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ION DIFFUSION
RELATED TO STRUCTURE IN MOLTEN SALTS

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ABSTRACT

A model first developed by Zwanzig to derive transport coefficients in cold dense fluids directly from the Green-Kubo time correlation formulae allows one to relate macroscopic diffusion coefficients to the local fluid structure. Applications to various ionic diffusion processes in molten salts are reviewed. Consequences of partial structural quenching are also discussed.

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1. Introduction

As is well known, the self-diffusion coefficient of an atom in a fluid is a macroscopic manifestation of the autocorrelations of the particle velocity in time. The main focus of the present short review is on a model invoking a combination of vibrational and jumping motions of the ions in a molten salt for the purpose of evaluating the ionic diffusion coefficients. The model was originally developed by Zwanzig [1] starting from an idea of Stillinger and Weber [2] and was used by him to derive a Stokes-Einstein-type relation between diffusion coefficient and shear viscosity in a cold dense liquid directly from the Green-Kubo time correlation formulae for transport coefficients. Further analysis and applications to monatomic fluids have been given by Mohanty [3] and by Tankeshwar *et al.* [4-6].

In essence, 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 free energy hypersurface. The configuration of the melt remains near one of these minima, performing approximate harmonic vibrations about it until a saddle point is found. Diffusion occurs at that point as a jump process out of the local free energy minimum into another cell, the effects of the jump being to rearrange the local configuration of the particles in some subvolume V* and to interrupt the oscillations within it so that the motions in V* before and after the jump are uncorrelated.

As extended by Tankeshwar and Tosi [7] to ion diffusion in bulk molten salts, the model involves a characteristic Einstein vibrational frequency and a characteristic residence time for each ionic species. With the help of sum rules these parameters can be evaluated in terms of pair potentials and partial pair distribution functions for the ionic species in the melt. Through this connection with local liquid structure the model accounts for (i) the large difference in mobilities of the two ionic species in superionic-conductor melts such as molten AgI or CuCl [7], and (ii) the so-called Chemla effect, i.e. the reversal of the mobilities of the two cations with varying concentration in liquid (Li,K)Cl mixtures [8]. These results, as well as their extension to evaluate the anisotropic diffusion coefficients of ions in a model electrical double layer [9], are briefly reviewed below. Finally, in the light of such relations between structure and mobilities the behaviours of an equilibrium melt and an ionic glass are contrasted by examining the structural consequences of quenching the chlorine component in molten CuCl [10].

2. Ionic diffusion in bulk 1:1 melts

The Green-Kubo formula for the diffusion coefficients $D_{\pm}$ of cations and anions is

$$D_{\pm} = \frac{k_B T}{N_{\pm} m_{\pm}} \int_0^{\infty} dt \sum_{i=1}^{N} < v_i^{\pm}(o) v_i^{\pm}(t) > / < (v_i^{\pm})^2 > \tag{1}$$

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where $m_\pm$ and $v_i^\pm(t)$ are the masses and the velocities of cations and anions. The realization of Zwanzig's model replaces the sum over the ions in Eq. (1) by a sum over a frequency spectrum for normal modes localized in subvolumes V* and describing optic-like rattling motions of the ions in the structural cages provided by their neighbours. Approximating the spectrum by two Einstein frequencies $\omega_\pm$ and introducing a waiting time distribution of the form sech($t/\tau_\pm$) for cell jumps destroying coherence in any V*, we have

$$D_\pm = \frac{\pi k_B T \tau_\pm}{2m_\pm} \mathrm{sech}(\pi \omega_\pm \tau_\pm / 2) \quad . \tag{2}$$

Evidently, many of the details of the ionic motions become irrelevant in performing the time integral in Eq. (1).

The Einstein frequencies and the relaxation times can now be evaluated from the short-time expansion of the velocity autocorrelation functions, with the results [7]

$$\omega_\alpha^2 = [5A_\alpha^2 - B_\alpha]/(4A_\alpha) \tag{3}$$

and

$$1/\tau_\alpha^2 = [B_\alpha - A_\alpha^2]/(4A_\alpha) \tag{4}$$

where

$$A_\alpha = \frac{1}{m_\alpha} \sum_{\alpha'} n_{\alpha'} \int dr g_{\alpha\alpha'}(r) \frac{\partial^2 U_{\alpha\alpha'}(r)}{\partial r_x^2} \tag{5}$$

and

$$B_\alpha \approx \frac{1}{2} A_\alpha^2 + \frac{1}{m_\alpha} \sum_{\alpha'} n_{\alpha'} (\frac{1}{m_\alpha} + \frac{1}{m_{\alpha'}}) \sum_{x'} \int dr g_{\alpha\alpha'}(r) \left(\frac{\partial^2 U_{\alpha\alpha'}}{\partial r_x \partial r_{x'}} \right)^2 \quad . \tag{6}$$

In these equations $g_{\alpha\beta}(r)$ are the pair distribution functions and $U_{\alpha\beta}(r)$ are the interionic pair potentials. From this formulae it is evident that the main contributions to the model parameters for each species, and hence to its diffusion coefficient come from the shells of first (unlike) neighbours and of second (like) neighbours. From Eq. (3) and (4) we also see that for $B_\alpha \to 5A_\alpha^2$ the Einstein frequency vanishes yielding gas-like behaviour, while for $B_\alpha \to A_\alpha^2$ the waiting time diverges yieldding solid-like behaviour.

For an illustration of the quantitative usefulness of the theory one may take a simple molten salt such as NaCl: at T = 1340.5 K one finds [7] D_+ = 16 and D_- = 13 against values of 14.1 and 12.2 from molecular dynamics and values of 17.3 and 12.9 from experiment (here and in the following, diffusion coefficients are in units of 10^{-5} cm^2 s^{-1}). Evidently, neither the theory nor the simulation are fully quantitative. The calculation shows that (i) the contributions from the Coulomb part of the interionic potentials largely cancel out as a consequence of charge neutrality, thus emphasizing the role of short-range interactions and hence, in essence, of ionic sizes; and (ii) the observed similarity of $g_{NaNa}(r)$ and $g_{ClCl}(r)$ in molten NaCl implies similar back-scattering for each ionic species from its shell of second neighbours and hence a reduction of the ratio D_+/D_- to a value of order 1.3, appreciably smaller than one may surmise from ionic

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sizes and ionic masses.

2.1 Diffusion in superionic-conductor melts

In contrast to the observation made just above for molten NaCl, a strong asymmetry in the diffusion coefficients for the ionic species in the melts of superionic conducting solids was emphasized in molecular dynamics work by Trullas *et al.* [11]. As can be seen from Table 1, they found that the ratio D_+/D_- is of order 4 in molten CuCl and CuBr and reaches a value of order 10 in molten AgI. The theory connects this liquid-state remnant of superionic behaviour in the hot solid to the strong asymmetry in the pair distribution functions for like neighbours, which is well known from neutron diffraction experiments carried out on molten CuCl by the isotopic enrichment technique [12, 13]. The diffraction data show typical molten-salt ordering in the Cu-Cl and Cl-Cl correlations combined with a broad, featureless and heavily damped Cu-Cu structure factor. The Cu-Cu distribution function shows little structure except for excluded volume. Structural backscattering of a Cu ion by its second-neighbour shell of Cu ions is therefore very ineffective, yielding a relatively low vibrational frequency and a relatively high jump frequency.

A quantitative comparison between the model and the data from molecular dynamics is reported in Table 1 [7]. The calculated values of the ratio D_+/D_- are in good agreement with the data, whereas the absolute values of the diffusion coefficients are not consistently reasonable. In summary, the theory relates the residual traces of solid-state superionic behaviour in the melt to the poor short-range order in the fast ion component. Of course, both the structural and the transport properties ultimately derive from special features in the pair potentials, which are grossly summarized in an unexpectedly small effective size for the Cu ion.

2.2 The Chemla effect in molten (Li,K)Cl mixtures

In measurements of the electrical mobilities of Li^+ and K^+ ions in molten (Li,K)Br mixtures Pèriè and Chemla [14] observed that the mobility of K^+ overtakes that of Li^+ with increasing content of KBr. The Chemla effect has since been reported for many other melts with two monovalent cations and a common anion (see e.g. [15]).

It has been proposed [8] that this phenomenon is the liquid-state analogue of the so-called "off-centre" ions in the crystalline state (see e.g. [16]). A well-known instance of the latter is provided by KCl:Li, where the Li^+ impurity can occupy sites displaced along the eight equivalent <111> directions from a cation site and tunnel between them. The locking of Li^+ in this configuration arises from the combined effect of its small radius, allowing close approach to Cl^- ions, and of the polarization energy gain ensuing from the off-centre displacement.

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The transport behaviour of the two cations in the molten mixture is related to the structural features of the cation-anion distribution function, combined with the volume dilation which accompanies the increase of KCl content. Computer simulation studies [17, 18] and x-ray diffraction experiments [19] show that the first-neighbour peak in the Li-Cl distribution function is considerably sharper and lies at a considerably shorter distance than that in the K-Cl distribution function and that the coordination of Li^+ by chlorines is approximately fourfold rather than sixfold. From the simulation study of Lantelme and Turq [18] it is also seen that the velocity autocorrelation function for Li^+ shows marked remnants of an oscillatory behaviour at short times.

Table 2 reports a comparison between the values of the ionic diffusion coefficients calculated form the pair distribution functions in the liquid mixture [8] and those obtained directly from the simulated velocity autocorrelation functions [18]. It is seen from the Table that at 1096 K the diffusion coefficient of Li^+ becomes smaller than that of K^+ as the KCl content increases above 50-60 % and that lowering the temperature shifts this crossover towards lower KCl content. The behaviour of the diffusion coefficients with composition and temperature is a consequence of the special sharpness of the first-neighbour Li-Cl structural correlations, which increases with decreasing mole fraction of LiCl and with decreasing temperature. This yields a relatively high vibrational frequency and a relatively long waiting time between jumps for the Li^+ ion. It should also be noticed from the Table, however, that the magnitudes of all the calculated diffusion coefficients exceed those from the simulation study by roughly a factor 2.

3. Ionic diffusion in the double layer at an electrode/molten-salt interface

Because of the complexity of real electrochemical systems, computer simulations of greatly simplified models of electrified metal-electrolyte interfaces have had a very useful role in providing controlled data to test advances in statistical mechanics (see e.g. [20]). Esnouf *et al.* [21] (see also Williams [22]) have extended such studies to the molten-salt regime of the electrolyte. In their model a slab of ionic liquid representing molten KCl is enclosed between two oppositely charged hard walls. The single-particle density profiles show layering of the charge density in the melt along the z direction perpendicular to the walls and the diffusion coefficients of the two ionic species, which are obtained from their mean square displacements as functions of time, show appreciable anisotropy.

In extending the model reviewed in § 2 to diffusion in a slab one needs to introduce local vibrational and jump frequencies for each species, which are different for diffusion parallel or perpendicular to the walls [9]. For instance, for the parallel motion of a K^+ ion at position z_1 the quantity in Eq. (5) is first replaced by

$$A_{K\parallel}(z_1) = \frac{1}{m_K} \int\limits_{-\infty}^{+\infty} dx_{12} \int\limits_{-\infty}^{+\infty} dy_{12} \int\limits_{-\ell/2}^{\ell/2} dz_2 [\frac{\rho_{KCl}(z_1,\mathbf{r}_{12})}{\rho_K(z_1)} \frac{\partial^2 U_{KCl}(r_{12})}{\partial x_{12}^2} + \frac{\rho_{KK}(z_1,\mathbf{r}_{12})}{\rho_K(z_1)} \frac{\partial^2 U_{KK}(r_{12})}{\partial x_{12}^2}] \quad (7)$$

involving the inhomogeneous one-body and two-body densities, with ℓ the separation distance between the walls. An average over the one-particle distribution yields

$$A_{K\parallel} = [\int\limits_{-\ell/2}^{\ell/2} dz_1 \rho_K(z_1) A_{K\parallel}(z_1)] / [\int\limits_{-\ell/2}^{\ell/2} dz_1 \rho_K(z_1)] \quad . \quad (8)$$

The approximation

$$\rho_{\alpha\beta}(z_1,\mathbf{r}_{12}) \cong \rho_\alpha(z_1)\rho_\beta(z_2)g_{\alpha\beta}(r_{12}) \quad (9)$$

for the two-body densities in terms of bulk distribution functions then allows an evaluation of the anisotropic diffusion coefficients in the slab.

The results are shown in Table 3 in comparison with the simulation data, at various values of the wall charge qe/ℓ^2 per unit area and of the temperature. The trends shown in the Table arise from the layering of the charge density in the molten salt slab parallel to the walls. For any given ion in a layer, the most effective back-scattering comes from its unlike neighbours lying in the same layer for parallel diffusion and in the two adjacent layers for perpendicular diffusion. The back-scattering becomes relatively more important for perpendicular diffusion with increasing charge density on the electrodes, so that the ratios $D_{\parallel}/D_{\pi}$ are larger than unity and increase with the electrode charge density. Allowing for spill out of electrons at the electrodes in a jellium model reinforces these trends, by favouring increased layering in the liquid slab through increased adsorption of counterions at the electrodes [9].

Tankeshwar and Tosi [9] have also taken advantage of the fact that in some of the simulation runs of Esnouf *et al.* [19] the liquid slab is quite thick to construct local diffusion coefficients for counter-ions and co-ions in a single double layer from quantities such as $A_{\parallel}(z)$ in Eq. (7), thus correlating local diffusivity with local single-particle densities. While parallel diffusion is found to change relatively little with distance from the charged wall across the layered charge density profile, strong correlations are found between the perpendicular diffusion processes and the local structure in the double layer. The correlation is similar for counter-ions and co-ions, except for their relative phase difference, and is simply summarized by the observation that perpendicular diffusion of each ionic species is slowed down in the regions where its density piles up.

4. Quenching of halogen framework in molten CuCl

Although no structural phase transition to a fast-ion conducting phase occurs in crystalline CuCl before melting, the mobility of the Cu^+ ions and the ionic conductivity reach rather high values in the crystal at high temperature. In comparison with other copper halides and AgI, it appears that melting pre-empts in CuCl such a phase transition in the solid state. The vast

amount of information which is available from experiment and simulation on molten CuCl has stimulated a theoretical study [10] of the consequences of quenching the chlorine component into a frozen disordered structure, within whose micropores the copper ions are allowed to reach a new state of equilibrium. The melt is thereby converted into a model superionic glass at the same temperature and density.

Recent developments in statistical mechanics have provided a solution for such a non-equilibrium structural problem from a variety of approaches, based on either the cluster expansion [23] or the replica method [24] or density functional theory [25]. In essence, the disordered system out of equilibrium can be mapped into a system in a state of full equilibrium. In particular, the Ornstein-Zernike relations which are appropriate for a binary system consisting of a fluid at equilibrium inside a quenched microporous matrix are mapped into those of a special three-component system at full equilibrium. Indeed, in the description of the structural correlations within the annealed fluid one needs to separately consider those that connect pairs of annealed particles separated from each other by quenched particles and those that are transmitted through successive layers of annealed particles.

In the case of CuCl the quenched chlorine matrix is first realized by treating the chlorines as an ionic fluid neutralized by a uniform background of positive charge. The replica Ornstein-Zernike equations for the Cu-Cl and the Cu-Cu correlations are then solved with the hypernetted chain closure. On comparing the results with those obtained for the fully equilibrated CuCl melt one finds that the Cl-Cl and Cu-Cl radial distribution functions are hardly changed. There are instead major changes in the Cu-Cu correlations: on chlorine quenching a major loss of short-range order within the copper component can be seen from the Cu-Cu structure factor and an enhanced delocalization of the copper ions is clearly visible from the Cu-Cu radial distribution function.

The enhanced structural delocalization of the copper ions on chlorine quenching corresponds to an increase in their diffusion coefficient. Similar calculations on entirely different models indicate that enhanced mobility is a rather general property of an annealed component adsorbed within a quenched matrix [26, 27]. Evidently, partial quenching decouples the motions of the annealed ions from those occurring within the quenched component, suppressing paired jump processes and allowing the annealed component to move more freely within the subsystem of favoured "structural holes" pre-existing in the matrix.

5. Concluding remarks

In this brief review I have stressed in a number of examples the connection between structure and ionic transport in disordered ionic systems. The simple formulae obtained for the diffusion coefficient in terms of pair potentials and radial distribution functions have allowed

us to highlight (i) the role of back-scattering by second neighbours in superionic-conductor melts, (ii) the role of structural trapping of small ions by their first neighbours in (Li,K)Cl mixtures, and (iii) the role of anisotropy and inhomogeneity in the double layer at a charged-wall/molten-salt interface. I have also touched upon a related new development in the theory of structure for non-equilibrium disordered systems.

Before closing it may be useful to explicitly recall that from a fundamental viewpoint structure in a fluid is a consequence of its dynamical and transport behaviour. However, models leading from structure to transport can be justified by the fact that structure is so much more easily accessible. Very recent work on a variety of liquids and disordered systems [28] has given evidence for an explicit relationship between the diffusion coefficient, reduced to a dimensionless form by scaling by the atomic collision frequency and the atomic diameter, and the pair distribution function through the excess entropy calculated in the two-particle approximation.

References

[1] R. Zwanzig, *J. Chem. Phys.* **79** (1983) 4507.

[2] F. H. Stillinger and T. A. Weber, *Phys. Rev.* A **28** (1983) 2408.

[3] U. Mohanty, *Phys. Rev.* A **32** (1985) 3054.

[4] K. Tankeshwar, K. N. Pathak and S. Ranganathan, *J. Phys.* C **20** (1987) 5748.

[5] K. Tankeshwar, B. Sigla and K. N. Pathak, *J. Phys.: Condens. Matter* **3** (1991) 3173.

[6] R. K. Sharma, K. N. Pathak, K. Tankeshwar and S. Ranganathan, *Phys. Chem. Liquids* **29** (1995) 59.

[7] K. Tankeshwar and M. P. Tosi, *J. Phys.: Condens. Matter* **3** (1991) 7511.

[8] K. Tankeshwar and M. P. Tosi, *Solid State Commun.* **84** (1992) 245.

[9] K. Tankeshwar and M. P. Tosi, *J. Phys.: Condens. Matter* **3** (1991) 9817.

[10] H. Tatlipinar, G. Pastore and M. P. Tosi, *Phil. Mag. Lett.* **68** (1993) 357; G. Pastore, H. Tatlipinar and M. P. Tosi, *Phys. Chem. Liquids* **31** (1996) 89.

[11] J. Trullas, A. Girò and M. Silbert, *J. Phys.: Condens. Matter* **2** (1990) 6643.

[12] I. D. Page and K. Mika, *J. Phys.* C **4** (1971) 3034.

[13] S. Eisenberg, S. F. Jal, J. Dupuy, P. Chieux and W. Knoll, *Phil. Mag.* A **46** (1982) 195.

[14] J. Pèriè and M. Chemla, *C. R. Acad. Sci.* **250** (1960) 3986.

[15] M. Chemla and I. Okada, *Electrochim. Acta* **35** (1990) 1761.

[16] A. M. Stoneham, *Theory of Defects in Solids*, Chap. 21 (Clarendon Press, Oxford 1965).

[17] C. Caccamo and M. Dixon, *J Phys.* C **13** (1980) 1887.

[18] F. Lantelme and P. Turq, *J. Chem. Phys.* **77** (1982) 3177.

[19] I. Okada, H. Okano, H. Ohtaki and R. Takagi, *Chem. Phys. Lett.* **100** (1983) 436.

[20] S. L. Carnie and G. M. Torrie, *Adv. Phys. Chem.* **56** (1984) 141.

[21] R. M. Esnouf, A. C. D. Smith and P. J. Grout, *Phil. Mag.* A **58** (1988) 27.

[22] D. I. T. Williams, *Ph. D. Thesis* (Oxford University, 1990).

[23] W. G. Madden and E. D. Glandt, *J. Stat. Phys.* **51** (1988) 537.

[24] J. A. Given and G. Stell, in *Condensed Matter Theories*, ed. L. Blum and F. Bary Malik (Plenum, New York 1993), p. 395,

[25] M. P. Tosi, *N. Cimento* D **16** (1994) 169.

[26] G. Pastore, H. Tatlipinar and M. P. Tosi, *Phys. Chem. Liquids* **31** (1996) 189.

[27] M. Cardenas and M. P. Tosi, *Physica* B **222** (1996) 143.

[28] M. Dzugutov, *Nature* **381** (1996) 137.

Table 1. Calculated self-diffusion coefficients in superionic-conductor melts (in units of 10^{-5} cm^2 s^{-1}), compared with the results of molecular dynamics (MD). From ref. [7].

Salt	T(K)	D_+	$(D_+)_{MD}$	D_-	$(D_-)_{MD}$	D_+/D_-	$(D_+/D_-)_{MD}$
AgI	873	3.6	3.8	0.34	0.3	11.	12.7
CuCl	773	20.	10.	4.3	2.5	4.8	4.0
CuBr	880	13.	10.	2.3	2.7	5.6	3.9
CuI	923	18.	8.8	2.2	1.3	8.1	6.8

Table 2. Calculated values of the self-diffusion coefficients in liquid (Li,K)Cl mixtures, compared with the results of molecular dynamics (in parentheses). The units are 10^{-5} cm^2 s^{-1}. From ref. [8].

MF of LiCl/T(K)	D_{Li}	D_K	D_{Cl}	D_K/D_{Li}
0.898/1096	14.7	13.4	19.4	0.91
	(11.1)	(10.1)	(8.95)	(0.91)
0.583/1096	11.2	13.0	18.6	1.16
	(7.78)	(7.57)	(7.06)	(0.97)
0.370/1096	8.2	12.8	19.7	1.56
	(5.95)	(7.02)	(6.68)	(1.18)
0.102/1096	4.7	12.5	14.1	2.65
	(2.91)	(7.05)	(6.85)	(2.42)
0.583/646	3.0	3.8	6.6	1.27
	(2.02)	(2.25)	(1.75)	(1.11)

Table 3. Anisotropic self-diffusion coefficients in model electrochemical cells in the molten salt regime, compared with the results of molecular dynamics (averages over the two ionic species, in parentheses). The units are 10^{-5} cm^2 s^{-1}. From ref. [9].

q/T(K)	$D_{K\parallel}$	$D_{K\pi}$	$D_{K\parallel}/D_{K\pi}$	$D_{Cl\parallel}$	$D_{Cl\pi}$	$D_{Cl\parallel}/D_{Cl\pi}$
0/1309	9.0	8.9	1.01	10.6	10.5	1.01
1/1326	9.1	8.7	1.04	10.8	10.5	1.03
2/1320	8.9	8.4	1.06	11.3	10.5	1.07
	(9.3)	(8.6)	(1.08)			
9/1406	11.6	7.4	1.58	14.7	10.3	1.43
	(12.9)	(8.9)	(1.45)			