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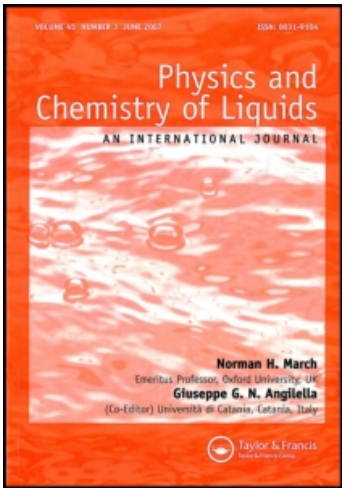

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Hydrodynamic correlation functions for molten salts

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Hydrodynamic Correlation Functions for Molten Salts†

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The linearized hydrodynamic equations for a binary ionic fluid, with specific reference to a dissociated molten salt, are used to evaluate correlation functions of local fluctuation variables and the corresponding response functions. Previous results for the instantaneous correlation functions are extended and connected with thermodynamic fluctuation theory. Different dynamical behaviours, depending on the relative magnitude of the relaxation frequency for charge fluctuations and the sound wave frequency, are demonstrated. When $4\pi\sigma/\epsilon \gg ck$, charge fluctuations are uncoupled from mass fluctuations, the latter being isomorphous to those of a one-component neutral fluid. Kubo relations for the transport coefficients are derived in this regime. When $4\pi\sigma/\epsilon \ll ck$, the behaviour of the ionic fluid becomes isomorphous to that of a neutral mixture, with electrical conduction playing a role analogous to interdiffusion and contributing, in particular, to the damping of sound waves. An interpolation formula between these two limiting behaviours of the relaxation frequencies is also derived. The consequences of these results for the light scattering spectrum of an ionic fluid are briefly discussed.

1 INTRODUCTION

The aim of the present work is to provide a comprehensive analysis of the correlation functions for fluctuations in the hydrodynamic regime for a realistic example of a charged fluid, that is a binary fluid of polarizable ions, with specific reference to a completely dissociated molten salt. A similar analysis for a two-component neutral fluid has been given recently by Cohen, Sutherland and Deutch[1] and by Bhatia, Thornton and March,[2] but

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the peculiarities which arise from the long range nature of the Coulomb interaction make it necessary to examine independently the case of the charged fluid.

Some of these characteristics have already been pointed out by Martin[3] in his discussion of a one-component charged fluid neutralized by a uniform, inert background. The charge relaxation mode frequency tends to a constant value, $4\pi\sigma/\epsilon$, rather than to a value vanishing as k^2 at long wavelengths. As a consequence, while the usual Kubo formula for the thermal conductivity[4] still holds, the electric conductivity and the thermoelectric coefficient are related to the Kubo limit of "screened" response functions. This form of the Kubo relations takes account of internal field correction terms in the driving forces.

In the present case the two-component nature of the fluid implies, of course, that the mass density and the charge density are distinct fluctuation variables, so that viscosity and electrostriction also play a role. As we shall see, the coupling between charge and mass fluctuations reflects directly the singularity in the Coulomb interaction. Physically different results are obtained in the two limiting situations $4\pi\sigma/\epsilon \ll ck$ and $4\pi\sigma/\epsilon \gg ck$ (here, σ is the electric conductivity, ϵ the dielectric constant, and c the long-wavelength sound velocity). In the former case, the time correlation functions are formally similar to those for a neutral mixture,[1] and in particular electric conduction is found to contribute to sound wave damping as is the case for interdiffusion in the mixture. However, this behaviour cannot be extrapolated to infinite wavelength, as signalled by the fact that the Kubo relations would be violated. In the opposite limit $4\pi\sigma/\epsilon \gg ck$, on the other hand, electrical effects do not contribute to the damping of sound waves. Numerical estimates indicate that this latter situation holds for molten salts at sonic wavelengths, but it appears that the transition from one regime to the other could be followed in sound attenuation or light scattering experiments on suitably chosen ionic fluids of low conductivity and high electrostriction.

With regard to polarization effects, very drastic simplifications are permissible for the fluid that we are considering. The vast difference in excitation energies for the electrons and for the ions ensures that, while the ions behave hydrodynamically, the polarization does not but enters only through a "high frequency" dielectric constant ϵ. Obviously, in the case of a partially associated ionic fluid or of an electrolytic solution, dynamical screening effects and diffusion of polarization may also occur. Caution should thus be exercized in applying our detailed results to more complex ionic systems.

The outline of the paper is briefly as follows. In section 2 we introduce the phenomenological equations of linearized hydrodynamics for the two-component charged fluid[5,6] and sketch the technique, well established since

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the work of Kadanoff and Martin,[7] by which one proceeds to derive the time correlation functions and the response functions of the liquid to a slowly varying perturbation, described in terms of an electric potential and of changes in pressure, temperature and electrochemical potential. In section 3 the instantaneous correlation functions entering the calculation are determined from the static limit of the hydrodynamic equations, with the help of Poisson's equation, the connexion with the results of thermodynamic fluctuation theory for a neutral mixture[8] being discussed in an Appendix. The analysis of the dispersion relation and the detailed expressions for the correlation spectra and the response functions are reported in section 4, while section 5 discusses the expressions of the transport coefficients in terms of response functions in the Kubo limit and section 6 discusses the optical properties in the appropriate low frequency region.

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2 LINEARIZED HYDRODYNAMIC EQUATIONS AND TIME CORRELATION FUNCTIONS

The linearized hydrodynamic equations for a molten salt[5,6] comprise the mass continuity equation,

$$\frac{\partial \rho(\underline{r}, t)}{\partial t} + \rho\psi(\underline{r}, t) = 0; \tag{2.1}$$

the Navier-Stokes equation from which we retain only the longitudinal part,

$$\rho\frac{\partial \psi(\underline{r},t)}{\partial t} = -\underline{\nabla}^2 p(\underline{r},t) + \rho b\, \underline{\nabla}^2\psi(\underline{r},t); \tag{2.2}$$

the continuity equation for the charge density,

$$\frac{\partial q(\underline{r},t)}{\partial t} + \underline{\nabla}\cdot \underline{j}(\underline{r},t) = 0; \tag{2.3}$$

and the heat transport equation,

$$\rho T\frac{\partial s(\underline{r},t)}{\partial t} = \kappa\nabla^2 T(\underline{r},t) - \frac{\alpha}{\sigma}\,\underline{\nabla}\cdot \underline{j}(\underline{r},t). \tag{2.4}$$

In these equations $\rho(\underline{r},t)$ and $q(\underline{r},t)$ are the mass density and the free charge density; $\psi(\underline{r},t)$ is the divergence of the local momentum per unit mass, and $\underline{j}(\underline{r},t)$ is the free-conduction current density; $p(\underline{r},t)$, $T(\underline{r},t)$ and $s(\underline{r},t)$ are the local pressure and temperature and the local entropy per unit mass; and $\rho = m_+n_+ + m_-n_- = n(m_+ + m_-) = nm$ is the mean mass density. The transport coefficients entering the equations are the longitudinal viscosity $\rho b = \frac{4}{3}\eta + \zeta$, where η and ζ are as usual the shear and bulk viscosities; the

electric conductivity σ, the thermal conductivity κ, and the thermoelectric coefficient α.

The form of Eqs. (2.1)–(2.4) is the same as for a two-component neutral fluid,[1] when the charge density and the electric current are replaced by the local concentration and the diffusion current, and α/σ is replaced by the appropriate transport coefficient involving the thermal diffusion ratio. The crucial difference between the charged fluid and the neutral fluid lies in the expression for the current, which in the present case is

$$\underline{j}(\underline{r}, t) = \sigma\left[\underline{E}(\underline{r}, t) - \frac{1}{e}\underline{\nabla}\mu(\underline{r}, t)\right] - \frac{\alpha}{T}\underline{\nabla}T(\underline{r}, t), \tag{2.5}$$

having made use of the Onsager symmetry relation for the thermoelectric coefficients. Here,[6]

$$\mu(\underline{r},t) = \frac{m_+ m_-}{m}\left[\mu_+(\underline{r},t) - \mu_-(\underline{r},t)\right] \tag{2.6}$$

is the electrochemical potential in terms of the local chemical potentials per unit mass of the two components. On the other hand, the electric field $\underline{E}(\underline{r},t)$ is related to the total charge density by Poisson's equation,

$$\underline{\nabla} \cdot \underline{E}(\underline{r},t) = 4\pi q_t(\underline{r},t) = \frac{4\pi}{\epsilon} q(\underline{r},t) \tag{2.7}$$

where ϵ is the dielectric constant. We can also write for the change in electrochemical potential

$$\delta\mu(\underline{r},t) = \left(\frac{\partial\mu}{\partial\rho}\right)_{T,q}\delta\rho(\underline{r},t) + \left(\frac{\partial\mu}{\partial q}\right)_{T,\rho}\delta q(\underline{r},t) + \left(\frac{\partial\mu}{\partial T}\right)_{\rho,q}\delta T(\underline{r},t) \tag{2.8}$$

so that Eq. (2.3) becomes

$$\frac{\partial q(\underline{r},t)}{\partial t} = \sigma\left[-\frac{4\pi}{\epsilon} + \frac{1}{e}\left(\frac{\partial\mu}{\partial q}\right)_{T,\rho}\nabla^2\right] q(\underline{r},t) + \lambda\sigma\nabla^2 T(\underline{r},t) + \nu\sigma\nabla^2\rho(\underline{r},t). \tag{2.9}$$

Here, the coefficient

$$\lambda = \frac{\alpha}{\sigma T} + \frac{1}{e}\left(\frac{\partial\mu}{\partial T}\right)_{\rho,q} \tag{2.10}$$

clearly describes the thermoelectric effects, and the coefficient

$$\nu = \frac{1}{e}\left(\frac{\partial\mu}{\partial\rho}\right)_{T,q} = \frac{1}{\rho}\left(\frac{\partial p}{\partial q}\right)_{T,\rho} \tag{2.11}$$

describes the electrostrictive effects. The term $-4\pi\sigma q(\underline{r},t)/\epsilon$ in the above equation, with its "anomalous" dependence on the wavelength of the fluctuation, is peculiar to the Coulomb fluid: the corresponding equation

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for the neutral mixture[1] contains only terms in $D\nabla^2 c(\underline{r},t)$, $c(\underline{r},t)$ being the local concentration and D the interdiffusion coefficient.

By expanding the pressure and entropy density fluctuations in a form analogous to eqn (2.8), eqns (2.2) and (2.4) are easily written

$$\frac{\partial \psi(\underline{r},t)}{\partial t} = -\frac{1}{\rho^2 K_T}\nabla^2\rho(\underline{r},t) - \frac{\alpha_T}{\rho K_T}\nabla^2 T(\underline{r},t) + b\nabla^2\psi(\underline{r},t) - \nu\nabla^2 q(\underline{r},t) \quad (2.12)$$

and

$$\frac{\partial T(\underline{r},t)}{\partial t} = \frac{\gamma\kappa}{\rho C_p}\nabla^2 T(\underline{r},t) + \frac{\gamma - 1}{\rho\alpha_T}\frac{\partial\rho(\underline{r},t)}{\partial t} + \frac{\gamma\lambda T}{\rho C_p}\frac{\partial q(\underline{r},t)}{\partial t}. \quad (2.13)$$

Here, K_T is the isothermal compressibility, $\gamma = C_p/C_V$ is the specific heat ratio, α_T is the thermal expansion, and use has been made of the thermodynamic identities

$$\left(\frac{\partial p}{\partial T}\right)_{\rho,q} = \rho\alpha_T\left(\frac{\partial p}{\partial \rho}\right)_{T,q} = \alpha_T/K_T, \quad (2.14)$$

$$\left(\frac{\partial s}{\partial \rho}\right)_{T,q} = -\frac{C_V}{T}\left(\frac{\partial T}{\partial \rho}\right)_{s,q} = \frac{C_V(1-\gamma)}{\rho T\alpha_T} \quad (2.15)$$

and

$$\left(\frac{\partial s}{\partial q}\right)_{T,\rho} = -\frac{1}{\rho e}\left(\frac{\partial \mu}{\partial T}\right)_{\rho,q}. \quad (2.16)$$

These involve the neutrality condition through the assumption that the internal electric potential is unchanged under changes of ρ or T at constant q.

Equations (2.1), (2.9), (2.12) and (2.13) give the basic form of the linearized hydrodynamic equations that we shall use in the subsequent evaluation of the correlation and response functions of the fluid. Denoting the four variables $\rho(\underline{r},t)$, $q(\underline{r},t)$, $T(\underline{r},t)$ and $\psi(\underline{r},t)$ by $A_i(\underline{r},t)$ with i = 1, 2, 3 and 4 respectively, and introducing their Fourier-Laplace transforms by

$$\hat{A}_i(\underline{k},z) = \int d\underline{r}\, \exp(i\underline{k}\cdot\underline{r}) \int_0^\infty dt\, \exp(-zt) A_i(\underline{r},t) \quad (2.17)$$

the hydrodynamic equations are compactly written

$$\sum_j M_{ij}(k,z)\,\hat{A}_j(k,z) = A_i(\underline{k}) \quad (2.18)$$

with

$$A_i(\underline{k}) = \int d\underline{r}\, \exp(i\underline{k}\cdot\underline{r})\, A_i(\underline{r},0). \quad (2.19)$$

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Here, the matrix $M(k,z)$ is explicitly given by

$$M(k,z) = \begin{bmatrix} z & 0 & 0 & \rho \\ \sigma\gamma k^2 & z + 4\pi\sigma(k)/\epsilon & \sigma\lambda k^2 & 0 \\ \gamma\sigma v\lambda Tk^2/(\rho C_p) & 4\pi\gamma\lambda T\sigma(\kappa)/(\epsilon\rho C_p) & z + \gamma(\kappa + \sigma\lambda^2 T)k^2/(\rho C_p) & (\gamma-1)/\alpha_T \\ -k^2/(\rho^2 K_T) & -\nu k^2 & -\alpha_T k^2/(\rho K_T) & z + bk^2 \end{bmatrix} \quad (2.20)$$

with

$$\sigma(k) = \sigma\left[1 + \frac{\epsilon}{4\pi e}\left(\frac{\partial\mu}{\partial q}\right)_{T,\rho} k^2\right]. \quad (2.21)$$

The formal solution of Eq. (2.18) can be written

$$\hat{A}_i(\underset{\sim}{k}z) = \sum_j N_{ij}(k,z)\, A_j(\underset{\sim}{k}) \quad (2.22)$$

where $N_{ij}(k,z) = |M|_{ij}/|M|$, $|M|_{ij}$ being the cofactor of $M_{ji}(k,z)$ in the determinant $|M|$ of the matrix $M(k,z)$. The Fourier-Laplace transforms of the correlation functions are then obtained as

$$\begin{aligned} \hat{S}_{ij}(k,z) &\equiv \langle \hat{A}_i(\underset{\sim}{k},z)\, A_j(-\underset{\sim}{k})\rangle \\ &= \sum_l N_{il}(k,z)\, S_{lj}(k) \end{aligned} \quad (2.23)$$

where

$$S_{lj}(k) = \langle A_l(\underset{\sim}{k})\, A_j(-\underset{\sim}{k})\rangle \quad (2.24)$$

are the instantaneous correlation functions. The van Hove functions $S_{ij}(k,\omega)$ follow from

$$S_{ij}(k,\omega) = 2\mathrm{Re}\,\hat{S}_{ij}(k,-i\omega) \qquad (i, j = 1,2,3;\ i = j = 4) \quad (2.25)$$

and

$$S_{ij}(k,\omega) = 2i\mathrm{Jm}\,\hat{S}_{ij}(k,-i\omega) \qquad (i = 1,2,3 \text{ and } j = 4) \quad (2.26)$$

The response functions of the fluid can then be calculated through the fluctuation-dissipation theorem and the Kramers-Kronig relations.

Before we carry out this program it is, however, necessary to discuss the instantaneous correlation functions introduced in Eq. (2.24).

3 INSTANTANEOUS CORRELATION FUNCTIONS

In the neutral fluid away from a critical point, it can be safely assumed that the range of intermolecular correlations is much shorter than k^{-1} in the

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hydrodynamic regime, and one can use thermodynamic fluctuation theory to determine the limiting values of the instantaneous correlation functions, as was first done for mixtures by Kirkwood and Buff.[8] The same theory cannot be straightforwardly applied to correlations involving charge density fluctuations, and indeed $S_{22}(k)$ is well known[9] to vanish as k^2 as a consequence of the long range nature of the Coulomb interaction. One can, however, determine this correlation function directly with the help of Poisson's equation, and similarly determine the other correlation functions from the static limit of the hydrodynamic equations in the presence of an external perturbation.

To evaluate $S_{22}(k)$ we consider the fluid in the presence of an external, static charge density $q_e(\underline{r})$, when the Poisson equation reads

$$\underline{\nabla} \cdot \underline{E}(\underline{r}) = \frac{4\pi}{\epsilon}\left[q(\underline{r}) + q_e(\underline{r})\right]. \tag{3.1}$$

The hydrodynamic equation (2.9) may then be written

$$\left[1 - \frac{\epsilon}{4\pi e}\left(\frac{\partial \mu}{\partial q}\right)_{T,\rho} \nabla^2 + \frac{\epsilon}{4\pi}\rho^2 v^2 K_T \nabla^2\right] q(\underline{r}) = -q_e(\underline{r}) \tag{3.2}$$

having made use of the other hydrodynamic equations and in particular of the relation

$$\nabla^2 \rho(\underline{r}) = -\rho^2 v K_T \nabla^2 q(\underline{r}) \tag{3.3}$$

which follows from (2.12). Equation (3.2) is solved to find

$$q(\underline{k}) = -\left[1 + k^2/k_s^2\right]^{-1} q_e(\underline{k}) \tag{3.4}$$

with

$$k_s^2 = \frac{4\pi e}{\epsilon}\left[\left(\frac{\partial \mu}{\partial q}\right)_{T,\rho} - e\rho^2 v^2 K_T\right]^{-1} = \frac{4\pi e}{\epsilon}\Bigg/\left(\frac{\partial \mu}{\partial q}\right)_{T,\rho} \tag{3.5}$$

This expression for the inverse screening length is soon shown to reduce for the one-component Coulomb fluid to the usual expression in terms of the isothermal compressibility.[3] Equation (3.4) thus embodies the perfect screening property of the conducting fluid, and through the fluctuation-dissipation theorem yields

$$S_{22}(k) = \frac{\epsilon k_B T k^2}{4\pi}(1 + k^2/k_s^2)^{-1}, \tag{3.6}$$

this result being in fact correct to order k^4.

A similar static calculation can be carried out for the other instantaneous correlation functions. From Eq. (3.3) we immediately see that $S_{12}(k)$ is

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related to $S_{22}(k)$ to order k^2,

$$S_{12}(k) = -\rho^2 \nu K_T \frac{\epsilon k_B T k^2}{4\pi} \tag{3.7}$$

Similarly, we find

$$S_{11}(k) = \rho^2 k_B T K_T, \tag{3.8}$$

$$S_{33}(k) = k_B T^2/(\rho C_v) \tag{3.9}$$

and

$$S_{44}(k) = -k_B T k^2/\rho, \tag{3.10}$$

while $S_{23}(k)$ is of order k^4 and $S_{13}(k)$ is of order at least k^2. However, to determine these latter correlation functions, as well as higher order terms in Eqs. (3.7)–(3.9), it would be necessary to go beyond the hydrodynamic equations.

Finally, we report the expressions for the partial ionic structure factors in the long wavelength limit, which follow by a straightforward calculation from the results given above. We find

$$S_{++}(k) = nk_B T K_T + \frac{\epsilon k_B T k^2}{4\pi n e^2}\left[\frac{m_-^2}{m^2} - 2m_- e n^2 \nu K_T + A\right], \tag{3.11}$$

$$S_{--}(k) = nk_B T K_T + \frac{\epsilon k_B T k^2}{4\pi n e^2}\left[\frac{m_+^2}{m^2} + 2m_+ e n^2 \nu K_T + A\right], \tag{3.12}$$

and

$$S_{+-}(k) = nk_B T K_T + \frac{\epsilon k_B T k^2}{4\pi n e^2}\left[-\frac{m_+ m_-}{m^2} + e n^2 \nu K_T (m_+ - m_-) + A\right], \tag{3.13}$$

where A is an unknown quantity determined by the unknown term of order k^2 in $S_{11}(k)$. The equality of these structure factors for $k \to 0$ is a well known consequence of charge neutrality. The first term in each square bracket agrees with the results obtained by Abramo, Parrinello and Tosi[10] on a plasmon-like model.

The connexion between the above expressions for the partial ionic structure factors and the thermodynamic fluctuation theory of Kirkwood and Buff[8] is discussed in the Appendix.

4 VAN HOVE FUNCTIONS AND RESPONSE FUNCTIONS

We are now in a position to evaluate the correlation spectra and the response functions of the Coulomb fluid in the hydrodynamic region. We write the

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dispersion relation of the fluid in the form

$$|M(k,z)| = \left(z + \frac{4\pi\sigma}{\epsilon} + z_1 k^2\right)(z + z_2 k^2)(z - ick + \Gamma k^2)(z + ick + \Gamma k^2) \tag{4.1}$$

where $c = [\gamma/(\rho K_T)]^{1/2}$ is the adiabatic sound velocity, and proceed to evaluate the coefficients of the k^2 relaxation terms by comparison with (2.20) under the assumption that these terms are small compared with ck. We must distinguish different regimes depending on the relative magnitude of the long-wavelength relaxation frequency $4\pi\sigma/\epsilon$ of the charge fluctuation mode and the sound wave frequency.

(i) *Kubo regime* ($4\pi\sigma/\epsilon \gg ck$). In this regime, which is relevant for the derivation of Kubo relations for the transport coefficients, the charge fluctuation mode is uncoupled from the mass and temperature fluctuation modes, which are in fact analogous to those of a one-component neutral fluid.[7] We find

$$z_1 = \sigma\left[\frac{4\pi}{k_s^2} + \frac{T\lambda_p^2}{\rho C_p} + \gamma K_T \rho^2 \tilde{\nu}^2\right], \tag{4.2}$$

$$z_2 = \kappa/(\rho C_p) \tag{4.3}$$

and

$$\Gamma = \tfrac{1}{2}[b + (\gamma - 1)\kappa/(\rho C_p)], \tag{4.4}$$

where

$$\lambda_p = \frac{\alpha}{\sigma T} + \frac{1}{e}\left(\frac{\partial\mu}{\partial T}\right)_{p,q} \tag{4.5}$$

and

$$\tilde{\nu} = \nu + \lambda_p T \alpha_T/(\rho^2 C_p K_T). \tag{4.6}$$

It should be noticed that the thermoelectric effects described by λ_p enter the charge fluctuation mode but do not affect the thermal mode. This result, which is confirmed by the Kubo relations to be derived in the next section, is at variance from the results of Corkum and McLennan,[11] who effectively assumed $z_1 = 0$.

(ii) *Two-component regime* ($4\pi\sigma/\epsilon \ll ck$). In this regime all the relaxation frequencies are small compared with the sound wave frequency and the behaviour of the charged fluid becomes similar to that of a two-component neutral fluid,[1] with electrical conduction playing the role of interdiffusion.

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We find

$$z_1 = \sigma\left[\frac{4\pi}{k_S^2} + \frac{T\lambda_p^2}{\rho C_p}\right], \tag{4.7}$$

$$z_2 = \kappa/(\rho C_p) \tag{4.8}$$

and

$$\Gamma = \tfrac{1}{2}[b + (\gamma - 1)\kappa/(\rho C_p) + \gamma K_T \rho^2 \tilde{v}^2 \sigma], \tag{4.9}$$

so that both electrostrictive and thermoelectric effects contribute to the damping of sound waves.

(iii) *Intermediate regime* ($4\pi\sigma/\epsilon \sim ck$). By analysing this case one finds an interpolation formula between the two previous limiting cases, which reads

$$z_1(k) = \sigma\left[\frac{4\pi}{k_S^2} + \frac{T\lambda_p^2}{\rho C_p} + \frac{(4\pi\sigma/\epsilon)^2}{(ck)^2 + (4\pi\sigma/\epsilon)^2}\gamma K_T \rho^2 \tilde{v}^2\right] \tag{4.10}$$

and

$$\Gamma(k) = \frac{1}{2}\left[b + (\gamma - 1)\frac{\kappa}{\rho C_p} + \frac{(ck)^2}{(ck)^2 + (4\pi\sigma/\epsilon)^2}\gamma K_T \rho^2 \tilde{v}^2 \sigma\right]. \tag{4.11}$$

With typical values for molten salts, that is $\sigma/\epsilon \sim 1$ ohm^{-1} cm^{-1} and $c \sim 10^5$ cm sec^{-1}, one finds a transition wavelength of the order of a few interionic distances. The hydrodynamic behaviour of these systems should thus be governed by Eqs. (4.2)–(4.4), but it may be possible to observe the transition from one regime to the other in ionic systems of low σ/ϵ and high $\tilde{v}$.

We give below the detailed expressions of the correlation spectra and the response functions, with special emphasis on the Kubo regime appropriate to molten salts.

4.1 Correlation functions

With the relaxation frequencies determined in Eqs. (4.2)–(4.4) or in Eqs. (4.7)–(4.9) to order k^2, the explicit solution of Eq. (2.23) yields the Fourier-Laplace transforms of the correlation functions in the general form

$$\tilde{S}_{ij}(k,z) = f_{ij}(k)\left[\frac{A_{ij}(k)}{z + z(k)} + \frac{B_{ij}(k)}{z + z_2 k^2} + \frac{C_{ij}(k)z + D_{ij}(k)}{z^2 + 2\Gamma k^2 z + c^2 k^2 + \Gamma^2 k^4}\right] \tag{4.12}$$

with $z(k) = 4\pi\sigma/\epsilon + z_1 k^2$. Correspondingly, the correlation spectra take the general form

$$S_{ij}(k,\omega) = f_{ij}(k)\left\{\frac{2A_{ij}(k)z(k)}{\omega^2 + z^2(k)} + \frac{2B_{ij}(k)z_2 k^2}{\omega^2 + (z_2 k^2)^2} + \right.$$

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TABLE I

Mode strengths in the correlation functions ($4\pi\sigma/\epsilon \gg ck$)†

$S_{ij}(k,\omega)$	$f_{ij}(k)$	$A_{ij}(k)$	$B_{ij}(k)$	$C_{ij}(k)$	$D_{ij}(k)$	$E_{ij}(k)$
$S_{11}(k,\omega)$	$S_{11}(k)$	$O(k^4)$	$1-\gamma^{-1}$	γ^{-1}	$\gamma^{-1}(4\Gamma-b)k^2$	$\gamma^{-1}(3\Gamma-b)k^2$
$S_{22}(k,\omega)$	$S_{22}(k)$	$1-\frac{\epsilon k^2}{4\pi}\left(\frac{T\lambda_p^2}{\rho C_p}+\gamma\rho^2\tilde{v}^2K_T\right)$	$\frac{\epsilon k^2}{4\pi}\left(\frac{T\lambda_p^2}{\rho C_p}\right)$	$\frac{\epsilon k^2}{4\pi}(\gamma\rho^2\tilde{v}^2K_T)$	$O(k^4)$	$O(k^4)$
$S_{12}(k,\omega)$	$S_{12}(k)$	$\frac{\tilde{v}}{v}\left(\frac{ck\epsilon}{4\pi\sigma}\right)^2$	$-(1-\gamma^{-1})\frac{\lambda_p}{\rho v\alpha_T}$	$\tilde{v}/v$	$\left(\frac{\epsilon c^2}{4\pi\sigma}+2\Gamma-\frac{T\lambda_p\alpha_T\kappa}{\rho^3C_p^2K_T\tilde{v}}\right)\frac{\tilde{v}}{v}k^2$	$\left(\frac{\epsilon c^2}{4\pi\sigma}+\Gamma-\frac{T\lambda_p\alpha_T\kappa}{\rho^3C_p^2K_T\tilde{v}}\right)\frac{\tilde{v}}{v}k^2$
$S_{33}(k,\omega)$	$S_{33}(k)$	$\frac{\epsilon k^2}{4\pi}\frac{T\lambda^2}{\rho C_v}$	γ^{-1}	$1-\gamma^{-1}$	$(1-\gamma^{-1})\left(b-\frac{2\kappa}{\rho C_p}\right)k^2$	$(1-\gamma^{-1})\left[\Gamma-(\gamma+1)\frac{\kappa}{\rho C_p}\right]k^2$
$S_{13}(k,\omega)$	$S_{33}(k)$	$O(k^4)$	$-\rho\alpha_T\gamma^{-1}$	$\rho\alpha_T\gamma^{-1}$	$\rho\alpha_T\gamma^{-1}\left(2\Gamma-\frac{\kappa}{\rho C_p}\right)k^2$	$\rho\alpha_T\gamma^{-1}\left(\Gamma-\frac{\kappa}{\rho C_p}\right)k^2$
$S_{23}(k,\omega)$	$S_{33}(k)$	$\frac{\epsilon k^2}{4\pi}\lambda$	$-\frac{\epsilon k^2}{4\pi}\frac{\lambda_p}{\gamma}$	$-\frac{\epsilon k^2}{4\pi}\rho\alpha_T\tilde{v}$	$O(k^4)$	$O(k^4)$

† The value of Γ is given in Eq. (4.4).

$$+ C_{ij}(k)\left[\frac{\Gamma k^2}{(\omega + ck)^2 + (\Gamma k^2)^2} + \frac{\Gamma k^2}{(\omega - ck)^2 + (\Gamma k^2)^2}\right] +$$

$$+ (ck)^{-1} E_{ij}(k)\left[\frac{\omega + ck}{(\omega + ck)^2 + (\Gamma k^2)^2} - \frac{\omega - ck}{(\omega - ck)^2 + (\Gamma k^2)^2}\right]\Bigg\} \quad (4.13)$$

with

$$E_{ij}(k) = D_{ij}(k) - \Gamma k^2 C_{ij}(k). \quad (4.14)$$

The values of the functions defining the strength of the various modes are collected in Table I for the Kubo regime and in Table II for the two-component regime. Of several entries in Table I we give only the order in k, as their determination would require the evaluation of the mode frequencies to order k^4 and higher order terms in the instantaneous correlation functions. The same comment applies to higher-order terms for the other entries. On the other hand, it is seen from Table II that in the two-component regime the charge fluctuation mode contributes terms of order k^2 to both $S_{11}(k,\omega)$ and $S_{12}(k,\omega)$. In fact, the structure of the correlation spectra in this regime

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TABLE II

Mode strengths in the correlation functions ($4\pi\sigma/\epsilon \ll ck$)†

$S_{ij}(k,\omega)$	$f_{ij}(k)$	$A_{ij}(k)$	$B_{ij}(k)$	$C_{ij}(k)$
$S_{11}(k,\omega)$	$S_{11}(k)$	$\frac{\epsilon k^2}{4\pi}\rho^2\bar{v}^2 K_T$	$1 - \gamma^{-1}$	γ^{-1}
$S_{22}(k,\omega)$	$S_{22}(k)$	$1 - \frac{\epsilon k^2}{4\pi}\frac{T\lambda_p^2}{\rho C_p}$	$\frac{\epsilon k^2}{4\pi}\frac{T\lambda_p^2}{\rho C_p}$	—
$S_{12}(k,\omega)$	$S_{12}(k)$	$\frac{\bar{v}}{v}\left\{1 + \frac{\epsilon k^2}{4\pi\sigma}\left[\frac{(1-\gamma^{-1})\kappa}{\rho\alpha_T\bar{v}} - T\lambda_p\sigma\right]\frac{\lambda_p}{\rho C_p}\right\}$	$-(1-\gamma^{-1})\frac{\lambda_p}{\rho v\alpha_T}$	—
$S_{33}(k,\omega)$	$S_{33}(k)$	$\frac{\epsilon k^2}{4\pi}\frac{T\lambda_p^2}{\gamma\rho C_p}$	γ^{-1}	$1 - \gamma^{-1}$
$S_{13}(k,\omega)$	$S_{33}(k)$	$-\frac{\epsilon k^2}{4\pi}\lambda_p\frac{\rho^2\bar{v}K_T}{\gamma}$	$-\rho\alpha_T\gamma^{-1}$	$\rho\alpha_T\gamma^{-1}$
$S_{23}(k,\omega)$	$S_{33}(k)$	$\frac{\epsilon k^2}{4\pi}\frac{\lambda_p}{\gamma}$	$-\frac{\epsilon k^2}{4\pi}\frac{\lambda_p}{\gamma}$	—

† The value of Γ is given in Eq. (4.9). Missing entries are of higher order in the transport coefficients.

is wholly analogous to that reported by Bhatia, Thornton and March[2] for a two-component neutral liquid.

4.2 Response functions and dielectric function

We define, as usual the response function $\mathcal{X}_{ij}(k,\omega)$ as relating the change in the mean value of the variable $A_i(\underset{\sim}{k},t)$ to a weak external perturbation coupled to the variable $A_j(\underset{\sim}{k},t)$. The fluctuation-dissipation theorem yields

$$\mathrm{Jm}\,\mathcal{X}_{ij}(k,\omega) = \frac{\omega}{2k_B T} S_{ij}(k,\omega) \qquad (i,j = 1, 2, 3; i = j = 4) \tag{4.15}$$

whence, using the Kramers-Kronig relations

$$\mathrm{Re}\mathcal{X}_{ij}(k,\omega) - \mathcal{X}_{ij}(k,\infty) = \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{\mathrm{Jm}\mathcal{X}_{ij}(k,\omega')}{\omega' - \omega} \tag{4.16}$$

we have

$$\mathcal{X}_{ij}(k,\omega) - \mathcal{X}_{ij}(k,\infty) = (k_B T)^{-1}[S_{ij}(k) + i\omega\,\tilde{S}_{ij}(k, -i\omega)]. \tag{4.17}$$

$D_{ij}(k)$	$E_{ij}(k)$
$\gamma^{-1}(4\Gamma - b)k^2$	$\gamma^{-1}(3\Gamma - b)k^2$
—	—
$\frac{4\pi\sigma}{\epsilon}\frac{\tilde{v}}{v}\left(1 + \frac{k^2}{k_S^2}\right)$	$\frac{4\pi\sigma}{\epsilon}\frac{\tilde{v}}{v}\left(1 + \frac{k^2}{k_S^2}\right)$
$(1 - \gamma^{-1})\left(b - \frac{2\kappa}{\rho C_p} - \frac{2\rho\tilde{v}K_T\sigma\lambda_p}{\alpha_T}\right)k^2$	$(1 - \gamma^{-1})\left(b - \Gamma - \frac{2\kappa}{\rho C_p} - \frac{2\rho\tilde{v}K_T\sigma\lambda_p}{\alpha_T}\right)k^2$
$\frac{\rho\alpha_T}{\gamma}\left(2\Gamma - \frac{\kappa}{\rho C_p} - \frac{\rho\tilde{v}K_T\sigma\lambda_p}{\alpha_T}\right)k^2$	$\frac{\rho\alpha_T}{\gamma}\left(\Gamma - \frac{\kappa}{\rho C_p} - \frac{\rho\tilde{v}K_T\sigma\lambda_p}{\alpha_T}\right)k^2$
$-\rho\tilde{v}\alpha_T\sigma k^2$	$-\rho\tilde{v}\alpha_T\sigma k^2$

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Detailed expressions are immediately obtained from Eqs. (3.6)–(3.9) and Eq. (4.12).

Of course, by "infinite" frequency we mean frequencies which are much higher than sound wave frequencies and yet much smaller than the frequencies of the other real excitation processes of the system. In practice, since the hydrodynamic equations do not contain the possibility of a plasmon-like mode of the ionic system, the upper cut-off frequency must be much smaller than the frequency of this possible mode, of order $10^{13}\,\mathrm{sec}^{-1}$. Thus, in deriving the dielectric function $\epsilon(\mathrm{k},\omega)$, which is related to the *total* charge response $\chi(\mathrm{k},\omega)$ by

$$\epsilon^{-1}(\mathrm{k},\omega) = 1 - \frac{4\pi}{\mathrm{k}^2}\chi(\mathrm{k},\omega), \tag{4.18}$$

we must set

$$\chi(\mathrm{k},\infty) = (1 - \epsilon^{-1})\frac{\mathrm{k}^2}{4\pi}. \tag{4.19}$$

We can also use

$$\chi(\mathrm{k},\omega) - \chi(\mathrm{k},\infty) = \epsilon^{-2}\chi_{22}(\mathrm{k},\omega) \tag{4.20}$$

on account of the fact that $\chi_{22}(\mathrm{k},\omega)$ describes the response of the *free* charge, with $\chi_{22}(\mathrm{k},\infty) = 0$. From Eq. (4.17) we find

$$\chi_{22}(\mathrm{k},\omega) = \frac{\sigma \mathrm{k}^2}{\mathrm{z}(\mathrm{k}) - \mathrm{i}\omega} \qquad (\omega \neq 0) \tag{4.21}$$

neglecting the thermal conduction mode and the sound wave mode which at finite ω contribute only terms of order k.[6] We thus find

$$\epsilon(\mathrm{k},\omega) = \epsilon + 4\pi\mathrm{i}\sigma/\omega \qquad (\omega \neq 0) \tag{4.22}$$

in accord with the well known expression.

On the other hand, in the static case the contributions of the thermal mode and of the mass fluctuation mode become of order k^4. Use of the fluctuation-dissipation theorem yields directly

$$\chi_{22}(\mathrm{k},0) = (\mathrm{k_B T})^{-1}\mathrm{S}_{22(\mathrm{k})} \tag{4.23}$$

whence

$$\epsilon(\mathrm{k},0) = \epsilon(1 + \mathrm{k}_\mathrm{S}^2/\mathrm{k}^2). \tag{4.24}$$

Similar caution in the static limit is necessary for the other response functions.

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4.3 Screened response functions

The screened response functions, that we shall need for the subsequent discussion of the Kubo relations, relate the change in the mean value of a fluctuation variable to the *internal* value of a weak perturbation coupled to another fluctuation variable, which differs from the external perturbation because of screening. The screened response function $\tilde{\chi}_{AB}(k,\omega)$ for two generic variables denoted by A and B can be evaluated by[3]

$$\tilde{\chi}_{AB}(k,\omega) = \chi_{AB}(k,\omega) + \frac{4\pi}{k^2}\epsilon(k,\omega)\chi_{Aq_t}(k,\omega)\chi_{q_tB}(k,\omega) \tag{4.25}$$

where q_t denotes the fluctuation in the total charge density.† In the particular case where one of the variables is the total charge density, this expression simplies to

$$\tilde{\chi}_{Aq_t}(k,\omega) = \epsilon(k,\omega)\chi_{Aq_t}(k,\omega) \tag{4.26}$$

on account of Eq. (4.18).

On taking in the present case $\chi_{Aq_t}(k,\infty) = 0$ for $A \neq q_t$, we have

$$\chi_{Aq_t}(k,\omega) = \epsilon^{-1}\chi_{A2}(k,\omega) \qquad (A \neq q_t) \tag{4.27}$$

which allows the explicit evaluation of the screened response functions from the results reported in the previous sections. On the other hand, we have

$$\tilde{\chi}(k,\omega) = \epsilon(k,\omega)\chi(k,\omega) = \frac{k^2}{4\pi}[\epsilon(k,\omega) - 1]. \tag{4.28}$$

5 KUBO RELATIONS

It is evident from the foregoing discussion that the longitudinal viscosity and the thermal conductivity in the ionic fluid are related to the Kubo limit of the correlation spectra in exactly the same manner as in a neutral one-component fluid, that is

$$\lim_{\omega\to 0}\omega^4\left[\lim_{k\to 0} k^{-4}S_{11}(k,\omega)\right] = 2k_BT\left(\frac{4}{3}\eta + \zeta\right), \tag{5.1}$$

$$\lim_{\omega\to 0}\omega^2\left[\lim_{k\to 0} k^{-2}S_{33}(k,\omega)\right] = 2k_B\left(\frac{T}{\rho C_V}\right)^2\kappa \tag{5.2}$$

† Equation (4.25) includes in the internal field correction the screening of the Coulomb potential but still excludes thermodynamic corrections to the driving forces (see Kubo[12] for a discussion on the one-component charged fluid). These two alternative definitions of the internal fields are, however, equivalent to the order in k of present interest.

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and

$$\lim_{\omega\to 0}\omega^4\left[\lim_{k\to 0}k^{-4}S_{13}(k,\omega)\right] = 2\rho\left(\frac{\partial T}{\partial \rho}\right)_{s,q}\left(b + \frac{\kappa}{\rho C_V}\right). \tag{5.3}$$

On the other hand, as discussed in detail by Martin,[3] meaningful Kubo relations for electrical transport coefficients can be obtained only from the screened response functions. One easily finds from the results reported above the following relations:

$$\lim_{\omega\to 0}\omega\left[\lim_{k\to 0}k^{-2}\,\mathrm{Jm}\,\tilde{\chi}_{q_tq_t}(k,\omega)\right] = \sigma, \tag{5.4}$$

$$\lim_{\omega\to 0}\omega^3\left[\lim_{k\to 0}k^{-4}\,\mathrm{Jm}\,\tilde{\chi}_{12}(k,\omega)\right] = \gamma\rho\tilde{v}\epsilon\sigma, \tag{5.5}$$

and

$$\lim_{\omega\to 0}\omega\left[\lim_{k\to 0}k^{-2}\,\mathrm{Jm}\,\tilde{\chi}_{23}(k,\omega)\right] = \frac{\epsilon T}{\rho C_V}(\lambda\sigma). \tag{5.6}$$

Kubo relations are in fact more usefully derived in terms of current response functions. In particular, introducing the heat flux $\underline{J}(\underline{r},t)$ through

$$\underline{\nabla}\cdot\underline{J}(\underline{r},t) = -\rho T\frac{\partial s(\underline{r},t)}{\partial t} = \frac{T\alpha_T}{\rho K_T}\frac{\partial\rho(\underline{r},t)}{\partial t} + \frac{T}{e}\left(\frac{\partial\mu}{\partial T}\right)_{\rho,q}\frac{\partial q(\underline{r},t)}{\partial t} - \rho C_V\frac{\partial T(\underline{r},t)}{\partial t} \tag{5.7}$$

we see that we can evaluate response functions involving this flux, of the type $\chi_{AJ}(k,\omega)$, through

$$\chi_{AJ}(k,\omega) = -\frac{\omega}{k}\left\{\frac{T\alpha_T}{\rho K_T}\chi_{A\rho}(k,\omega) + \frac{T}{e}\left(\frac{\partial\mu}{\partial T}\right)_{\rho,q}\chi_{Aq}(k,\omega) - \rho C_V\,\chi_{AT}(k,\omega)\right\} \tag{5.8}$$

and similarly for $\chi_{JJ}(k,\omega)$. The relation (5.2) becomes

$$\lim_{\omega\to 0}\omega^{-1}\,\mathrm{Jm}\,\chi_{JJ}(0,\omega) = T\kappa \tag{5.9}$$

and, in addition, one has the relation

$$\lim_{\omega\to 0}\omega^{-1}\,\mathrm{Jm}\,\tilde{\chi}_{JJ}(0,\omega) = T\tilde{\kappa} \tag{5.10}$$

with $\tilde{\kappa} = \kappa + \alpha^2/(T\sigma)$. The meaning of these relations becomes apparent if one notices that the phenomenological equation relating the heat flux to the driving forces reads[5]

$$\underline{J} = \alpha(\underline{E} - \underline{\nabla}\mu) - \tilde{\kappa}\,\underline{\nabla}T \tag{5.11}$$

so that the screening effected in eqn (5.10) separates from the observed

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thermal conductivity κ the term $-\alpha^2/(T\sigma)$ arising from the dynamical coupling between temperature and charge fluctuations. On the other hand, the thermoelectric coefficient α is given directly by the relation

$$\lim_{\omega\to 0} \omega^{-1}\, \mathrm{Jm}\, \tilde{X}_{j_t j_t}(0,\omega) = \alpha \tag{5.12}$$

where j_t is the total charge density current.

6 LIGHT SCATTERING SPECTRUM

We conclude this analysis of hydrodynamic behaviour by a brief discussion of the light scattering spectrum of the ionic liquid. As is well known, this is determined by the spectrum $S(k,\omega)$ of correlations between fluctuations in the dielectric function. By writing these fluctuations in the form

$$\delta\epsilon(\underline{k},\omega) = \left(\frac{\partial\epsilon}{\partial\rho}\right)_{T,q} \delta\rho(\underline{k},\omega) + \left(\frac{\partial\epsilon}{\partial q}\right)_{T,\rho} \delta q(\underline{k},\omega) + \left(\frac{\partial\epsilon}{\partial T}\right)_{\rho,q} \delta T(\underline{k},\omega) \tag{6.1}$$

we have

$$\begin{aligned} S(k,\omega) = {} & \left(\frac{\partial\epsilon}{\partial\rho}\right)^2_{T,q} S_{11}(k,\omega) + \left(\frac{\partial\epsilon}{\partial q}\right)^2_{T,\rho} S_{22}(k,\omega) + \left(\frac{\partial\epsilon}{\partial T}\right)^2_{\rho,q} S_{33}(k,\omega) + \\ & + 2\left(\frac{\partial\epsilon}{\partial\rho}\right)_{T,q}\left(\frac{\partial\epsilon}{\partial q}\right)_{T,\rho} S_{12}(k,\omega) + 2\left(\frac{\partial\epsilon}{\partial\rho}\right)_{T,q}\left(\frac{\partial\epsilon}{\partial T}\right)_{\rho,q} S_{13}(k,\omega) + \\ & + 2\left(\frac{\partial\epsilon}{\partial q}\right)_{T,\rho}\left(\frac{\partial\epsilon}{\partial T}\right)_{\rho,q} S_{23}(k,\omega). \end{aligned} \tag{6.2}$$

The results reported in section 4 yield for the spectrum in the Kubo regime

$$\begin{aligned} S(k,\omega) = {} & 2k_B T\left[\left(\frac{\partial\epsilon}{\partial q}\right)_{S,\rho} + \frac{\alpha/\sigma}{\rho C_V}\left(\frac{\partial\epsilon}{\partial T}\right)_{\rho,q}\right]^2 \frac{\sigma k^2}{\omega^2 + z^2(k)} + \\ & + \frac{2k_B T^2}{\rho C_p}\left(\frac{\partial\epsilon}{\partial T}\right)^2_{p,q} \frac{\kappa k^2/\rho C_p}{\omega^2 + (z_2 k^2)^2} \\ & + \frac{\gamma k_B T}{K_T}\left(\frac{\partial\epsilon}{\partial p}\right)^2_{S,q}\left[\frac{\Gamma k^2}{(\omega + ck)^2 + (\Gamma k^2)^2} + \frac{\Gamma k^2}{(\omega - ck)^2 + (\Gamma k^2)^2}\right] \\ & + K_T \frac{\rho^2 k_B T}{\gamma} B \frac{k}{c}\left[\frac{\omega + ck}{(\omega + ck)^2 + (\Gamma k^2)^2} - \frac{\omega - ck}{(\omega - ck)^2 + (\Gamma k^2)^2}\right] \end{aligned} \tag{6.3}$$

with

$$\begin{aligned} B = {} & (3\Gamma - b)\left(\frac{\partial\epsilon}{\partial\rho}\right)^2_{T,q} + 2\left(2\Gamma - \frac{\kappa}{\rho C_p}\right)\frac{T\alpha_T}{\rho^2 C_V K_T}\left(\frac{\partial\epsilon}{\partial\rho}\right)_{T,q}\left(\frac{\partial\epsilon}{\partial T}\right)_{\rho,q} + \\ & + \left(\frac{T\alpha_T}{\rho^2 C_V K_T}\right)^2\left(b - \Gamma - \frac{2\kappa}{\rho C_p}\right)\left(\frac{\partial\epsilon}{\partial T}\right)^2_{\rho,q}, \end{aligned} \tag{6.4}$$

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having omitted the term arising from $S_{12}(k;\omega)$, which is of order k^4. The last three terms on the right-hand side of eq. (6.3) give, as in a one-component neutral fluid, a Rayleigh peak determined by thermal fluctuations and a Brillouin doublet distorted from a Lorentzian shape by coupling between thermal and pressure fluctuations. The new feature of the charged fluid is the contribution of charge fluctuations to the Rayleigh peak, given by the first term in eq. (6.3), which differs qualitatively from the thermal contribution because its width becomes constant at long wavelength.

In the opposite limit $4\pi\sigma/\epsilon \ll ck$, the light scattering spectrum has again a structure similar to eq. (6.3). The new qualitative feature is the broadening of the Brillouin doublet which arises from the coupling between mass and charge fluctuations, according to eq. (4.9).

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Appendix. Partial Ionic Structure Factors and Thermodynamic Fluctuation Theory

The partial structure factors at long wavelength represent correlations between fluctuations in the numbers of particles from the average, and thermodynamic fluctuation theory yields[8] for a two-component fluid

$$\lim_{k\to 0} S_{\alpha\beta}(k) = \frac{\langle \Delta N_\alpha \Delta N_\beta \rangle}{[\langle N_\alpha \rangle \langle N_\beta \rangle]^{1/2}} = \frac{k_B T}{n m_\beta}\left(\frac{\partial n_\alpha}{\partial \mu_\beta}\right)_{T,n_{\bar\alpha}} \tag{A.1}$$

Here, $\bar\alpha$ denotes the component different from α, and μ_α denotes as in the main text the chemical potential of component α *per unit mass*. This relation can be inverted for a neutral mixture to yield

$$\left(\frac{\partial \mu_\beta}{\partial n_\alpha}\right)_{T,n_{\bar\alpha}} = \frac{k_B T}{n m_\beta} \lim_{k\to 0} \frac{(-1)^{\alpha+\beta} S_{\bar\alpha\bar\beta}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)} \tag{A.2}$$

whence, in terms of variables $\rho = m_1 n_1 + m_2 n_2$ and $x = n_1 - n_2$ we find:

$$\left.\frac{\partial(m_1\mu_1 + m_2\mu_2)}{\partial \rho}\right|_{T,x} = \frac{k_B T}{\rho} \lim_{k\to 0} \frac{S_{11}(k) + S_{22}(k) - 2S_{12}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)}, \tag{A.3}$$

$$\left.\frac{\partial(m_1\mu_1 + m_2\mu_2)}{\partial x}\right|_{T,\rho} = \frac{k_B T}{\rho} \lim_{k\to 0} \frac{m_2 S_{22}(k) - m_1 S_{11}(k) + (m_1 - m_2)S_{12}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)}, \tag{A.4}$$

$$\left.\frac{\partial(m_1\mu_1 - m_2\mu_2)}{\partial \rho}\right|_{T,x} = \frac{k_B T}{\rho} \lim_{k\to 0} \frac{S_{22}(k) - S_{11}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)}, \tag{A.5}$$

and

$$\left.\frac{\partial(m_1\mu_1 - m_2\mu_2)}{\partial x}\right|_{T,\rho} = \frac{k_B T}{\rho} \lim_{k\to 0} \frac{m_1 S_{11}(k) + m_2 S_{22}(k) + (m_1 + m_2)S_{12}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)} \tag{A.6}$$

If we apply these relations to an ionic fluid, the expression (A.2), as well as (A.6), diverges on account of charge neutrality yielding

$$\lim_{k\to 0} S_{\alpha\beta}(k) = n k_B T K_T. \tag{A.7}$$

However, we shall now see that the expressions (3.11)–(3.13) of the partial ionic structure factors to order k^2, when used in Eqs. (A.3)–(A.5), yield agreement with the thermodynamic values of the left-hand side of these equations.

Indeed, from the Gibbs-Duhem relation for the ionic fluid,[6] which to first order in the electromagnetic terms reads

$$\rho_1 \delta\mu_1 + \rho_2 \delta\mu_2 = -\rho s \delta T + \delta p \tag{A.8}$$

one finds at once

$$\left.\frac{\partial(m_1\mu_1 + m_2\mu_2)}{\partial \rho}\right|_{T,x} = (\rho n K_T)^{-1} \tag{A.9}$$

and

$$\left.\frac{\partial(m_1\mu_1 + m_2\mu_2)}{\partial x}\right|_{T,\rho} = em\nu \tag{A.10}$$

Similarly, using Eq. (A.8) in the differential of the electrochemical potential μ defined in Eq. (2.6), one finds

$$\left.\frac{\partial(m_1\mu_1 - m_2\mu_2)}{\partial \rho}\right|_{T,x} = 2e\nu + \frac{m_1 - m_2}{\rho^2 K_T}. \tag{A.11}$$

The same results follow from Eqs. (A.3)–(A.5) by using the expressions (3.11)–(3.13) of the partial ionic structure factors.

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