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## CONCENTRATION TIME CORRELATION FUNCTIONS OF BINARY LIQUIDS: IONIC MELTS AND MIXTURES OF NEUTRAL PARTICLES

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Analytical expressions that satisfy the sum rules up to the fourth order included have been obtained for the time correlation functions of binary liquid mixtures composed of either charged or neutral particles. Calculations were performed for an extended set of dynamic variables which, along with the concentration density, includes also its first and second time derivatives. The results of calculations were used to make a comparative analysis between the dynamic behaviors of ionic melts and binary mixtures of neutral particles. It was shown that, owing to specific features of interactions in ionic melts, there is a number of important differences between the behaviors of those two kinds of liquids. In particular, the obtained results demonstrate an incomprehensive character and inconsistency of the standard hydrodynamic approach for the description of ionic melts.

For the description of the dynamic behavior of multicomponent – in particular, ionic – liquids, time correlation functions play an important role. For instance, the time correlation functions of partial densities are related to dynamic structural factors, knowing which one can properly analyze scattering experiments [1–4]. A special place among multicomponent liquids is occupied by ionic melts, the behavior of which demonstrates a number of substantial differences from that of neutral particle mixtures [5–7]. As the simplest model of the ionic melt – among other nontrivial ones – which is widely applied to simulating salt melts, we can consider a binary mixture of opposite charged particles in a dielectric medium with a constant dielectric constant, so that the system as a whole is electrically neutral.

Dynamic properties of binary liquids have been a subject of especially active researches within the last

quarter of a century [8–11]. Interest to this subject was inspired, first of all, by the phenomenon of “fast sound”, which was observed in the mixtures of neutral particles characterized by a large difference between the masses of particles involved. In the course of light-scattering experiments, the positions of side peaks in the dynamic structural factor of such liquids were found to shift almost linearly as the wave number  $k$  increases, and the coefficient of proportionality can considerably exceed the adiabatic speed of sound in the mixture, being close to the sound speed in the lighter component [4, 10]. In order to explain this effect, which does not fall within the framework of the standard hydrodynamic description, a number of theories has been proposed. They differ from one another already at the level of an underlying physical mechanism, which was taken into consideration: from simple “mechanistic” models of binary liquid to models, where a nonlinear interaction between hydrodynamic modes should play a crucial role [2]. Things have been put right in this problem relatively recently, when a rather simple approach to the description of binary liquids has been proposed [5, 7, 12]. The approach is based on the same concept, as the method of generalized collective modes does, and provides the explicit consideration to concentration waves in the mixture, which are a prototype of optical phonon vibrations in binary crystals.

Excitations of the optical type have been identified in ionic melts even earlier [8, 9] – at the beginning

of the 1970s – when studying the dynamic “charge-charge” structural factors. The latter can be easily expressed in terms of the corresponding concentration time correlation functions, and it was found that the behaviors of concentration correlation functions in a Coulomb system and in a mixture of neutral particles are essentially different from each other even in the hydrodynamic limit [5, 6]. For the case of a neutral mixture, typical is a purely exponential decay in time, whereas, in the case of a Coulomb mixture, an oscillatory component is observed, which evidences the availability of an additional propagator mode belonging to the optical type. Such qualitative discrepancies follow from both the results of light-scattering experiments and those obtained making use of computer simulation methods [5, 6, 13]. Similarly to what occurred in the case of binary mixtures of neutral particles, the attempts to describe these features in ionic melts theoretically turned out substantially different in both their underlying assumptions and their interpretations of the results obtained (see, e.g., works [8–11]).

We have already mentioned that the standard hydrodynamic description gives no opportunity to explain the difference in the behaviors of those two classes of systems – ionic liquids and binary mixtures of neutral particles. In particular, in the framework of the hydrodynamic approach, we can find – in both cases – a relaxation mode [6] which governs the evolution of the concentration time correlation function. The difference is that the relaxation mode in the Coulomb system has a finite lifetime even in the hydrodynamic limit [6]. A more detailed description of dynamic properties can be done in the framework of the method of generalized collective modes [14] and making use of an extended set of dynamic variables, which allows the effects of the kinetic origin to be adequately taken into consideration as well. The results of our previous researches [5] showed that the longitudinal dynamics of binary mixtures can be described with a high accuracy in the framework of the eight-variable model in the whole range of wave number variation – from the hydrodynamic mode to the kinetic regime. The purpose of this work consists in studying a simplified dynamic model for a binary mixture. This approach enables an analytical consideration to be carried out and the explanation for the main differences in the behavior of concentration time correlation functions, which were discussed above, to be given.

## 1. Formalism of the Generalized Hydrodynamic Description: Basic Dynamic Model

Let us define the time correlation functions

$$\mathbf{F}^{(l \times l)}(k, t) = \langle \Delta \hat{\mathbf{P}}_{\mathbf{k}} \exp\{-iL_N t\} \Delta \hat{\mathbf{P}}_{\mathbf{k}}^+ \rangle \quad (1)$$

and their Laplace transforms

$$\tilde{\mathbf{F}}^{(l \times l)}(k, z) = \int_0^{\infty} dt \exp\{-zt\} \mathbf{F}^{(l \times l)}(k, t) \quad (2)$$

for a definite set of dynamic variables  $\hat{\mathbf{P}}_{\mathbf{k}} = \{\hat{P}_{\mathbf{k}}^{(1)}, \hat{P}_{\mathbf{k}}^{(2)}, \dots, \hat{P}_{\mathbf{k}}^{(l)}\}$  which describe the longitudinal dynamics of the system; in Eq. (1),  $\Delta \hat{\mathbf{P}}_{\mathbf{k}} = \hat{\mathbf{P}}_{\mathbf{k}} - \langle \hat{\mathbf{P}}_{\mathbf{k}} \rangle$ , and  $L_N$  is the Liouville operator. Then, the equations for the Laplace transforms of those functions can be written down in the form [6, 14, 15]

$$\begin{aligned} \left\{ z \mathbf{I}^{(l \times l)} - i \Omega^{(l \times l)}(k) + \tilde{\Phi}^{(l \times l)}(k, z) \right\} \tilde{\mathbf{F}}^{(l \times l)}(k, z) &= \\ &= \mathbf{F}^{(l \times l)}(k, 0), \end{aligned} \quad (3)$$

where  $\mathbf{I}^{(l \times l)}$ ,  $\Omega^{(l \times l)}(\mathbf{k})$ , and  $\tilde{\Phi}^{(l \times l)}(\mathbf{k}, z)$  are the identity, frequency, and memory function matrices, respectively. The matrices  $i \Omega^{(l \times l)}(\mathbf{k})$  and  $\tilde{\Phi}^{(l \times l)}(\mathbf{k}, z)$  are evidently determined on the set of dynamic variables  $\hat{\mathbf{P}}_{\mathbf{k}}$ .

In the Markovian approximation, when the approximate equality  $\tilde{\Phi}^{(l \times l)}(\mathbf{k}, z) \approx \tilde{\Phi}^{(l \times l)}(\mathbf{k}, 0)$  is supposed to hold true, the matrix equation (3) acquires a simple form

$$\left\{ z \mathbf{I}^{(l \times l)} + \mathbf{T}^{(l \times l)}(k) \right\} \tilde{\mathbf{F}}(k, z) = \mathbf{F}(k, 0), \quad (4)$$

where  $\mathbf{T}^{(l \times l)}(k)$  is the so-called generalized hydrodynamic matrix which is determined by the expression

$$\begin{aligned} \mathbf{T}^{(l \times l)}(k) &= -i \Omega^{(l \times l)}(k) + \tilde{\Phi}^{(l \times l)}(k, 0) = \\ &= \mathbf{F}^{(l \times l)}(k, 0) \left[ \tilde{\mathbf{F}}^{(l \times l)}(k, 0) \right]^{-1}. \end{aligned}$$

The matrix equation (4) allows an analytical solution to be found, provided that the eigenvalues  $z_{\alpha}$  and the corresponding eigenvectors  $\tilde{\mathbf{X}}_{j, \alpha}$  of the matrix equation

$$\sum_{j=1}^l \mathbf{T}_{ij}^{(l \times l)}(k) \tilde{\mathbf{X}}_{j, \alpha}(k) = z_{\alpha}(k) \tilde{\mathbf{X}}_{i, \alpha}(k) \quad (5)$$

are known. In this case, for the Laplace transforms of the correlation functions, we find

$$\tilde{\mathbf{F}}_{ij}(k, z) = \sum_{\alpha=1}^l \frac{\mathbf{G}_{\alpha}^{ij}(k)}{z + z_{\alpha}(k)}, \quad (6)$$

where

$$\mathbf{G}_{\alpha}^{ij}(k) = \sum_{q=1}^l \hat{\mathbf{X}}_{i,\alpha} [\hat{\mathbf{X}}]_{\alpha,q}^{-1} \mathbf{F}_{qj}(k, 0) \quad (7)$$

are the amplitudes which describe the contribution of the collective mode  $z_{\alpha}$  to the time correlation function

$$\mathbf{F}_{ij}(k, t) = \sum_{\alpha=1}^l \mathbf{G}_{\alpha}^{ij}(k) \exp(-z_{\alpha}(k)t). \quad (8)$$

It is clear that the structure of the equations cited above is rather general, being typical of linear response theories [16], so that their practical application to describe a specific physical system would require, first of all, a proper choice of the set of dynamic variables  $\hat{\mathbf{P}}_{\mathbf{k}}$ . This set must include the slowest variables which would ensure, in particular, an opportunity to use the Markovian approximation for memory functions. On the other hand, the choice of dynamic variables is also dictated by the specific features of the problem to be considered. For instance, if the case in point is the calculation of the partial dynamic structural factors of mixtures, the set of dynamic variables must include all partial densities, for which the dynamic structural factors are determined, as well as all the densities of additive integrals of motion and their time derivatives. The inclusion of the latter makes it possible to use the Markovian approximation for higher memory functions, which do govern dissipative processes in the system. The issues associated with this problem were discussed in detail in a number of our previous works [6, 14, 15] in the framework of the Zubarev nonequilibrium statistical operator method.

Our previous researches of the dynamics of binary mixtures [5] testified that the optimum set of dynamic variables which can provide a reliable quantitative description for the time correlation functions, the spectra of collective excitations, and the generalized transfer coefficients in the whole variation ranges of the spatial and time scales can be implemented in the framework of the eight-variable model (these are the total particle density  $\hat{n}_{\mathbf{k}}$  and its derivatives to the second order included, the mass-concentration density  $\hat{x}_{\mathbf{k}}$  and its derivatives to the second order included, as well as

the energy density  $\hat{\varepsilon}_{\mathbf{k}}$  and the energy flow). For all partial time correlation functions, the sum rules are obeyed exactly for the frequency momenta up to the fourth order included. At the same time, such a model is rather complicated for analytical researches, which makes the analysis of the basic mechanisms that are responsible for the formation of collective processes governing the longitudinal fluctuation dynamics in that or another range of the wave numbers  $k$  and frequencies  $\omega$  more difficult. Therefore, in what follows, we consider a certain simplified model, where (i) interaction of the thermal, concentration, and viscoelastic processes is not taken into consideration explicitly; and (ii) the dynamics of concentration fluctuations is described making use of the extended set of dynamic variables which includes the mass-concentration density

$$\hat{x}_{\mathbf{k}} = \frac{1}{\bar{m}} [(x_2 m_1) \hat{n}_{\mathbf{k},1} - (x_1 m_2) \hat{n}_{\mathbf{k},2}] \quad (9)$$

and its time derivatives up to the second order included (a three-variable model). In expression (9), the following notation is used:  $x_{\alpha} = c_{\alpha} m_{\alpha} / \bar{m}$ ,  $\bar{m} = \sum_{\alpha} m_{\alpha} c_{\alpha}$ ,  $c_{\alpha} = N_{\alpha} / N$  is the concentration of particles of the  $\alpha$ -th kind, and  $\hat{n}_{\mathbf{k},\alpha}$  is the corresponding partial density of these particles. The inclusion of the mass-concentration density (9) into the basic set of variables is caused by the fact that, in the case of an ionic binary mixture, this parameter is directly connected with the charge density:

$$\hat{q}_{\mathbf{k}} = q_1 \hat{n}_{\mathbf{k},1} + q_2 \hat{n}_{\mathbf{k},2} = \bar{m} I \hat{x}_{\mathbf{k}}, \quad (10)$$

where  $I = q_1 / m_1 - q_2 / m_2$ , and  $q_1$  and  $q_2$  are the ionic charges. Therefore, its behavior is identical to that of the charge density, which is of importance while comparing the dynamic properties of ionic and neutral liquids.

The extended set of dynamic variables, which will be used for the model description of mixture dynamics, includes three variables; these are  $\hat{x}_{\mathbf{k}}$ ,  $iL_N \hat{x}_{\mathbf{k}}$ , and  $[iL_N]^2 \hat{x}_{\mathbf{k}}$ . The analytical consideration is more convenient to be carried out using the orthogonalized variables  $\hat{\mathbf{P}}_{\mathbf{k}} = \{\hat{P}_{\mathbf{k}}^{(1)}, \hat{P}_{\mathbf{k}}^{(2)}, \hat{P}_{\mathbf{k}}^{(3)}\}$ , where

$$\hat{P}_{\mathbf{k}}^{(1)} = \hat{x}_{\mathbf{k}}, \quad \hat{P}_{\mathbf{k}}^{(2)} = iL_N \hat{x}_{\mathbf{k}},$$

$$\hat{P}_{\mathbf{k}}^{(3)} = [iL_N]^2 \hat{x}_{\mathbf{k}} - \frac{\langle [iL_N]^2 \hat{x}_{\mathbf{k}} \hat{x}_{-\mathbf{k}} \rangle}{\langle \hat{x}_{\mathbf{k}} \hat{x}_{-\mathbf{k}} \rangle} \hat{x}_{\mathbf{k}},$$

and for which the matrix of static correlation functions  $\mathbf{F}^{(3 \times 3)}(k, 0)$  is diagonal, i.e.  $\langle \hat{P}_{\mathbf{k}}^{(i)} \hat{P}_{-\mathbf{k}}^{(j)} \rangle = \delta_{ij} \langle \hat{P}_{\mathbf{k}}^{(i)} \hat{P}_{-\mathbf{k}}^{(i)} \rangle$ . The general case of the construction of orthogonal

variables with the help of projective operators of the Mori type was discussed in work [14].

In the space of orthogonal dynamic variables, the structures of the frequency matrix  $i\Omega^{(3\times 3)}(k)$  and the memory function matrix  $\Psi^{(3\times 3)}(k, z)$  become simpler, and we find for them

$$i\Omega^{(3\times 3)}(k) = \begin{pmatrix} 0 & 1 & 0 \\ -\Gamma_1(k) & 0 & 1 \\ 0 & -\Gamma_2(k) & 0 \end{pmatrix}, \quad (11)$$

$$\tilde{\Psi}^{(3\times 3)}(k, z) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \tilde{\Phi}_2(k, z) \end{pmatrix}, \quad (12)$$

where

$$\Gamma_1(k) = \frac{\langle iL_N \hat{x}_{\mathbf{k}} iL_N \hat{x}_{-\mathbf{k}} \rangle}{\langle \hat{x}_{\mathbf{k}} \hat{x}_{-\mathbf{k}} \rangle},$$

$$\Gamma_2(k) = \frac{\langle [iL_N]^2 \hat{x}_{\mathbf{k}} [iL_N]^2 \hat{x}_{-\mathbf{k}} \rangle}{\langle iL_N \hat{x}_{\mathbf{k}} iL_N \hat{x}_{-\mathbf{k}} \rangle} - \frac{\langle iL_N \hat{x}_{\mathbf{k}} iL_N \hat{x}_{-\mathbf{k}} \rangle}{\langle \hat{x}_{\mathbf{k}} \hat{x}_{-\mathbf{k}} \rangle}$$

are the quantities directly related to the frequency momenta of the concentration correlation function. For the orthogonalized set of variables, the expression for the mode amplitudes (7) also becomes simpler:

$$\mathbf{G}_{\alpha}^{ij}(k) = \hat{\mathbf{X}}_{i,\alpha} \hat{\mathbf{X}}_{\alpha,j}^{-1} \mathbf{F}_{jj}(k, 0). \quad (13)$$

As a result, the equation for the eigenvalues of matrix  $\mathbf{T}^{(3\times 3)}(k)$ , taking into account Eqs. (11) and (12), looks like

$$\begin{vmatrix} z & -1 & 0 \\ \Gamma_1(k) & z & -1 \\ 0 & \Gamma_2(k) & z + \tilde{\Phi}_2(k, 0) \end{vmatrix} = 0. \quad (14)$$

Whence, we find three eigenvalues  $z_{\alpha}(k)$  which characterize the spectrum of collective excitations in the system obtained in the framework of the three-variable model used by us for the description of the concentration fluctuation dynamics. The eigenvectors  $\hat{\mathbf{X}}_{\alpha}(k) = \{\hat{\mathbf{X}}_{1,\alpha}, \hat{\mathbf{X}}_{2,\alpha}, \hat{\mathbf{X}}_{3,\alpha}\}$ , which correspond to the eigenvalues  $z_{\alpha}(k)$ , are determined by solving the matrix equation (5) and taking expressions (11) and (12) into account. It is easy to verify that the matrix  $\hat{\mathbf{X}}(k)$ , the columns of which are the solutions  $\{\hat{\mathbf{X}}_{\alpha}\}$ , can be written down in the form

$$\hat{\mathbf{X}} = \begin{pmatrix} x_0 & x_0 & x_0 \\ z_1 x_0 & z_2 x_0 & z_3 x_0 \\ (z_1^2 + \Gamma_1)x_0 & (z_2^2 + \Gamma_1)x_0 & (z_3^2 + \Gamma_1)x_0 \end{pmatrix}, \quad (15)$$

where  $x_0$  is an arbitrary constant.

## 2. Analytical Expressions for Time Correlation Functions and Sum Rules

Now, making use of expressions (13) and (8), we can calculate the mode amplitudes  $\mathbf{G}_{\alpha}^{ij}(k)$  and, hence, obtain expressions for the concentration time correlation functions which are the immediate subject of our interest. First of all, we are interested in the amplitudes  $\mathbf{G}_{\alpha}^{11}(k)$ . In order to calculate them, it is necessary to find the matrix elements  $\hat{\mathbf{X}}_{\alpha,1}^{-1}$  of the inverse matrix  $\hat{\mathbf{X}}^{-1}$ . It is easy to demonstrate that the expressions for them can be written down in a compact form making use of the known Levi-Civita symbol, i.e. an absolutely antisymmetric unity tensor  $\varepsilon_{\alpha\beta\gamma}$ , the components of which are equal to unity for  $(\alpha, \beta, \gamma) = (1, 2, 3)$  and other combinations of those subscripts obtained as a result of their cyclic permutation, to minus unity for all cyclic permutations of the combination  $(\alpha, \beta, \gamma) = (3, 2, 1)$ , and to zero in all other cases. Then, we have

$$\begin{aligned} \hat{\mathbf{X}}_{\alpha,1}^{-1} &= \frac{1}{x_0} \frac{\sum_{\beta,\gamma} \varepsilon_{\alpha\beta\gamma} z_{\beta} (z_{\gamma}^2 + \Gamma_1)}{\sum_{\beta,\gamma,\delta} \varepsilon_{\beta\gamma\delta} z_{\gamma} (z_{\delta}^2 + \Gamma_1)} = \\ &= \frac{1}{x_0} \frac{\sum_{\beta,\gamma} \varepsilon_{\alpha\beta\gamma} z_{\beta} (z_{\gamma}^2 + \Gamma_1)}{\sum_{\beta,\gamma,\delta} \varepsilon_{\beta\gamma\delta} z_{\gamma} z_{\delta}^2}. \end{aligned} \quad (16)$$

The latter equality stems from the fact that, since  $\varepsilon_{\alpha\beta\gamma} z_{\beta} = -\varepsilon_{\gamma\beta\alpha} z_{\beta}$ , so that  $\sum_{\alpha,\beta,\gamma} \varepsilon_{\alpha\beta\gamma} z_{\beta} = 0$  when summing up over all subscripts, the denominator's summands including  $\Gamma_1$  can be omitted. Hence, we obtain

$$\mathbf{G}_{\alpha}^{11}(k) = \frac{\sum_{\beta,\gamma} \varepsilon_{\alpha\beta\gamma} z_{\beta} (z_{\gamma}^2 + \Gamma_1)}{\sum_{\beta,\gamma,\delta} \varepsilon_{\beta\gamma\delta} z_{\gamma} z_{\delta}^2} \mathbf{F}_{11}(k, 0), \quad (17)$$

where  $\mathbf{F}_{11}(k, 0) = \mathbf{F}_{11}(k) = \langle \hat{x}_{\mathbf{k}} \hat{x}_{-\mathbf{k}} \rangle$ .

The amplitudes  $\mathbf{G}_{\alpha}^{11}(k)$  describe the contributions made by collective modes  $z_{\alpha} = z_{\alpha}(k)$ , so that the mass-concentration correlation function can now be written, according to expression (8), in the form

$$\mathbf{F}_{xx}(k, t) \equiv \mathbf{F}_{11}(k, t) = \sum_{\alpha=1}^3 \mathbf{G}_{\alpha}^{11}(k) \exp(-z_{\alpha}(k)t), \quad (18)$$

where  $\mathbf{G}_\alpha^{11}(k)$  are given by expressions (17).

At this stage, one can verify the validity of the sum rules for the momenta of the time correlation function (18) up to the fourth order included. For example, by putting  $t = 0$  in Eq. (18), the evident identity law

$$\mathbf{F}_{11}(k, t) |_{t=0} = \sum_{\alpha=1}^3 \mathbf{G}_\alpha^{11}(k) = \mathbf{F}_{11}(k), \quad (19)$$

is to be obtained, which is just the sum rule of the zero order. Really, substituting the amplitudes  $\mathbf{G}_\alpha^{11}(k)$  found from Eq. (17) into Eq. (19), we have

$$\begin{aligned} \left( \frac{\mathbf{F}_{11}(k, t)}{\mathbf{F}_{11}(k)} \right)_{t=0} &= \frac{\sum_{\alpha, \beta, \gamma} \varepsilon_{\alpha\beta\gamma} z_\beta (z_\gamma^2 + \Gamma_1)}{\sum_{\beta, \gamma, \delta} \varepsilon_{\beta\gamma\delta} z_\gamma z_\delta^2} = \\ &= \frac{\sum_{\alpha, \beta, \gamma} \varepsilon_{\alpha\beta\gamma} z_\beta (z_\gamma^2 + \Gamma_1)}{\sum_{\beta, \gamma, \delta} \varepsilon_{\beta\gamma\delta} z_\gamma (z_\delta^2 + \Gamma_1)} = 1. \end{aligned} \quad (20)$$

The first sum rule for expression (18) asserts that, owing to the even parity of this function with respect to the time inversion, the first term of its expansion in  $t$  must be equal to zero. Really, by differentiating Eq. (18) with respect to time and putting  $t = 0$ , we find

$$\begin{aligned} \frac{1}{\mathbf{F}_{11}(k)} \left( \frac{d}{dt} \mathbf{F}_{11}(k, t) \right)_{t=0} &= -\frac{1}{\mathbf{F}_{11}(k)} \sum_{\alpha=1}^3 z_\alpha \mathbf{G}_\alpha^{11}(k) = \\ &= \frac{\sum_{\alpha, \beta, \gamma} \varepsilon_{\alpha\beta\gamma} z_\alpha z_\beta (z_\gamma^2 + \Gamma_1)}{\sum_{\beta, \gamma, \delta} \varepsilon_{\beta\gamma\delta} z_\gamma z_\delta^2} = 0, \end{aligned} \quad (21)$$

because, owing to the antisymmetry of the Levi-Civita symbol, the summands  $\varepsilon_{\alpha\beta\gamma} z_\alpha z_\beta$  and  $\varepsilon_{\beta\alpha\gamma} z_\alpha z_\beta$  in the numerator of this expression compensate each other in pairs, so that the equality  $\sum_{\alpha, \beta} A_\gamma \varepsilon_{\alpha\beta\gamma} z_\alpha z_\beta = 0$  holds true at every fixed  $\gamma$ .

The essence of the second sum rule is that the exact function  $\mathbf{F}_{xx}(k, t)$  must satisfy the equality  $d^2 \mathbf{F}_{xx}(k, t) / dt^2 |_{t=0} = -\langle \hat{x}_k \hat{x}_{-k} \rangle$ . Hereafter, the standard notation for the time derivatives – namely,  $iL_N \hat{x}_k = \dot{\hat{x}}_k$  and  $[iL_N]^2 \hat{x}_k = \ddot{\hat{x}}_k$  – is used. Really, the straightforward calculations on the basis of expression (18) give rise to

$$\frac{1}{\mathbf{F}_{11}(k)} \left( \frac{d^2}{dt^2} \mathbf{F}_{11}(k, t) \right)_{t=0} = \frac{1}{\mathbf{F}_{11}(k)} \sum_{\alpha=1}^3 z_\alpha^2 \mathbf{G}_\alpha^{11}(k) =$$

$$= -\Gamma_1 = -\frac{\langle \dot{\hat{x}}_k \dot{\hat{x}}_{-k} \rangle}{\langle \hat{x}_k \hat{x}_{-k} \rangle}, \quad (22)$$

which was to be proved. This result follows from the general expression (17), if one opens the  $(z_\gamma^2 + \Gamma_1)$ -brackets in it and takes the antisymmetric properties of the Levi-Civita symbol – namely,  $\varepsilon_{\alpha\beta\gamma} z_\alpha^2 z_\gamma^2 = -\varepsilon_{\gamma\beta\alpha} z_\alpha^2 z_\gamma^2$  and  $\varepsilon_{\alpha\beta\gamma} z_\alpha^2 z_\beta = -\varepsilon_{\gamma\beta\alpha} z_\alpha^2 z_\beta$  – into account. Then, the first summand with  $z_\gamma^2$  vanishes, and the sums in the numerator and denominator of the second summand, after taking  $\Gamma_1$  out of the brackets, become mutually cancelled.

Concerning the third sum rule

$$\left( \frac{d^3}{dt^3} \mathbf{F}_{11}(k, t) \right)_{t=0} = -\sum_{\alpha=1}^3 z_\alpha^3 \mathbf{G}_\alpha^{11}(k) = 0, \quad (23)$$

its validity can be easily checked up by expressing  $z_\alpha^3$  from the eigenvalue equation (14) in terms of lower powers of  $z_\alpha$  and the corresponding momenta and by applying the sum rules obtained before. A similar procedure is applied to prove the sum rule of the fourth order. In so doing, when considering the contributions proportional to  $z_\alpha^4 = z_\alpha z_\alpha^3$ , the quantity  $z_\alpha^3$  should again be expressed from Eq. (14) in terms of lower powers of  $z_\alpha$  and the corresponding momenta, which makes it possible to obtain the expression

$$\begin{aligned} \frac{1}{\mathbf{F}_{11}(k)} \left( \frac{d^4}{dt^4} \mathbf{F}_{11}(k, t) \right)_{t=0} &= \frac{1}{\mathbf{F}_{11}(k)} \sum_{\alpha=1}^3 z_\alpha^4 \mathbf{G}_\alpha^{11}(k) = \\ &= \frac{\langle \ddot{\hat{x}}_k \ddot{\hat{x}}_{-k} \rangle}{\langle \hat{x}_k \hat{x}_{-k} \rangle}, \end{aligned} \quad (24)$$

so that  $d^4 \mathbf{F}_{xx}(k, t) / dt^4 |_{t=0} = \langle \ddot{\hat{x}}_k \ddot{\hat{x}}_{-k} \rangle$ .

Therefore, we managed to derive the analytical solutions for time correlation functions in a simple three-variable dynamic model which describes mass-concentration fluctuations and to demonstrate that the expression found by us for the function  $\mathbf{F}_{xx}(k, t)$  exactly reproduces the corresponding sum rules up to the fourth order included in the whole range of wave vector variation.

### 3. Comparative Analysis of Binary Mixtures Composed of Neutral and Charged Particles in the Hydrodynamic Limit

Now, let us come back to the analysis of the spectrum of longitudinal collective excitations  $\{z_\alpha\}$  which is obtained in the framework of the three-variable model and is composed of the solutions of Eq. (14). After expanding the determinant in this equation, we come to the cubic equation

$$z^3 + z^2\phi_2(k) + z[\Gamma_1(k) + \Gamma_2(k)] + \Gamma_1(k)\phi_2(k) = 0, \quad (25)$$

where  $\phi_2(k) \equiv \tilde{\Phi}_2(k, 0)$ . Let us analyze this equation in more details in the hydrodynamic limit  $k \rightarrow 0$  and consider the cases of binary mixtures composed of either charged or neutral particles separately. Such a study will enable us to detect the appearance of a difference between the behaviors of ionic liquids and neutral binary mixtures in the long-wave asymptotics which originates from the difference between the dependences of  $\Gamma_1(k)$ ,  $\Gamma_2(k)$ , and  $\phi_2(k)$  coefficients on  $k$ .

For an ionic mixture, the extended set of dynamic variables is often more convenient to be constructed on the basis of the charge density  $\hat{q}_k$ . However, as was already pointed out, in accordance with the electroneutrality condition, the charge density  $\hat{q}_k$  is proportional to the mass-concentration one  $\hat{x}_k$  [see Eq. (10)]. Therefore, without loss of universality, we come to the following expressions for the required elements of the frequency and memory function matrices:

$$\Gamma_1(k) = \frac{\langle \hat{q}_k \hat{q}_{-k} \rangle}{\langle \hat{q}_k \hat{q}_{-k} \rangle} \equiv \omega_x^2,$$

$$\Gamma_2(k) = \frac{\langle \hat{q}_k \ddot{\hat{q}}_{-k} \rangle}{\langle \hat{q}_k \hat{q}_{-k} \rangle} - \frac{\langle \ddot{\hat{q}}_k \hat{q}_{-k} \rangle}{\langle \hat{q}_k \hat{q}_{-k} \rangle} \equiv \omega_j^2 - \omega_x^2,$$

$$\phi_2(k) = \frac{\int_0^\infty \langle \hat{y}_k^{(2)} e^{-iL_N t} \hat{y}_{-k}^{(2)} \rangle dt}{\langle \hat{q}_k \hat{q}_{-k} \rangle},$$

where  $\hat{y}_k^{(2)} = \ddot{\hat{q}}_k - \langle \ddot{\hat{q}}_k \hat{q}_{-k} \rangle \langle \hat{q}_k \hat{q}_{-k} \rangle^{-1} \hat{q}_k$ . Further, we are going to calculate the static correlation functions entering into these expressions in the hydrodynamic limit.

The static charge-charge correlation function, according to the Stillinger-Lovett rules [19] (see also

work [6]), is proportional to  $k^2$  in the long-wave limit. In particular,

$$\langle \hat{q}_k \hat{q}_{-k} \rangle = NS_{qq}(k) |_{k \rightarrow 0} \simeq \frac{N\varepsilon}{4n\pi\beta} k^2 = N\kappa_D^2 k^2,$$

where  $n = N/V$ , and  $\kappa_D$  is the Debye radius. Respectively, we have  $\langle \hat{q}_k \hat{q}_{-k} \rangle = k^2 \langle \hat{J}_{k,q} \hat{J}_{-k,q} \rangle$ , where the charge flow  $\hat{J}_{k,q}$  can be determined from the equation  $\hat{q}_k = ik\hat{J}_{k,q}$  and is directly connected with the mass-concentration flow  $\hat{J}_{k,x} = x_2\hat{J}_{k,1} - x_1\hat{J}_{k,2}$ ; besides,  $\hat{x}_k = (ik/\bar{m})\hat{J}_{k,x}$ , and  $\hat{J}_{k,l}$  are the partial density flows ( $l = 1, 2$ ). The correlator  $\langle \hat{J}_{k,x} \hat{J}_{-k,x} \rangle$  can be easily calculated [15], and we find that

$$\langle \hat{J}_x \hat{J}_x \rangle = x_2^2 \langle \hat{J}_1 \hat{J}_1 \rangle + x_1^2 \langle \hat{J}_2 \hat{J}_2 \rangle = N \frac{x_1 x_2 \bar{m}}{\beta},$$

where  $\beta = 1/k_B T$  is the inverse temperature. Taking into account the expressions obtained above, we have – in the long-wave limit –

$$\Gamma_1 = \omega_x^2 = \frac{\langle \hat{q} \hat{q} \rangle}{\langle \hat{q} \hat{q} \rangle} \simeq \frac{x_1 x_2 \bar{m} I^2}{\beta \kappa_D^2} = \frac{4\pi}{\varepsilon} n I^2 \bar{m} x_1 x_2. \quad (26)$$

To evaluate the correlator in the long-wave limit, we have to calculate the correlator  $\langle \hat{J}_x \hat{J}_x \rangle = x_2^2 \langle \hat{J}_1 \hat{J}_1 \rangle + x_1^2 \langle \hat{J}_2 \hat{J}_2 \rangle - 2x_1 x_2 \langle \hat{J}_1 \hat{J}_2 \rangle$ . Taking the total momentum conservation law into account, we find that  $\langle \hat{J}_1 \hat{J}_1 \rangle = \langle \hat{J}_2 \hat{J}_2 \rangle = -\langle \hat{J}_1 \hat{J}_2 \rangle \equiv N\bar{F}^2$ , where  $\bar{F}^2$  is the mean-square value of the interaction force between individual components of the mixture. Hence, we eventually obtain that

$$\langle \hat{J}_{k,x} \hat{J}_{-k,x} \rangle |_{k \rightarrow 0} \simeq N\bar{F}^2$$

and

$$\langle \ddot{\hat{q}}_k \ddot{\hat{q}}_{-k} \rangle |_{k \rightarrow 0} \simeq k^2 I^2 N\bar{F}^2.$$

Therefore, at  $k \rightarrow 0$ ,

$$\Gamma_2 = \omega_j^2 - \omega_x^2 \simeq \frac{\bar{F}^2 \beta}{\bar{m} x_1 x_2} - \frac{4\pi}{\varepsilon} n I^2 \bar{m} x_1 x_2. \quad (27)$$

On the basis of recurrent relations for memory functions [6, 14], the memory function  $\phi_2(k)$  at  $z = 0$  and small  $k$  can be rewritten in the form

$$\phi_2(k) = \frac{\Gamma_2}{\Gamma_1} \frac{\int_0^\infty \langle \hat{x}_k e^{-iL_N t} \hat{x}_{-k} \rangle dt}{\langle \hat{x}_k \hat{x}_{-k} \rangle} =$$

$$= \frac{\Gamma_2}{\Gamma_1} \frac{\int_0^\infty \langle \hat{q}_{\mathbf{k}} e^{-iL_N t} \hat{q}_{-\mathbf{k}} \rangle dt}{\langle \hat{q}_{\mathbf{k}} \hat{q}_{-\mathbf{k}} \rangle}. \quad (28)$$

In its turn, the integral in the numerator of the last expression can be easily presented in terms of the conductivity  $\sigma$  of an ionic liquid by a formula of the Green–Kubo type, namely,

$$\sigma = (\beta/V) \int_0^\infty \langle \hat{J}_q e^{-iL_N t} \hat{J}_q \rangle dt.$$

Then, bearing in mind the Stillinger–Lovett rules mentioned above [19], we arrive at a final expression applicable in the long-wave limit:

$$\phi_2|_{k \rightarrow 0} = \frac{4\pi\sigma}{\varepsilon} \frac{\Gamma_2}{\Gamma_1} = \frac{1}{\tau_0} \left[ \frac{\omega_j^2}{\omega_x^2} - 1 \right], \quad (29)$$

where  $\tau_0 = \varepsilon/(4\pi\sigma)$  is the time of hydrodynamic relaxation of the charge density [5, 6]. In addition, it is worth noting that the ionic conductivity is readily expressed in terms of the mutual diffusion coefficient  $\sigma = nDI^2\beta$ .

Therefore, all nontrivial elements in the frequency and memory function matrices are different from zero in the hydrodynamic limit for a binary ionic system, so that Eq. (25) is a cubic one, where all the coefficients are nonzero:

$$z_\alpha^3 + \frac{1}{\tau_0} \left[ 1 - \frac{\omega_j^2}{\omega_x^2} \right] z_\alpha^2 + \omega_j^2 z_\alpha + \frac{\omega_x^2}{\tau_0} \left[ 1 - \frac{\omega_j^2}{\omega_x^2} \right] = 0. \quad (30)$$

This equation is used to find all  $z_\alpha$ -values which enter into expression (18).

A cubic equation is known to possess three roots in the general case; if the polynomial coefficients are real and different from zero, either all the three roots are real and different, or one root is real and the two others are complex and mutually conjugate. This means that there must be at least one real solution associated with a relaxation mode of the  $e^{-z_1 t}$ -type. Let us denote it as  $z_1 \equiv d = 1/\tau_0 + \delta$ , where the term  $1/\tau_0$  corresponds to a trivial case of the one-variable model, and  $\delta$  is a correction to this trivial solution due to the dynamic extension of the model. For such a solution, the left-hand side of Eq. (30) can be factorized,

$$(z_1 - d)(z_\alpha^2 + pz_\alpha + g) = 0, \quad (31)$$

and two other solutions of Eq. (30) – with  $\alpha = 2$  and  $3$  – can be determined by solving the quadratic equation

$z_\alpha^2 + pz_\alpha + g = 0$ . Opening the brackets in Eq. (31) and comparing the coefficients at identical powers of  $z$  in this equation and Eq. (30), we find

$$p = \frac{1}{\tau_0} \left[ 2 + \delta\tau_0 - \frac{\omega_j^2}{\omega_x^2} \right], \quad g = \frac{\omega_j^2 - \omega_x^2}{1 + \delta\tau_0},$$

as well as the condition

$$g = \omega_j^2 + dp$$

which can be regarded as an equation to find the correction  $\delta$ . Accordingly, we obtain  $z_{2,3} = -p/2 \pm \sqrt{p^2/4 - g}$ .

It should be noted that, since  $\langle \hat{y}_{\mathbf{k}}^{(2)} \hat{y}_{-\mathbf{k}}^{(2)} \rangle \geq 0$ , we have  $\Gamma_2 = \omega_j^2 - \omega_x^2 \geq 0$ , which gives rise to the inequality  $p - d = (1/\tau_0)(1 - \omega_j^2/\omega_x^2) \leq 0$ . Moreover, in order that the decay coefficient should be positive, there must be  $p \leq 0$  and  $d > 0$ , which could be proved valid in the general case even at the matrix level. If the discriminant  $D = p^2/4 - g = p^2/4 - \omega_j^2 - dp$  of the quadratic equation is negative, the corresponding solutions will be complex-conjugate:

$$z_{2,3} = \Gamma_0 \pm i\omega_0,$$

where

$$\omega_0 = \sqrt{\frac{\omega_j^2 - \omega_x^2}{1 + \delta\tau_0} - \Gamma_0^2} \quad (32)$$

is the characteristic frequency of the corresponding excitations, and

$$\Gamma_0 \equiv -\frac{p}{2} = \frac{\omega_j^2 - \omega_x^2(2 + \delta\tau_0)}{2\tau_0\omega_x^2} \geq 0 \quad (33)$$

is the coefficient of their decay.

Therefore, in the case of ionic liquid, the spectrum of excitations, which describe the charge fluctuation dynamics, is determined in the long-wave limit by the following solutions:

$$z_1 = \frac{1}{\tau_0} + \delta, \quad z_\pm = \Gamma_0 \pm i\omega_0, \quad (34)$$

where  $\omega_0$  and  $\Gamma_0$  are determined by expressions (32) and (33), respectively.

Now, we can calculate the corresponding amplitudes and express them in terms of the quantities included into expressions (32) and (33). Substituting solutions (34) into Eq. (17), we obtain

$$\frac{\mathbf{G}_1^{11}(k)}{\mathbf{F}_{11}(k)} = \frac{\Gamma_0^2 + \omega_0^2 - \omega_x^2}{\omega_0^2 + [d - \Gamma_0]^2},$$

$$\frac{\mathbf{G}_{2,3}^{11}(k)}{\mathbf{F}_{11}(k)} = \frac{1}{2} \frac{d^2 + \omega_x^2 - 2\Gamma_0 d}{\omega_0^2 + [d - \Gamma_0]^2} \mp$$

$$\mp \frac{i}{2\omega_0} \frac{(\Gamma_0 - d)(\omega_x^2 - \Gamma_0 d) + d\omega_0^2}{\omega_0^2 + [d - \Gamma_0]^2}. \quad (35)$$

The amplitudes found can be substituted into expression (18) for the time correlation function. Changing over from complex exponents  $\exp(\pm i\omega_0 t)$  to trigonometric functions, we find that

$$\begin{aligned} \frac{\mathbf{F}_{qq}(k, t)}{\mathbf{F}_{qq}(k)} &= \frac{\Gamma_0^2 + \omega_0^2 - \omega_x^2}{\omega_0^2 + [d - \Gamma_0]^2} e^{-dt} + \\ &+ e^{-\Gamma_0 t} \times \left[ \frac{d^2 + \omega_x^2 - 2\Gamma_0 d}{\omega_0^2 + [d - \Gamma_0]^2} \cos \omega_0 t + \right. \\ &\left. + \frac{(\Gamma_0 - d)(\omega_x^2 - \Gamma_0 d) + d\omega_0^2}{\omega_0(\omega_0^2 + [d - \Gamma_0]^2)} \sin \omega_0 t \right]. \end{aligned} \quad (36)$$

It is of interest to compare this result, which has been derived for an ionic liquid, with a similar expression for the mass-concentration time correlation function  $\mathbf{F}_{xx}(k, t)$  which corresponds to the case of a binary mixture of neutral particles. For a mixture of neutral particles, the structures of the frequency and memory function matrices are the same [see Eqs. (11) and (12)], but the dependence of their nonzero elements on  $k$  in the long-wave limit is different. The key difference between neutral and ionic systems is that the static structural factor  $S_{xx}(k)$  tends to a nonzero value at  $k \rightarrow 0$  [17], i.e.  $S_{xx}(0) = \text{const} \neq 0$ . As a consequence, in the long-wave limit, we have  $\Gamma_1 = \langle \hat{x}_{\mathbf{k}} \hat{x}_{-\mathbf{k}} \rangle / \langle \hat{x}_{\mathbf{k}} \hat{x}_{-\mathbf{k}} \rangle |_{k \rightarrow 0} \simeq \omega_x^2 k^2$  and  $\Gamma_2 = \omega_j^2 - k^2 \omega_x^2 \simeq \omega_j^2$ , where  $\omega_x^2 = x_1 x_2 k_B T / \bar{m} S_{xx}(0)$  and  $\omega_j^2 = \langle \hat{J}_x \hat{J}_x \rangle / \langle \hat{J}_x \hat{J}_x \rangle$  [7, 17].

Evidently, this circumstance cardinaly changes the character of the  $k$ -dependence of the solutions of Eq. (25). First, the relaxation mode  $z_1 = Dk^2$  in a system of neutral particles turns out typically hydrodynamic; hence, the relaxation time of mass-concentration excitations  $\tau_0 = (Dk^2)^{-1}$  is proportional to  $k^{-2}$  and, at small  $k$ , becomes extremely large, unlike that for an ionic system, where  $\tau_0 = \text{const}$  even in the hydrodynamic limit. Second, the complex-conjugate propagator modes  $z_{\pm}$  emerge [7] in a binary system of uncharged particles only under definite conditions; but even more important is the fact that their amplitudes  $G_{\pm}$  become infinitesimally small as compared with the hydrodynamic mode amplitude  $G_1$ , and that they vanish

as  $k^2$ , if  $k \rightarrow 0$ . Therefore, we find that  $F_{xx}(k, t) \simeq e^{-Dk^2 t}$  for small  $k$ , and it is a well-known result of the standard hydrodynamic theory [17, 18].

The memory function of a binary mixture of neutral particles also has its characteristic feature in comparison with that for the ionic liquid case. Recall that we are interested in an expression for

$$\phi_2(k)|_{k \rightarrow 0} \simeq \frac{k^2}{S_{xx}(0)} \frac{\Gamma_2}{\Gamma_1} \int_0^{\infty} \langle \hat{J}_x e^{-iL_N t} \hat{J}_x \rangle dt =$$

$$= \frac{\omega_j^2}{S_{xx}(0)\omega_x^2} \int_0^{\infty} \langle \hat{J}_x e^{-iL_N t} \hat{J}_x \rangle dt \equiv d_0.$$

The collective modes of the system, which are the solutions of Eq. (25), look like  $z_1 = Dk^2$  and  $z_{\pm} = \bar{\Gamma} \pm i\bar{\omega} = d_0/2 \pm i\sqrt{\omega_j^2 - d_0^2/4}$ , where  $D = (\omega_x^2/\omega_j^2)d_0$ . It should be noted that, in this case, the quantity

$$D = \frac{\beta}{V} \int_0^{\infty} \langle \hat{J}_x e^{-iL_N t} \hat{J}_x \rangle dt$$

is the hydrodynamic coefficient of mutual diffusion in a binary mixture [18].

Hence, the mass-concentration time correlation function of a binary mixture of neutral particles can be written down in the form

$$\begin{aligned} \frac{\mathbf{F}_{xx}(k, t)}{\mathbf{F}_{xx}(k, 0)} &= \left( 1 - \frac{\omega_x^2 - (\omega_x^2/\omega_j^2)d_0^2}{\omega_j^2} k^2 \right) e^{-Dk^2 t} + \\ &+ k^2 e^{-(d_0/2)t} \left( \frac{\omega_x^2 - (\omega_x^2/\omega_j^2)d_0^2}{\omega_j^2} \cos \bar{\omega} t + \right. \\ &\left. + \frac{3\omega_x^2 d_0 - (\omega_x^2/\omega_j^2)d_0^3}{2\bar{\omega}\omega_j^2} \sin \bar{\omega} t \right) \end{aligned} \quad (37)$$

with an accuracy to within terms of the  $k^2$ -order. By comparing expressions (37) and (36), we would like to emphasize once more that the second summand in Eq. (37) describes a contribution of propagator modes which is proportional to  $k^2$ , so that the dominant contribution in the long-wave limit is given by the hydrodynamic mode. On the other hand, in the case of ionic liquid (36), all the modes are characterized by their nonvanishing contributions even at  $k \rightarrow 0$ .



#### 4. Discussion of Results and Conclusions

Summarizing the results of this research, we can draw conclusion that the behaviors of time correlation functions for ionic liquids and binary mixtures of neutral particles are essentially different in the hydrodynamic limit. A difference between Coulomb systems and neutral mixtures consists, first of all, in that the hydrodynamic mode  $Dk^2$  in ionic liquids degenerates into the relaxation one characterized by a finite lifetime. Moreover, propagator oscillatory modes, which are not always maintained in neutral particle mixtures, start to play an important role in ionic liquids. The contributions made by those modes remain finite even in the hydrodynamic limit, which is also specific only to the mixtures of charged particles with long-range Coulomb interactions. The availability of such differences is evidenced by both the old experimental results on light scattering and the results of recent researches executed in the framework of the molecular dynamics method [5, 6, 13].

Our studies have demonstrated that the standard hydrodynamic approach does not enable one to reveal and to correctly describe propagator collective excitations which play an important role at quitting the hydrodynamic mode, in both cases of binary mixtures – with either charged or neutral particles. On the basis of an idea of generalized hydrodynamic description using the extended set of dynamic variables, we have proposed rather a simple dynamic model which allows all the principal features in the dynamics of mass-concentration fluctuations to be properly reproduced at a qualitative level for both cases concerned – ionic liquids and binary mixtures of neutral particles. In the framework of the model proposed, analytical expressions for the spectra of collective excitations and the time correlation functions have been derived. In addition, this model can be used to analyze the results of researches which are based upon more complicated dynamic models; for example, it is an eight-variable model of transverse dynamics, which provides a good quantitative agreement with the data of computer simulations [5]. While considering more complicated models, the obtained analytical results can also be useful for carrying out the analytical calculations on the basis of perturbation theory. The development of the theory along the directions indicated above will be the subject of a separate study.

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#### КОНЦЕНТРАЦІЙНІ ЧАСОВІ КОРЕЛЯЦІЙНІ ФУНКЦІЇ БІНАРНИХ ПЛИНІВ: ІОННІ РОЗПЛАВИ І СУМІШІ НЕЙТРАЛЬНИХ ЧАСТИНОК

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#### Резюме

Отримано аналітичні вирази для концентраційних часових кореляційних функцій бінарних плинів заряджених та нейтральних частинок, для яких точно виконуються правила сум до четвертого порядку включно. Розрахунки виконано з використанням розширеного набору динамічних змінних, який крім концентраційної густини включає в себе її першу та другу часові похідні. На цій основі проведено порівняльний аналіз динамічної поведінки іонних розплавів та бінарних сумішей нейтральних частинок. Показано, що внаслідок специфіки взаємодій у іонних розплавах, їх поведінка має низку важливих відмінностей. Зокрема, отримані результати демонструють обмеженість стандартного гідродинамічного підходу до опису іонних розплавів.