20.5	10.0[a]	4.26	2.5[a]	4.81	4.0[a]
			(14.4)		(5.21)		(2.76)	
CuBr	880	0.0350	12.6	10.5[a]	2.26	2.7[a]	5.57	3.9[a]
			(10.7)		(3.6)		(2.97)	
CuI	923	0.0304	17.9	8.8[a]	2.20	1.3[a]	8.14	6.8[a]
			(16.0)		(3.75)		(4.27)	
NaCl	1340.5	0.0286	12.4	14.1[b]	10.5	12.2[b]	1.18	1.15[b]
			(13.8)	(17.3[c])	(11.0)	12.9[c]	(1.25)	1.34[c]

[a] From Trullàs *et al* [4].
[b] From Lantelme *et al* [5].
[c] Experimental values from J O'M Bockris *et al* [22].

by simulation. The results obtained are reported in table 1. In order to test the applicability of our model on a 'normal' melt, we have also done calculations for NaCl, taking the potentials and partial distribution functions from the MD work of Lantelme *et al* [5]. The results are also given in table 1. We have omitted in these calculations the triplet contributions to C_4, which are discussed in the appendix.

The difference between a normal melt and the superionic-conductor melts emerges from the behaviour of the second sum rule, on which the diffusion constants depend strongly. We see from table 1 that the ratio $[C_2^{+(+)}m_+]/[C_2^{-(-)}m_-]$ is very small ($<10^{-3}$) in the superionic-conductor melts, whereas it is 0.36 in NaCl. This difference arises directly from the cation–cation pair potential and radial distribution function. The role of structure is evident from the character of $g_{++}(r)$, which is essentially structureless in superionic-conductor melts and very similar to $g_{--}(r)$ in NaCl. To clarify the role of the potential, we point out that the electrostatic contribution to $C_2^{+(+)}$ and $C_2^{+(-)}$ (as well as those to $C_2^{-(-)}$ and $C_2^{-(+)}$) cancel each other by charge neutrality, so that only the short-range parts of the potential, and hence primarily an ion-size effect, enter the calculation. The consequences of the smallness of the quantity $[C_2^{+(+)}m_+]$ in superionic-conductor melts can be seen from equations (3)–(7). It leads to a relatively low vibrational frequency

and relatively high jumping frequency for the cation, and hence to a relatively high self-diffusion coefficient.

The self-diffusion coefficients obtained from (3) and (4), using the numerical values of the sum rules from table 1, are given in table 2. It can be seen from the table that our model successfully predicts the large differences in self-diffusion constants for the cation and the anion in copper halides and silver iodide. The calculated ratios D_+/D_- are found to be in good agreement with the simulation results of Trullas et al [4]. The absolute values of D_+ and D_- are found to be in good agreement with the simulation results on AgI and CuBr as well as with those in NaCl. However, the calculated absolute values of the self-diffusion constants in CuCl and CuI are about twice the simulation values. This discrepancy may indicate a limitation in our model for systems where the mass difference between the two ionic species is large.

The sensitivity of our results to the type of theoretical approach may be tested by using the same sum rules within the Mori–Zwanzig formalism, combined with a simple phenomenological ansatz for the memory functions. This is a hyperbolic secant form, which has recently been successful in the calculation of the transport coefficients for the Lennard-Jones fluids [20]. The expressions for the self-diffusion coefficients in a molten salt follow as

$$D_+ = \frac{2\,k_B T}{\pi\,m_+} \frac{(C_4^+ - (C_2^+)^2)^{1/2}}{(C_2^+)^{3/2}} \tag{11}$$

and

$$D_- = \frac{2\,k_B T}{\pi\,m_-} \frac{(C_4^- - (C_2^-)^2)^{1/2}}{(C_2^-)^{3/2}} \tag{12}$$

The results obtained from (11) and (12) are given in table 2 in round brackets. The main consequence is a large increase of the calculated D_- for superionic-conductor melts, leaving only qualitative agreement with the MD data on the ratio D_+/D_-. This suggests that the memory effects may be stronger for the anion than for the cation.

4. Summary and concluding remarks

We have used a simple model for the diffusional dynamics in molten salts and related its vibrational and jumping-frequency parameters to sum rules describing the short-time behaviour of velocity autocorrelations, in order to derive expressions for the self-diffusion coefficients of the two ionic species which explicitly contain pair potentials and pair distribution functions. These expressions have allowed us to separate the constraining effects of the first-neighbour shell of unlike ions, which aside from mass factors are similar for the two ionic species, from those of the shell of second-neighbour-like ions. The large magnitude of the ratio D_+/D_- in the melts of fast-cation conductors, as contrasted with 'normal' melts, has thus been related to the character of the liquid structure through the very different strengths of backscattering for cations by cations and for anions by anions. Our approach interprets the residual traces of solid-state superionic behaviour in the melt as a consequence of the poor short-range order in the fast-ion component, and hence ultimately as a consequence of the effective interactions which determine it.

The numerical results that we have obtained are quite satisfactory for the ratio D_+/D_-, but not consistently reasonable for the absolute magnitudes of D_+ and D_- in all the melts that we have considered. We have illustrated the sensitivity of the calculation by reporting results obtained in a more conventional memory function approach to ionic diffusion and by trying to assess the magnitude of three-body corrections to our main formulae.

Acknowledgments

Appendix

The triplet contribution to the fourth sum rule C_4^+ is obtained from

$$C_{4(3)}^+ = \frac{1}{m_+^2} \sum_{j=k=1}^{N} \left\langle \frac{d^2 U(r_{1j})}{dr_{1x}\,dr_{1\alpha}} \frac{d^2 U(r_{1k})}{dr_{1x}\,d_{1\alpha}} \right\rangle \tag{A1}$$

where the particle 1 is taken to be a cation, while particles j and k may be of either species. Separating out the various choices of particles j and k and writing the averages in terms of distribution functions, we obtain

$$C_{4(3)}^+ = \frac{n^2}{4m_+^2} \iint dr_1\,dr_2 g_3(r_1, r_2) U_{1x\alpha}^{++} U_{2x\alpha}^{++}$$

$$+ \frac{n^2}{4m_+^2} \iint dr_1\,dr_2 g_3(r_1, r_2) U_{1x\alpha}^{+-} U_{2x\alpha}^{+-}$$

$$+ \frac{n^2}{2m_+^2} \iint dr_1\,dr_2 g_3(r_1, r_2) U_{1x\alpha}^{++} U_{2x\alpha}^{+-} \tag{A2}$$

where $g_3(r_1, r_2)$ are the triplet distribution functions and $U_{1x\alpha} = d^2 U(r_1)/(dr_{1x}\,dr_{1\alpha})$, $U_{2x\alpha} = d^2 U(r_2)/(dr_{2x}\,dr_{2\alpha})$. The expression for $C_{4(3)}^-$ is obtained from (A2) by interchanging $+$ and $-$ in the superscripts.

The integrals in (A2) can only be evaluated by using an approximate closure for the triplet correlation functions. We have tried to estimate these by means of the superposition approximation. The magnitudes of $C_{4(3)}$ appear to be small compared with $C_{4(2)}$ (of the order of 10%).

A simple decoupling approximation on (A1), which amounts to neglecting the correlations between particles j and k, has been suggested in earlier work in simple Lennard-Jones fluids [21]. In the molten salts of present interest, it implies neglecting correlations between cations and anions, leading to

$$C_{4(3)}^+ = \tfrac{1}{2}(C_2^+)^2. \tag{A3}$$

Inclusion of triplet correlations in this approximation yields for molten NaCl at 1340.5 K

the values $D_{Na} = 16 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ and $D_{Cl} = 13 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$. Comparison with the results in table 2 again indicates that the inclusion of triplet correlations in our calculation should have no major consequences, especially with regards to the ratio D_+/D_-.

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