Collective excitations in molten NaCl and NaI: A theoretical generalized collective modes study

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A theoretical analysis of dispersion for two branches of propagating collective excitations in molten NaCl and NaI is performed using an approach of generalized collective modes. Two molten salts with different mass ratios were studied in order to clarify reported "fast sound" in molten NaCl [F. Demmel, S. Hosokawa, M. Lorenzen, and W.-C. Pilgrim, Phys. Rev. B **69**, 012203 (2004)]. Contributions of low- and high-frequency branches to partial dynamical structure factors in molten salts are discussed.

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The interest to collective dynamics in many-component liquids has been revived because of recent neutron-scattering experiments in K-Cs (Ref. 1) and Na-Sn (Ref. 2) liquid alloys as well as inelastic x-ray-scattering experiments in vitreous silica[3] and a molten salt NaCl.[4] Thus far the theory of collective processes in binary liquids has been far behind the requirements of real and computer experiments. Analytical expressions for dynamical structure factors of binary liquids and molten salts are well known only in hydrodynamic limit,[5,6] when the binary liquid is treated as continuum without atomic structure. However, the real scattering experiments and molecular-dynamics (MD) computer simulations cover a window of wave numbers k, which is behind the hydrodynamic region. That is why a generalized model of collective dynamics in many-component liquids must be used for analysis of experimental data. The generalized model should take into account main dynamical processes that contribute to the shape of dynamical structure factors beyond the hydrodynamic region. One of the most promising theoretical approaches is based on a concept of generalized collective excitations (GCM),[7,8] which treats the collective dynamics beyond the hydrodynamic region as a variety of microscopic processes between generalized hydrodynamic excitations and so-called kinetic ones, which can exist only beyond hydrodynamic window of wave numbers and frequencies. As an example of kinetic propagating processes one can mention heat waves[9] and optic phononlike excitations in binary liquids,[10] whereas the most obvious kinetic relaxing process not taken into account in hydrodynamics is structural relaxation.[9]

This paper was initiated by a recent report[4] on experimental study of propagating particle density fluctuations in molten NaCl. One of the conclusions was about a "fast sound" found in this molten salt, which was interpreted as "the Na^+ subsystem moving independent on the anionic background at high frequencies." Following the conclusions of Ref. 4 it seems that there does not exist a clear understanding of the role played by light and heavy subsystems in binary ionic melts, and the issue of spatial scales on which one can observe the dynamics of partial densities should be clarified.

The fast sound phenomenon was reported from analysis of MD-derived partial dynamical structure factors in molten metallic alloy Li_4Pb,[11] for which the mass ratio of Pb and Li atoms is about 30. The fast sound in Ref. 11 was implied by the behavior of two almost linear dispersion laws with essentially different slopes in the small-wave-number region, obtained for two branches of collective excitations in the small-wave-number region: the high-frequency branch was named as a fast sound, whereas the low-frequency branch was supposed to match hydrodynamic dispersion law. It is worth noting that in Ref. 11 and following MD studies[12] of collective dynamics in molten Li_4Pb, the dispersion laws of the two branches was obtained either from the maxima positions of current spectral functions $C_{\alpha\alpha}(k,\omega)$, $\alpha=\mathrm{Li,Pb}$, or Brillouin peak location on the shape of partial dynamical structure factors $S_{\alpha\alpha}(k,\omega)$. It is necessary to mention that analysis of the last neutron-scattering experiments[13] on Li_4Pb implied a nonacoustic origin of high-frequency excitations reflecting "localized out-of-phase atomic motions."

The goal of this study was to perform a theoretical GCM analysis of dispersion of collective excitations in molten salts NaCl and NaI. They essentially differ by a mass ratio of heavy and light components $R=m_h/m_l$: 1.54 for NaCl and 5.52 for NaI. We will show how the difference in mass ratio is reflected in the behavior of high- and low-frequency branches. Mode contributions to partial spectral functions in the long-wavelength region will be discussed.

MD simulations for NaCl at 1260 K and NaI at 1080 K were performed in the standard microcanonical ensemble on a model systems of 1000 particles in a cubic box subject to periodic boundary conditions. Potentials in the Tosi-Fumi form for NaCl and NaI were taken from Ref. 14. The long-range interaction was treated by the Ewald method, and the short-range parts of two-body potentials were cut off at 12.66 Å for NaCl and at 14.39 Å for NaI. The smallest wave numbers $k_{\min}$ reached in the MD simulations were 0.19 $Å^{-1}$ for NaCl and 0.17 $Å^{-1}$ for NaI, respectively. The main aim of the MD simulations was to obtain the time evolution of all hydrodynamic and short-time extended dynamical variables, forming the following eight-variable basis set $\mathbf{A}^{(8)}(k,t)$ used for our study of collective dynamics within the GCM approach:

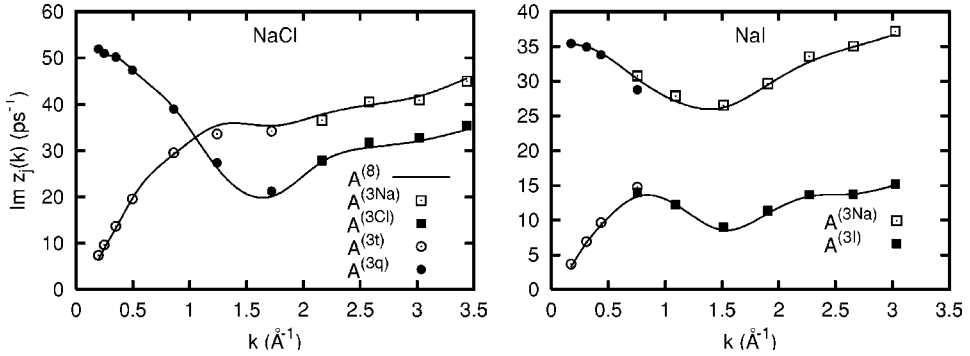

FIG. 1. Dispersion of two branches of propagating collective excitations in molten NaCl at 1260 K (left) and NaI at 1080 K (right). Imaginary parts of complex eigenmodes obtained in eight-variable treatment (1) of collective dynamics are shown by the spline-interpolated solid line. Results of projected on "partial" and "intrinsic collective" basis sets are plotted as follows: open circles correspond to the projection $\mathbf{A}^{(3t)}$; filled circles, $\mathbf{A}^{(3q)}$; open boxes, projection on partial dynamics of light (Na^+) subsystem; filled boxes, projection on partial dynamics of heavy (Cl^- or I^-) subsystem.

$$\mathbf{A}^{(8)}(k,t) = \{n_t(k,t), n_q(k,t), J_t^L(k,t), J_q^L(k,t), \varepsilon(k,t), \dot{J}_t^L(k,t), \dot{J}_q^L(k,t), \dot{\varepsilon}(k,t)\}, \quad (1)$$

where the hydrodynamic variables of total particle density $n_t(k,t)$, charge density $n_q(k,t)$, longitudinal total momentum density $J_t^L(k,t)$, and energy density $\varepsilon(k,t)$ are defined in the standard way,[6] and the extended dynamical variables are represented by the time derivatives of hydrodynamic variables. The choice of the eight-variable basis set (1) is defined in several ways: (i) it must contain all hydrodynamic variables; (ii) fluctuations of the total mass and charge currents and their time derivatives must be treated on the same level of approximation; (iii) we may restrict our GCM treatment of short-time processes with the first time derivatives of the currents and energy, because our previous GCM studies of pure and binary liquids[15,9] revealed that faster fluctuations are not so important for treatment of main dynamical processes.

We estimated directly from MD the time correlation functions and relevant static averages needed for the estimation of matrix elements of the 8×8 matrices of time correlation functions $\mathbf{F}(k,t)$ and their Laplace transforms $\tilde{\mathbf{F}}(k,z)$ and calculation of GCM replicas of relevant time correlation functions. Eigenvalues and eigenvectors of a generalized hydrodynamic matrix[8]

$$\mathbf{T}(k) = \mathbf{F}(k,t=0)\tilde{\mathbf{F}}^{-1}(k,z=0)$$

were calculated for each k point sampled in MD. Thus, in our approach there were no fitting or free parameters. The set of eigenvalues $z_j(k)$ [purely real eigenvalues $d_j(k)$ and complex-conjugated pairs $\sigma_j(k)\pm i\omega_j(k)$] of generalized hydrodynamic matrix $\mathbf{T}(k)$ formed the spectrum of collective excitations. Any MD-derived time correlation function of interest within the GCM approach has its GCM replica represented as the sum over the mode contributions,

$$F_{\alpha\beta}^{(\mathrm{GCM})}(k,t) = \sum_{j=1}^{8} G_{\alpha\beta}^{j}(k) e^{-z_j(k)t}, \quad (2)$$

where in general complex amplitudes $G_{\alpha\beta}^{j}(k)$ were estimated from the eigenvectors of $\mathbf{T}(k)$ associated with the relevant eigenvalue $z_j(k)$.[8,16] Note, that Eq. (2) permits estimation of mode contributions from propagating and relaxation processes to the shape of time correlation functions of interest and relevant dynamical structure factors $S_{\alpha\beta}(k,\omega)$.

Dispersion of two branches of propagating excitations obtained from the eight-variable GCM treatment of collective dynamics in molten NaCl and NaI is shown in Fig. 1. In order to estimate the main dynamical processes responsible for the dispersion law in different regions of wave numbers, we have performed additional GCM studies on the projected-out subsets of dynamical variables, namely, for four different three-variable subsets $\mathbf{A}^{(3\alpha)}(k,t)$,

$$\mathbf{A}^{(3\alpha)}(k,t) = \{n_\alpha(k,t), J_\alpha^L(k,t), \dot{J}_\alpha^L(k,t)\}, \quad \alpha = t,q,\mathrm{Na},\mathrm{Cl},\mathrm{I}, \quad (3)$$

connected solely with total (t) and charge (q) densities, partial density of light (Na), and heavy (Cl or I) components. The results are presented in Fig. 1 by corresponding symbols. A clear picture of the origin of two branches of propagating excitations immediately follows from such a projected approach. In the small-wave-number region the low-frequency branch has almost linear dispersion and corresponds to propagating sound modes, whereas the high-frequency branch is completely determined by charge current fluctuations and is an analogy of longitudinal optic phonons in ionic crystals. Unlike in crystals, where the periodicity of dispersion curves is defined by the Brillouin zone, in molten salts the branches have dispersion in the large-wave-number region, which is completely defined by dynamics of partial quantities: the low- or high-frequency branch reflects solely the heavy or light subsystem, respectively. The role of the mass ratio of components in molten salts is twofold: it defines the gap between low- and high-frequency branches in the large-wave-number region and changes the width of the

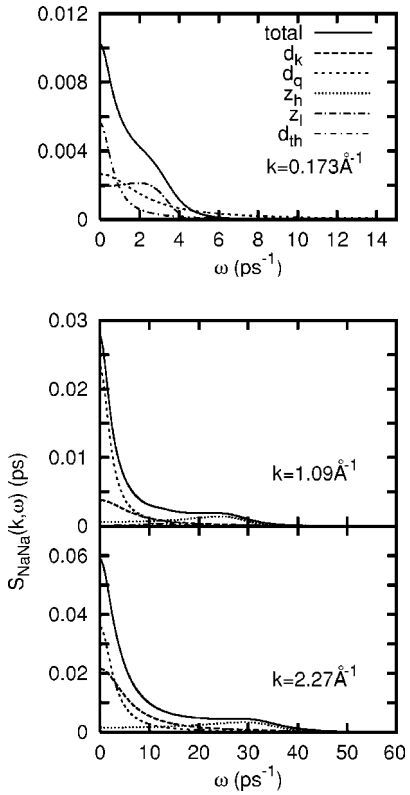

FIG. 2. Contributions from propagating collective excitations and relaxing modes to the shape of partial dynamical structure factor $S_{\mathrm{NaNa}}(k,\omega)$ of the light component (solid line) in molten NaI at 1080 K for three wave numbers. The $z_h(k)$ and $z_l(k)$ denote contributions from high- and low-frequency propagating excitations, respectively. The contributions from relaxing processes of thermal diffusivity, conductivity, and the kinetic process of structural relaxation were marked as d_{th}, d_q, and d_k, respectively.

region where dynamics corresponds to either t-q (implicit collective) or A-B (partial) type. In the studied case of molten NaCl and NaI we observe the reduction of the t-q region from about 1.7 Å^{-1} in NaCl to about 0.7 Å^{-1} in NaI, while the region of "partial" dynamics becomes more wide. This conclusion is in agreement with our recent study on mass ratio dependence of spectra in Lennard-Jones liquid mixtures.[19] Thus, we do not observe fast-sound-like behavior in the high-frequency branch in molten NaCl in the long-wavelength region, and for $k<1.7$ Å^{-1} the two branches correspond to acoustic and optic phononlike collective excitations. An interesting issue is the propagation speed of acoustic excitations at the smallest wave numbers sampled in the MD simulations. Estimated values for molten NaCl and NaI are 3294 m/s and 1930 m/s, respectively. The propagation speed of low-frequency excitations in NaCl is in agreement within 7–8% with numerical MD results by Ciccotti *et al.*,[14] whereas the frequency of opticlike excitations is in much better agreement. The difference perhaps is the consequence of different sizes and cutoff radii of the short-range part of the two-body potentials. GCM results on dispersion of acoustic excitations in NaCl are in better agreement with results by Demmel *et al.*,[4] estimated from the peak positions of fitted current spectral functions $j(k,\omega)=\omega^2 I(k,\omega)$, where $I(k,\omega)$ is the spectral function of the damped harmonic-oscillator model. Note that more correct numerical procedures of dispersion estimation should take into account contributions from both branches with amplitudes taken as parameters. We would also like to stress that the dispersion (shown in Fig. 1 by open circles) reflects projected-out propagating total density fluctuations, for which an analytical three-variable treatment $\mathbf{A}^{(3t)}(k,t)$ in $k\to 0$ limit results in propagation speed c_∞, known as the high-frequency speed of sound. Thus, our eight-variable GCM results in the long-wavelength region show, in Fig. 1, that the propagation speed of acoustic excitations (solid lines) is close to the high-frequency speed of sound with a tendency of decreasing toward the hydrodynamic window of wavenumbers.

The opticlike branch in molten salts belongs to kinetic propagating excitations, which one cannot observe in a hydrodynamic window of frequencies and wave numbers. However, the kinetic excitations contribute significantly to the shape of time correlation functions and dynamical structure factors beyond the hydrodynamic region. Since in the original paper on fast sound in two-component liquids[11] the dispersion curve for high-frequency excitations was obtained from the positions of Brillouin peak on the partial dynamical structure factor of light component, we show in Fig. 2 the contributions from different propagating and relaxing processes to the shape of partial dynamical structure factor $S_{\mathrm{NaNa}}(k,\omega)$ in molten NaI because NaI has larger mass ratio. In general, any dynamical structure factor defined on dynamical variables from the chosen set (1) can be represented within the GCM approach as follows:

$$\frac{S_{\alpha\beta}(k,\omega)}{S_{\alpha\beta}(k)} = \sum_{j}^{N_r} A^j_{\alpha\beta}\frac{d_j(k)}{\omega^2+d_j^2(k)} + \sum_{j,\pm}^{N_p}\frac{B^j_{\alpha\beta}\sigma_j(k)+D^j_{\alpha\beta}[\omega\pm\omega_j(k)]}{[\omega\pm\omega_j(k)]^2+\sigma_j^2(k)}, \quad \alpha,\beta=\{A_i(k,t)\}, \tag{4}$$

which generalizes the four-term hydrodynamic expressions onto a more general case of N_r relaxing and N_p pairs of propagating generalized hydrodynamic and kinetic collective excitations, $N_r+2N_p=N_v$. The amplitudes of mode contributions $A^j(k)$, $B^j(k)$, $D^j(k)$ (frequently called mode strengths) from collective modes can be estimated numerically from $G^j_{\alpha\beta}(k)$ in (2) for any k point sampled in real or computer experiments, that permit representation of measured dynamical structure factors $S_{\alpha\beta}(k,\omega)$ in terms of separated mode contributions being extremely important for experimentalists.

From Fig. 2 one can conclude that in the region of intermediate and large wave numbers, the central peak of $S_{\mathrm{NaNa}}(k,\omega)$ is formed by two main relaxing contributions coming from conductivity $d_q(k)$ and the kinetic process of structural relaxation $d_k(k)$, whereas the side peak is completely due to propagating high-frequency excitations $z_h(k)$. However, for small wave numbers (upper frame in Fig. 2) only the hydrodynamic processes form the shape of $S_{\mathrm{NaNa}}(k,\omega)$: the central peak because of thermal diffusivity

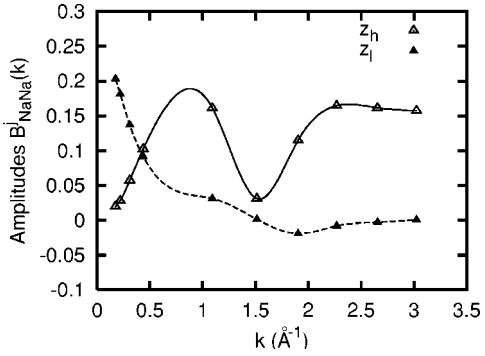

FIG. 3. Amplitudes of contributions (mode strengths) of high-frequency $z_h(k)$ and low-frequency $z_l(k)$ propagating collective excitations to the shape of partial dynamical structure factor $S_{\mathrm{NaNa}}(k,\omega)$ in molten NaI at 1080 K.

$d_{th}(k)$ and electric conductivity $d_q(k)$, and a shoulder because of acoustic low-frequency propagating excitations. An important point is that the high-frequency branch does not contribute to the partial dynamical structure factor in long-wavelength region. A more general picture of contributions from propagating excitations to the shape of $S_{\mathrm{NaNa}}(k,\omega)$ one can be obtained from Fig. 3, where mode strengths $B^j_{\mathrm{NaNa}}(k)$ of high- and low-frequency branches are shown as functions of k. An obvious crossover in contributions coming from high- and low-frequency branches exists at about 0.5 Å^{-1}, which means that in the long-wavelength limit even the partial dynamical structure factor of the light component does not contain the contribution from the kinetic high-frequency branch and only generalized sound excitations form the side shoulder. It is interesting that the vanishing in long-wavelength contributions from opticlike excitations to partial spectral functions seem to be a specific feature of the liquid state because recent analysis of MD-derived current spectral functions in crystals composed of disparate-mass particles[17] revealed well-defined peaks from high-frequency excitations, even in long-wavelength regions.

In summary, we have performed a theoretical GCM study of collective propagating excitations in molten salts NaCl and NaI and shown that the high-frequency branch of collective excitations corresponds in small-wave-number region to optic phononlike excitations and cannot be interpreted as a "fast sound." We observed in NaCl a clear separation of collective dynamics into partial ones only for large wave numbers, namely, for $k > 1.7$ Å^{-1}. For smaller wave numbers there are no reasons to talk about a light subsystem moving independent of a heavy one. The contributions of propagating modes to the shape of partial dynamical structure factors of the light component make evident that in the small-wave-number region the inelastic peak on its shape is due to low-frequency sound excitations, but not to partial dynamics of the light component. We would like to stress that these GCM results were obtained using two-body interactions within the simple Tosi-Fumi model of rigid ions. More precise dispersion curves can be obtained by inclusion into treatment polarization effects[18] or performing GCM analysis of *ab initio* MD-derived time correlation functions, which would reflect polarization effects.

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