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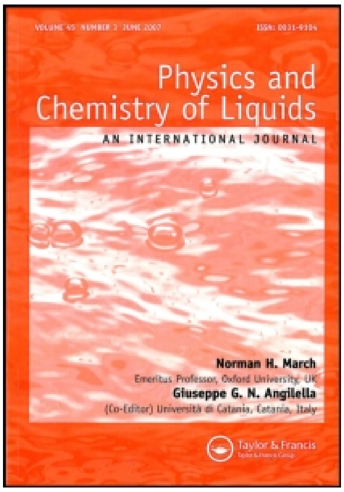

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Mass-charge Coupling and Ionic Dynamics in Molten Salts

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Mass-charge Coupling and Ionic Dynamics in Molten Salts

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Mass-density and charge-density current fluctuations are approximately independent collective dynamical variables at wavelengths greater than several mean interionic spacings. For shorter wavelengths this is no longer true, and they can interact strongly. We have investigated the effect of this mass-charge coupling on single particle motion in molten NaCl. Its influence on the diffusion coefficients, in this case, is quite small, but it significantly changes the form of the velocity autocorrelation functions. It is clear that the effect of mass-charge coupling must be included in microscopic theories of ionic dynamics.

1 INTRODUCTION

In microscopic studies of ionic dynamics in molten salts, the quantities of primary interest are the mass and charge density correlation functions, and the interplay between mass and charge effects. Even when attention is concentrated on single particle motion, through the velocity autocorrelation function, the coupling of an individual ion to mass and charge current density fluctuations is emphasised.

Recent theories of ionic dynamics have been largely confined to the simple molten salt (SMS), where the two ion species differ only in the sign of the charge they carry.[1–3] Despite the simplification, there is disagreement about the way in which the coupling to mass and charge current fluctuations is manifested in the velocity correlation function. In Munakata's and Bosse's work,[2] charge density fluctuations appear explicitly, through the memory function. In contrast, Gaskell and Woolfson[3] express the correlation function entirely in terms of the mass current fluctuations, and the charge is significant through its effect on the structure of the liquid. The reason for this is that charge ordering effects tend to suppress the mass density fluctuations, with the result that individual ionic motion is not coupled to well defined collective modes. This, it is argued, explains why the velocity autocorrelation function shows no tendency to oscillate as it decays, in agreement with computer simulation data.

The latter authors have extended their work to a more realistic model of a binary salt and derived the following expressions for the velocity autocorrelation functions.

$$\psi^{+}(t) = \frac{1}{3kTm}\frac{1}{(2\pi)^3}\int d\mathbf{q}\tilde{f}(q)\left[\frac{m^{+}}{m}C^{MM}(q,t) + \frac{m^{+}m^{-}}{2m}\Delta m C^{QQ}(q,t) + \frac{m^{+}}{2m}(\Delta m + 2m^{-})C^{MQ}(q,t)\right]F_s^{+}(q,t) \tag{1.1}$$

$$\psi^{-}(t) = \frac{1}{3kTm}\frac{1}{(2\pi)^3}\int d\mathbf{q}\tilde{f}(q)\left[\frac{m^{-}}{m}C^{MM}(q,t) - \frac{m^{+}m^{-}}{2m}\Delta m C^{QQ}(q,t) + \frac{m^{-}}{2m}(\Delta m - 2m^{+})C^{MQ}(q,t)\right]F_s^{-}(q,t) \tag{1.2}$$

where

$$\begin{aligned} C^{MM}(q,t) &= \frac{\langle \mathbf{J}^{M}_{-\mathbf{q}}(0)\cdot\mathbf{J}^{M}_{\mathbf{q}}(t)\rangle}{N} \\ C^{QQ}(q,t) &= \frac{\langle \mathbf{J}^{Q}_{-\mathbf{q}}(0)\cdot\mathbf{J}^{Q}_{\mathbf{q}}(t)\rangle}{N} \\ C^{MQ}(q,t) &= \frac{\langle \mathbf{J}^{M}_{-\mathbf{q}}(0)\cdot\mathbf{J}^{Q}_{\mathbf{q}}(t)\rangle}{N} \end{aligned} \tag{1.3}$$

$\mathbf{J}^{M}_{\mathbf{q}}(t)$ and $e\mathbf{J}^{Q}_{\mathbf{q}}(t)$ are momentum and charge current density fluctuations, $m = (m^{+} + m^{-})/2$ is the mean mass of an ion pair, $\Delta m = m^{-} - m^{+}$ and N is the total number of ions. Finally $F_s(q, t)$ refers to the Fourier transform of a self-correlation function, and $\tilde{f}(q)$ essentially that of a step function (introduced in the definition of the velocity field) whose width is the ion-sphere radius, $a = (3/4\pi n)^{1/3}$, n being the total number density.

These results were applied to NaCl,[4] but in the absence of computer data of the low order moments, we used results for the functions $C^{MM}(q, t)$ and $C^{QQ}(q, t)$ from current models appropriate to the SMS. Because of the relatively small mass difference between the ions in NaCl, it was argued that this would be a reasonable first approximation. One problem, however, is avoided in this liquid model. Because of the symmetry in the SMS, the mass and charge currents are independent so that $C^{MQ}(q, t) = 0$ for all t, and mass-charge coupling effects are completely ignored.

In the long wavelength limit the coupling between mass and charge fluctuation variables is small. At shorter wavelengths, however, mass and charge fluctuations interact strongly, and in more realistic models such cross-correlations inevitably appear. Their effects can be important at small t, as pointed out in the latter reference. For example, the inclusion of $C^{MQ}(q, t)$ is essential to obtain the correct coefficient of t^2, in the small t expansion of $\psi^+(t)$ and $\psi^-(t)$ from (1.1) and (1.2). It was decided, therefore, to make a more thorough assessment of their significance in ionic dynamics. We construct more realistic estimates for the low order moments appearing in the current correlation functions (more details are given in Section 2), and at the same time include the cross term $C^{MQ}(q, t)$. It is shown that the effects of mass-charge coupling are significant.

In Section 2 we outline the framework used. It was originally proposed by Abramo *et al.*,[5] to calculate the partial structure factors in a binary salt. The idea is to construct two dynamical variables which are linear combinations of the cation and anion density fluctuations, with wavevector-dependent coefficients which are chosen so that the linear combinations are approximately independent. The longitudinal component of $C^{MQ}(q, t)$ is easily obtained from the partial structure factors, although the memory functions we use are different from those suggested in the above reference. The technique is extended to the transverse components, and in Section 3, the results we obtain for the velocity autocorrelation functions in NaCl, are reported.

2 THEORETICAL FRAMEWORK

Each of the currents in Eqs. (1.3) is expressed as one longitudinal and two transverse components, defined with respect to the direction of the wavevector $\mathbf{q}$. The longitudinal components are essentially second time derivatives of the appropriate density fluctuations, and we discuss this type of current autocorrelation function first.

Longitudinal components

Defining the Fourier components of the cation and anion densities as

$$n_{\mathbf{q}}^+(t) = \sum_{i=1}^{N^+} \exp(i\mathbf{q} \cdot \mathbf{r}_i^+(t)), \qquad n_{\mathbf{q}}^-(t) = \sum_{j=1}^{N^-} \exp(i\mathbf{q} \cdot \mathbf{r}_j^-(t))$$

the appropriate linear combinations are

$$\begin{aligned} A_{\mathbf{q}}^1(t) &= (m^+)^{1/2} \sin \theta_q n_{\mathbf{q}}^+(t) + (m^-)^{1/2} \cos \theta_q n_{\mathbf{q}}^-(t) \\ A_{\mathbf{q}}^2(t) &= (m^+)^{1/2} \cos \theta_q n_{\mathbf{q}}^+(t) - (m^-)^{1/2} \sin \theta_q n_{\mathbf{q}}^-(t) \end{aligned} \tag{2.1}$$

As stated above, at long wavelengths the mass and charge density fluctuations are approximately independent. An imposed requirement, therefore, is that $A^1_{\mathbf{q}}(t)$ and $A^2_{\mathbf{q}}(t)$ should be proportional to mass and charge density fluctuations as $q \to 0$. At the other extreme the ions behave as free particles. In this limit appropriate independent variables are proportional to $n^+_{\mathbf{q}}(t)$ and $n^-_{\mathbf{q}}(t)$. Hence θ_q should have the following 'boundary' conditions.

i) $$\lim_{q\to 0} \sin\theta_q = \left(\frac{m^+}{2m}\right)^{1/2}, \qquad \lim_{q\to 0} \cos\theta_q = \left(\frac{m^-}{2m}\right)^{1/2}$$

so that

$$\lim_{q\to 0} A^1_{\mathbf{q}}(t) = \frac{1}{(2m)^{1/2}}(m^+ n^+_{\mathbf{q}}(t) + m^- n^-_{\mathbf{q}}(t))$$

and

$$\lim_{q\to 0} A^2_{\mathbf{q}}(t) = \left(\frac{m^+ m^-}{2m}\right)^{1/2}(n^+_{\mathbf{q}}(t) - n^-_{\mathbf{q}}(t))$$

ii) $$\lim_{q\to\infty} \sin\theta_q = 0, \qquad \lim_{q\to\infty} \cos\theta_q = 1$$

so that

$$\lim_{q\to\infty} A^1_{\mathbf{q}}(t) = (m^-)^{1/2} n^-_{\mathbf{q}}(t)$$

and

$$\lim_{q\to\infty} A^2_{\mathbf{q}}(t) = (m^+)^{1/2} n^+_{\mathbf{q}}(t)$$

We can regard the dynamical variables $A^1_{\mathbf{q}}(t)$, $A^2_{\mathbf{q}}(t)$ as the components of a column matrix, and describe their time evolution by a generalized Langevin equation. The matrix of correlation functions can be formally expressed in terms of a hierarchy or memory function matrices. The reader is referred to the paper by Abramo *et al.*[5] for details.

We write $S_{\alpha\beta}(q, t) = \langle A^{\alpha}_{-\mathbf{q}}(0) A^{\beta}_{\mathbf{q}}(t)\rangle/N$, where the brackets denote a canonical ensemble average over the initial phase space. Equal time values will be referred to as $S_{\alpha\beta}(q)$, and its Fourier-Laplace transform as $\bar{S}_{\alpha\beta}(q, \omega)$. Ideally, the mixing parameter θ_q is chosen to diagonalize the matrix $S_{\alpha\beta}(q, t)$. The above limits on θ_q can be met, and the diagonalization very nearly achieved, by chosing

$$\omega^{\infty}_{12}(q) = \omega^{0}_{12}(q) \tag{2.2}$$

Following the notation of Abramo *et al.*, we have introduced the quantities

$$\omega^{\infty}_{\alpha\beta}(q) = \frac{1}{kTq^2}\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, \omega^4 \bar{S}_{\alpha\beta}(q, \omega)$$

and

$$\omega^0_{\alpha\beta}(q) = (-1)^{\alpha+\beta} kTq^2 S_{\bar{\alpha}\bar{\beta}}(q)[S_{11}(q)S_{22}(q) - S^2_{12}(q)]^{-1}$$

with $\bar{\alpha}$ denoting the component different from α. Condition (2.2) is equivalent to diagonalization of the dynamical matrix for longitudinal modes in the lattice vibration problem of ionic crystals. Simplifications are made, on the basis of symmetry requirements, by neglecting off-diagonal, second order memory functions.

The expressions for the dynamic structure factor then become

$$S_{\alpha\alpha}(q, \omega) = \frac{kTq^2}{2\pi\omega}\,\mathrm{Im}\left[\frac{\omega^2 - i\omega\Gamma^{(1)}_{\bar{\alpha}\bar{\alpha}}(q, \omega) - \omega^0_{\bar{\alpha}\bar{\alpha}}(q)}{D(q, \omega)}\right] \tag{2.3}$$

$$S_{\alpha\bar{\alpha}}(q, \omega) = -\frac{kTq^2}{2\pi\omega}\,\omega^0_{12}(q)\,\mathrm{Im}[D^{-1}(q, \omega)] \tag{2.4}$$

where

$$D(q, \omega) = [\omega^2 - i\omega\Gamma^{(1)}_{11}(q, \omega) - \omega^0_{11}(q)][\omega^2 - i\omega\Gamma^{(1)}_{22}(q, \omega) - \omega^0_{22}(q)] - [\omega^0_{12}(q)]^2 \tag{2.5}$$

$\Gamma^{(1)}_{\alpha\alpha}(q, t)$ are first order memory functions which appear in the generalized Langevin equations. Finally, we obtain the longitudinal currents $C^L_{\alpha\beta}(q, t)$, through the equation

$$C^L_{\alpha\beta}(q, t) = -\frac{1}{q^2}\ddot{S}_{\alpha\beta}(q, t) = \frac{1}{q^2}\int_{-\infty}^{\infty} \mathrm{d}\omega\,\omega^2 S_{\alpha\beta}(q, \omega)\exp(-i\omega t) \tag{2.6}$$

Now the quantities $\mathbf{J}^M_\mathbf{q}(t)$ and $\mathbf{J}^Q_\mathbf{q}(t)$, which we introduced in Section 1, are given by

$$\mathbf{J}^M_\mathbf{q}(t) = m^+\mathbf{j}^+_\mathbf{q}(t) + m^-\mathbf{j}^-_\mathbf{q}(t)$$

$$\mathbf{J}^Q_\mathbf{q}(t) = \mathbf{j}^+_\mathbf{q}(t) - \mathbf{j}^-_\mathbf{q}(t)$$

where

$$\mathbf{j}^+_\mathbf{q}(t) = \sum_{i=1}^{N^+} \mathbf{v}^+_i(t)\exp(i\mathbf{q}\cdot\mathbf{r}^+_i(t))$$

and

$$\mathbf{j}^-_\mathbf{q}(t) = \sum_{j=1}^{N^-} \mathbf{v}^-_j(t)\exp(i\mathbf{q}\cdot\mathbf{r}^-_j(t)) \tag{2.7}$$

Their longitudinal components are essentially linear combinations of the time derivations of $n^+_\mathbf{q}(t)$ and $n^-_\mathbf{q}(t)$. By inverting the transformation (2.1), we can readily express the current correlation functions (1.3) as linear combinations of the $C^L_{\alpha\beta}(q, t)$ defined in (2.6). In particular,

$$\begin{aligned} C^{MQ}_L(q, t) = {} & \frac{1}{2(m^+m^-)^{1/2}} [\Delta m \sin 2\theta_q - 2(m^+m^-)^{1/2} \cos 2\theta_q] \\ & \times [C^L_{11}(q, t) - C^L_{22}(q, t)] \\ & + \frac{1}{(m^+m^-)^{1/2}} [\Delta m \cos 2\theta_q + 2(m^+m^-)^{1/2} \sin 2\theta_q] c^L_{12}(q, t) \end{aligned} \tag{2.8}$$

Provided that we are able to construct the two memory functions $\Gamma^{(1)}_{11}(q, t)$ and $\Gamma^{(1)}_{22}(q, t)$, we can calculate the current correlation functions on the right hand side of the above equation. Abramo *et al.* assume a simple exponential time-dependence. The relaxation time is determined by a prescription proposed by Lovesey,[5] or a rather more elaborate alternative.[6] However, it is clear from the work of Adams *et al.*,[7] that a single relaxation time model is inadequate in molten salts. They demonstrate that a more appropriate form would be

$$\begin{aligned} \Gamma^{(1)}_{\alpha\alpha}(q, t) = {} & (\omega^\infty_{\alpha\alpha}(q) - \omega^0_{\alpha\alpha}(q)) \left[(1 - \beta(q)) \exp\left[- \left(\frac{t}{\tau^L_{1\alpha}(q)} \right)^2 \right] \right. \\ & \left. + \beta(q) \exp\left[- \frac{t}{\tau^L_{2\alpha}(q)} \right] \right] \end{aligned} \tag{2.9}$$

Although there is no computer simulation data of the parameter $\beta(q)$, or the relaxation times, we have this information for the mass and charge current autocorrelation functions.[7] We have utilized it in the following way, to estimate the memory functions.

i) For the thermodynamic state investigated by Adams *et al.*, both $C^{MM}_L(q, t)$ and $C^{QQ}_L(q, t)$ have the same, q-independent, value for $\tau^L_{2\alpha}(q)$. We also use it in (2.9).

ii) Data is available for $qa \leq 7$. For $qa > 7$ (where $\beta(q)$ is very small), we choose $\tau^L_{1\alpha}(q) = (\omega^\infty_{\alpha\alpha}(q) - \omega^0_{\alpha\alpha}(q))^{-1/2}$ a form which has proved useful before.[3]

iii) $C^L_{11}(q, t)$ and $C^L_{22}(q, t)$ may each be expressed as linear combinations of $C^{MM}_L(q, t)$, $C^{QQ}_L(q, t)$ and $C^{MQ}_L(q, t)$, with θ_q-dependent coefficients. Although $C^{MQ}_L(q, t)$ is significant, it is not the dominant term for $qa < 7$. We ignore its contribution, as a first approximation, and by means of a least squares fit to the $C^{MM}_L(q, t)$, $C^{QQ}_L(q, t)$ data, determine the parameters in the memory function. The $\tau^L_{1\alpha}(q)$ values obtained in this way turn out to be consistent with the above approximation for $qa \simeq 7$.

iv) Given the latter we calculate $C^L_{12}(q, t)$, and through Eq. (2.8) estimate the mass-charge coupling term $C^{MQ}_L(q, t)$. In principle this cycle can be repeated, but this time retaining our first approximation for $C_L^{MQ}(q, t)$ to obtain a more accurate memory function. It is a rather lengthy and tedious process, but we find after one cycle that $C^L_{\alpha\beta}(q, t)$ is very nearly diagonal. We take the results as adequate for our present purpose, bearing in mind the earlier simplifications which have been made in the theory.

It should be mentioned that the moments $\omega^{\infty}_{\alpha\alpha}(q)$ and $\omega^{0}_{\alpha\alpha}(q)$ can be calculated from the zeroth, second and fourth moments of $S^{MM}(q, \omega)$, $S^{QQ}(q, \omega)$ and $S^{MQ}(q, \omega)$. Formal expressions for these have been derived by Abramo *et al.*[8] In the absence of computer data for the moments in NaCl, we evaluate the expressions by using the radial distribution functions which have been tabulated for the SMS,[9] but with the correct mass-dependent coefficients of each term. The justification for the procedure stems from the predominant influence of the electrostatic component of the interionic interaction on the structure of the liquid.

Transverse components

The formalism outlined above can also be adapted to evaluate $C_T^{MQ}(q, t)$. In this case we choose the approximately independent variables to be

$$A^1_{\mathbf{q}}(t) = (m^+)^{1/2} \sin \theta_q \mathbf{j}^+_{\mathbf{q}T}(t) + (m^-)^{1/2} \cos \theta_q \mathbf{j}^-_{\mathbf{q}T}(t)$$

and

$$A^2_{\mathbf{q}}(t) = (m^+)^{1/2} \cos \theta_q \mathbf{j}^+_{\mathbf{q}T}(t) - (m^-)^{1/2} \sin \theta_q \mathbf{j}^-_{\mathbf{q}T}(t) \qquad (2.10)$$

where $\mathbf{j}^+_{\mathbf{q}T}(t)$, $\mathbf{j}^-_{\mathbf{q}T}(t)$ refer to the transverse components of the current density fluctuations defined in (2.7). In this case we introduce

$$C^T_{\alpha\beta}(q, t) = \langle A^{\alpha}_{-\mathbf{q}}(0) A^{\beta}_{\mathbf{q}}(t) \rangle / N$$

and $\bar{C}^T_{\alpha\beta}(q, w)$ as its Fourier–Laplace transform. At the limits of the wave-number range, $\sin \theta_q$ and $\cos \theta_q$ take the same values as for the longitudinal components. These will follow if we choose θ_q through the condition which is the transverse equivalent of (2.2), namely

$$\omega^T_{12}(q) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}\omega \, \omega^2 \bar{C}^T_{12}(q, \omega) = 0 \qquad (2.11)$$

Apart from the limits $q \to 0$ and $q \to \infty$, the angle θ_q will of course be different from that obtained for the longitudinal currents.

Unfortunately, we know only the zeroth and second moments of $\bar{C}^T_{\alpha\beta}(q, \omega)$, and we have to introduce approximations to the matrix of memory functions $\Gamma^{(1)}_{\alpha\beta}(q, t)$ (in the notation of Abramo *et al.*). Once again we neglect off-diagonal elements in this matrix. It follows from this, bearing in mind the constraint (2.11), that $\Gamma^{(0)}_{\alpha\bar{\alpha}}(q, t) = 0$, and because of the different structure of the equations in the transverse case that $C^T_{\alpha\bar{\alpha}}(q, t) = 0$. Thus as a consequence of our approximations, which are consistent with those made in our treatment of the longitudinal modes, there is no coupling between the variables $A^1_{\mathbf{q}}(t)$ and $A^2_{\mathbf{q}}(t)$. As a further consequence, we may show that

$$\bar{C}^T_{\alpha\alpha}(q, \omega) = \frac{C^T_{\alpha\alpha}(q, t = 0)}{i\omega + \bar{\Gamma}^{(0)}_{\alpha\alpha}(q, \omega)} \tag{2.12}$$

This memory function, $\bar{\Gamma}^{(0)}_{\alpha\alpha}(q, \omega)$, is related to $\bar{\Gamma}^{(1)}_{\alpha\alpha}(q, \omega)$ by the equation

$$\bar{\Gamma}^{(0)}_{\alpha\alpha}(q, \omega) = \frac{\omega^T_{\alpha\alpha}(q)}{i\omega + \bar{\Gamma}^{(1)}_{\alpha\alpha}(q, \omega)} \tag{2.13}$$

In the single relaxation-time approximation, $\bar{\Gamma}^{(1)}_{\alpha\alpha}(q, \omega)$ is replaced by a wave-number-dependent relaxation time. As before we believe that a more convincing form for the memory function is

$$\Gamma^{(0)}_{\alpha\alpha}(q, t) = \omega^T_{\alpha\alpha}(q)\left[(1 - \beta(q))\exp\left[-\left(\frac{t}{\tau^T_{1\alpha}(q)}\right)^2\right] + \beta(q)\exp\left[-\frac{t}{\tau^T_{2\alpha}(q)}\right]\right] \tag{2.14}$$

The parameters in this expression are determined in the way we outlined when discussing the longitudinal components. The one modification being that for $qa > 7$ we put $\tau^T_{1\alpha}(q) = (\omega^T_{\alpha\alpha}(q))^{-1/2}$. Our calculation of the mass-charge coupling also follows the same procedure, although because $C^T_{\alpha\bar{\alpha}}(q, t) = 0$, the latter is given by

$$C^{MQ}_T(q, t) = \frac{1}{2(m^+m^-)^{1/2}}[\Delta m \sin 2\theta_q - 2(m^+m^-)^{1/2} \cos 2\theta_q] \times [C^T_{11}(q, t) - C^T_{22}(q, t)] \tag{2.15}$$

In the next section we report some results for the velocity autocorrelations in NaCl, on the basis of Eqs. (1.1) and (1.2). The only remaining terms in the equations, which need to be specified, are the self correlation functions $F^+_s(q, t)$ and $F^-_s(q, t)$. We use the well-known Gaussian approximation to construct these, with appropriate values for the diffusion coefficients. Because the diffusion process is slow, compared to momentum transfer, the self correlation functions do not have a significant effect on the results. This point is demonstrated if we ignore diffusion by putting $F^+_s(q, t) = F^-_s(q, t) = 1$ (see Figure 3). Indeed, it is the great disparity between the diffusion rate and the rate of momentum transfer, which makes this method so effective in the discussion of velocity correlations in liquids.

3 RESULTS AND DISCUSSION

For the model investigated by Adams *et al.*,[7] the Coulombic coupling parameter $\Gamma = e^2/akT$ is 77.5, $n = 0.0308$ ions Å^{-3}, and the system simulates molten NaCl at a temperature of 1090 K. The time-dependent data is plotted

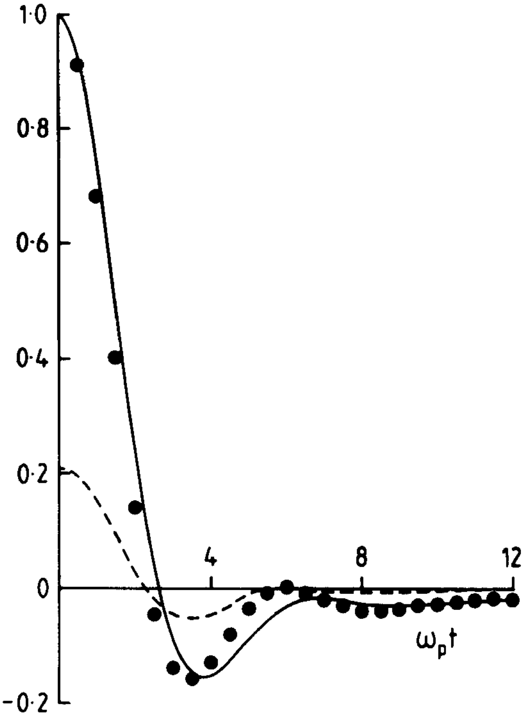

FIGURE 1 Normalized velocity autocorrelation function for Na^+ ion (dotted curve) obtained from Eq. (1.1). Also shown is the result (full curve) when mass-charge coupling term is omitted, and the contribution from charge current fluctuations (dashed curve).

in terms of $\omega_p t$, where $\omega_p = (2\pi n e^2/\mu)^{1/2}$ is the plasma frequency, $\mu = m^+ m^-/(m^+ + m^-)$ being the reduced mass. Under the conditions of the computer 'experiment,' $\omega_p = 4.4 \times 10^{13}\ s^{-1}$. We model the memory functions using this data; but in constructing the moments we have been obliged to use structure data from the SMS, for conditions in which $\Gamma = 64.6$.[9] Nevertheless, the fact that the structure data from these two sources is strikingly similar, leads us to believe that these inconsistencies will not be serious enough to invalidate our conclusions about the effect of the mass-charge coupling term.

In Figure 1 we show the velocity autocorrelation function for the Na^+ ion, as given by (1.1). We also include the result from (1.1) when the mass-charge coupling term is omitted, as well as the contribution from the charge current autocorrelation function $C^{QQ}(q, t)$. The same information for the Cl^- ion is reported in Figure 2. Because of the weak dependence of the results on $F_s^+(q, t)$, the coupling of the ionic motion to the charge current fluctuations has very nearly the same magnitude for each ion, but of opposite sign. Its contribution to the velocity correlation function is proportional to the mass

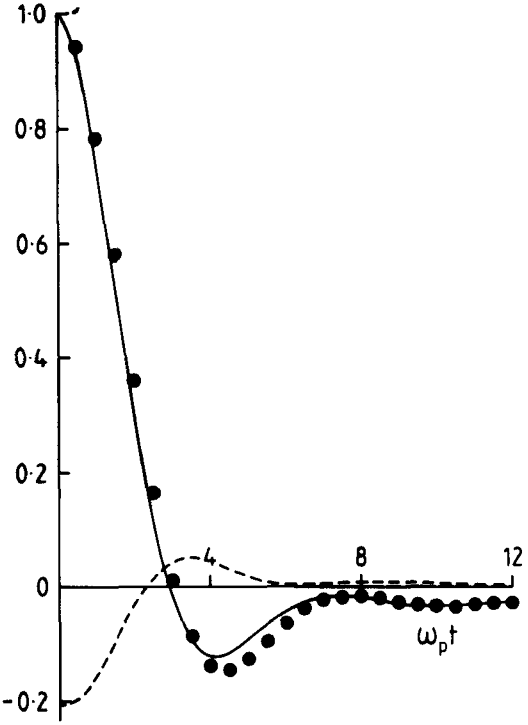

FIGURE 2 Normalized velocity autocorrelation function for Cl^- ion (dotted curve) obtained from (1.2). The full curve is the result when the mass-charge coupling term is omitted, and the dashed curve represents the contribution from the charge current fluctuations.

difference Δm, and in this application its effect is not very dramatic. It does, however, make a significant contribution to the depth of the first minimum in $\psi^+(t)$, whilst acting in the opposite sense for the heavier ion.

When the effect of the mass-charge contribution is compared in the two figures, its most important influence is in displacing the curves relative to the time axis, but in opposite directions for the respective ions. That is it separates $\psi^+(t)$ and $\psi^-(t)$ to a degree which brings the results more in line with computer simulation data. This is consistent with the behaviour at small t, as demonstrated by a direct calculation of the small t expansion of the autocorrelation functions. Including $C^{MQ}(q, t)$ increases the magnitude of the coefficient of t^2 for $\psi^+(t)$ and decreases it for $\psi^-(t)$. Clearly, if one attempts to explain computer data on velocity correlation functions on the basis of a theory which involves mass and charge fluctuations in the binary salt, the interaction of these variables must also be taken into account.

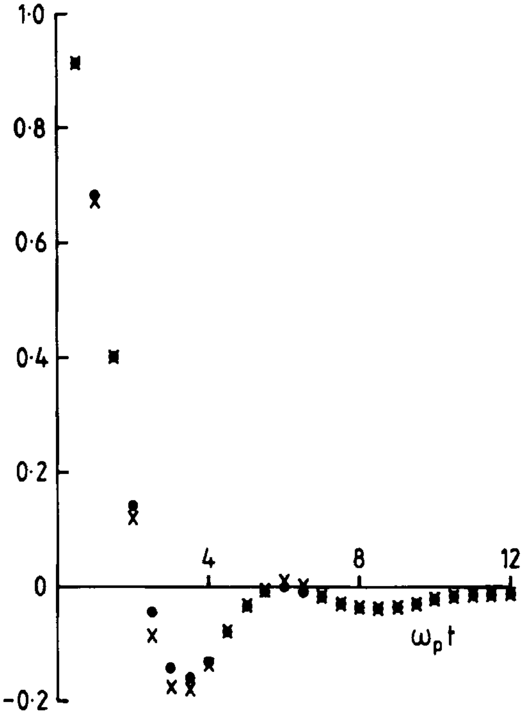

FIGURE 3 The dotted curve shows the velocity autocorrelation function for the Na$^+$ ion. The crosses give the result obtained from Eq. (1.1) with $F_s^+(q, t) = 1$.

Equations (1.1) and (1.2) contain a theory of the self-diffusion coefficient in the salt, and we conclude the discussion with the following remarks about the diffusion mechanism.

i) Assuming a value for the self-diffusion coefficient, D^+, of the Na$^+$ ions,[10] the root mean square displacement of an ion after 2.7×10^{-13} s (which is the period covered by the curves in Figures 1 and 2) is only 1.3 Å—about one third of the mean interionic separation. Not surprisingly, if we neglect the diffusion of the ion in our theory of the velocity autocorrelation function, the outcome is not significantly different. This is demonstrated explicitly in Figure 3, where we show the result obtained from (1.1) by putting $F_s^+(q, t) = 1$, which is its initial value. These observations will be valid for other liquids with similar packing fractions.

ii) The self-diffusion coefficients are obtained through the equation,

$$D^{\pm} = \frac{kT}{m^{\pm}} \int_0^{\infty} dt \psi^{\pm}(t)$$

If we use the simplification $F_s^{\pm}(q, t) = 1$, the time integral of the longitudinal component for each of the currents is zero. Even with the complete expressions for $\psi^+(t)$ and $\psi^-(t)$, it is clear that the transverse components largely determine the diffusion coefficients.

iii) The mass currents make virtually the same contribution to the self-diffusion coefficient of each type of ion. The charge current introduces a direct connection to the conductivity of the salt, and is most significant for the cation (being proportional to m^-). Its effect is to increase the ratio D^+/D^-. It is clear from Figures 1 and 2 that the mass-charge coupling term behaves in an oscillatory fashion, and in this application its influence on the diffusion coefficients is quite small, although acting in such a way as to reduce the ratio D^+/D^-.

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