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Collective excitations and generalized transport coefficients in a molten metallic alloy Li_4Pb

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Collective dynamics of a molten metallic alloy Li_4Pb is studied using a combination of analytical multivariable approach of generalized collective modes and molecular dynamics simulations. Dispersion and damping of two branches of propagating collective excitations are analyzed in a wide range of wavenumbers. The features in collective dynamics connected with the large difference in species mass are discussed. Generalized k-dependent transport coefficients for Li_4Pb are reported.

Key words: *collective dynamics, binary liquid, collective excitation, generalized transport coefficients*

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1. Introduction

A molten metallic alloy Li_4Pb has become well-known following the Letter by Bosse *et al* [1] in which the existence of “fast sound” collective excitations in disparate mass two-component liquids was suggested. The new collective excitation in Li_4Pb was interpreted as “a propagating lithium density fluctuations in a background of heavy lead ions, which do not participate, to an essential extent, in the high-frequency motion” [1]. Moreover, the frequency of “fast sound” excitations was found from the molecular dynamics (MD) simulations on a model system of 250 particles to follow the nearly linear law of dispersion in the region of small wavenumbers. This raised a question whether the fast-sound mode will disappear as the wavenumber decreases or alternatively, whether the fast-sound mode will continuously change its slope in the transition regime to merge into the ordinary Brillouin peak without ever disappearing [1].

Collective dynamics of binary liquids is so far well-known only in hydrodynamic limit when the liquid is treated as continuum. Four local conservation laws permit to obtain analytical expressions for hydrodynamic time correlation functions and dynamical structure factors $S_{ij}(k,\omega)$ in the limit $k \to 0, \omega \to 0$ (k and ω are the wavenumber and frequency, respectively) [2–4]. It is obvious that due to a very large mass difference for components in Li_4Pb the lithium (light) and lead (heavy) subsystems would clearly display different tendencies behind the hydrodynamic region. Computational studies of molten Li_4Pb using molecular dynamics simulations [5,6] did not shed the light on the problem of how the branches of collective excitations behave by approaching the hydrodynamic region because the numerical method of estimating the dispersion was not based in those studies on particular models of generalized hydrodynamics but simply traced out the maxima positions in relevant spectral functions. Therefore, the theoretical studies based on generalized hydrodynamics are extremely important in collective dynamics of disparate-mass binary liquids.

A theoretical analysis of collective dynamics in binary fluids, based on the generalized hydrodynamics, was for the first time applied in the study of another "fast sound" mixture He-Ne [7]. A *five-variable* kinetic approach was based on a simultaneous treatment of hydrodynamic and short-time (extended) dynamical variables and enabled one to obtain dynamical eigenmodes in the binary fluids as the eigenvalues of 5×5 generalized hydrodynamic matrix, as well as to estimate their contributions to all spectral functions of interest. However, the necessity to know *a priori* the transport coefficients of the studied mixture, or alternatively the presence of free parameters in the generalized hydrodynamic matrix, was a considerable drawback of the method proposed in [7]. Later, in [8] the parameter-free generalized collective modes (GCM) approach based on the original concept developed for simple fluids by de Schepper *et al* [9], in its parameter-free version [10], was employed in *seven-variable* approximation to study the binary mixture $He_{0.65}Ne_{0.35}$. In contrast to the study [7] all the elements of the generalized hydrodynamic matrix in [8] were calculated directly in MD. Following the collective excitation study in $He_{0.65}Ne_{0.35}$ an attempt was undertaken to calculate generalized (k,ω)-dependent transport coefficients in this gaseous binary mixture [11] based on generalized hydrodynamics of multicomponent liquids formulated in [12] within the GCM approach.

The GCM approach has proved to be applicable in the study of non-hydrodynamic collective processes in pure [13] and binary liquids [14,15], such as heat waves, transverse optic-like processes and kinetic modes connected with local structural relaxation. In [14] the GCM study of transverse dynamics in molten Li_4Pb at 1085 K permitted to identify the high-frequency branch in low-k region as the transverse optic-like excitations, caused by mass-concentration fluctuations. It was shown that in long-wavelength limit, the high-frequency branch in Li_4Pb tends to a finite frequency and can be described solely by treatment of transverse mass-concentration current fluctuations.

Thus, our aim is to apply the generalized hydrodynamic GCM approach to the study of collective dynamics in Li_4Pb. So far this approach turns out to be the most consistent method for analytical and numerical studies of collective kinetic modes, because it enables us to treat the hydrodynamic and more short-time processes in liquids on the same footing. We will obtain the spectrum of longitudinal collective excitations and find out the origin of each branch. For the first time we report herein the calculations of generalized transport coefficients in a "fast sound" liquid alloy.

2. The method

The method used in this work for a miscroscopic study of liquid dynamics is a combination of molecular dynamics simulations and multivariable kinetic approach for parameter-free analysis of MD-derived time correlation functions.

2.1. Molecular dynamics simulations

Computer simulations were performed in the standard microcanonical ensemble on a model system of 4000 particles in a cubic box subject to periodic boundary conditions at the temperature of 1085 K and mass-density of 3556.76 kg/m^3. The pair potentials $\Phi_{ij}(r)$, taken from [16], were the same as the ones used in previous studies of dynamics in Li_4Pb [1,5,6]. The functional form of $\Phi_{ij}(r)$ for molten Li_4Pb was suggested in [17] and consisted of a repulsive soft core term and a screened Coulomb potential in order to reflect the short-range charge neutrality. The fourth-order Gear algorithm with the time step $\delta t = 1 \cdot 10^{-15}$ s was used to integrate the equations of motion. Energy conservation in MD turned out to be very good. Over the length of production run of $3 \cdot 10^5$ steps, the total energy drift was on the level of 0.1%. The ratio of square roots of variances corresponding to fluctuations of total and potential energies was on the level of 0.13. The smallest wavenumber reached in MD simulations was $k_{\min} = 0.1414$ Å^{-1}.

The main purpose of MD simulations was to obtain the time evolution of hydrodynamic and short-time extended dynamic variables, to estimate time correlation functions and relevant static averages necessary for GCM analysis, and to compare MD-derived time correlation functions with their GCM-replicas. To reduce the dimension of relevant quantities, the following energy, mass, spatial and time scales were used in our simulations: $\epsilon = k_{\mathrm{B}}T$, $\mu = \bar{m} = 7.803 \cdot 10^{-26}$ kg, $\sigma = 4.455$ Å, $\tau = \sigma(\mu/\varepsilon)^{1/2} = 1.017$ ps.

2.2. Generalized collective modes approach

In this GCM study of generalized transport coefficients in molten Li_4Pb we have chosen the following eight-variable basis set of dynamic variables:

$$\mathbf{A}^{(8)}(k,t) = \{n_1(k,t), n_2(k,t), J_1^{\mathrm{L}}(k,t), J_2^{\mathrm{L}}(k,t), \varepsilon(k,t), \dot{J}_1^{L}(k,t), \dot{J}_2^{\mathrm{L}}(k,t), \dot{\varepsilon}(k,t)\} \ , \tag{1}$$

where the dynamic variables of partial number densities are defined as follows:

$$n_\alpha(k,t) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N_\alpha} \mathrm{e}^{\mathrm{i}\mathbf{k}\mathbf{r}_{\alpha,i}(t)} \ , \qquad \alpha = 1,2 \ .$$

Both partial densities $n_i(k,t)$ are hydrodynamic variables and, along with dynamic variables of total mass-current density $\mathbf{J}_t(k,t)$ and energy density $\varepsilon(k,t)$, they are used in the hydrodynamic description of any binary system in liquid state:

$$\mathbf{A}^{\rm hyd}(k,t) = \{n_1(k,t), n_2(k,t), J_t^{\rm L}(k,t), \varepsilon(k,t)\} \ .$$

These four dynamical variables from the hydrodynamic basis set describe the slowest miscroscopic processes in binary liquids. All the other dynamical variables from the basis set $\mathbf{A}^{(8)}(k,t)$, which are the time derivatives and linear combinations of hydrodynamic variables correspond to faster kinetic-like processes. The time evolution of dynamical variables from the basis set $\mathbf{A}^{(8)}(k,t)$ was obtained in MD simulations. All the static and time correlation functions necessary for the estimation of matrix elements of the 8×8 matrices of time correlation functions $\mathbf{F}(k,t)$ and their Laplace transforms $\tilde{\mathbf{F}}(k,z)$ were directly evaluated in computer simulations. Eigenvalues and eigenvectors of generalized hydrodynamic matrix [10]

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

were calculated for each k-point sampled in molecular dynamics. Thus, in our approach there was no fitting of free parameters. The set of eigenvalues $z_\alpha(k)$ 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 mode contributions:

$$F_{ij}^{\rm (GCM)}(k,t) = \sum_{\alpha=1}^{8} G_{ij}^{\alpha}(k){\rm e}^{-z_\alpha(k)t} \ , \tag{2}$$

where in general complex amplitudes $G_{ij}^{\alpha}(k)$ were estimated from the eigenvectors associated with the relevant eigenvalue $z_\alpha(k)$ [10,8].

3. Results and discussion

3.1. Static quantities

Three partial static structure factors $S_{ij}(k),\ i,j = \mathrm{Li},\mathrm{Pb}$, directly estimated in MD simulations are shown in figure 1. The difference in the size of components is clearly seen from the positions of the main peaks of static structure factors. Light subsystem of small Li atoms has its maximum of $S_{\rm LiLi}(k)$ at approximately 2.4 Å^{-1}, while the heavy large atoms of Pb have a corresponding maximum of $S_{\rm PbPb}(k)$ at approximately 1.55 Å^{-1}. The partial static structure factors can be used in calculating the Bhatia-Thornton "number-concentration" structure factors $S_{ij}(k)$ with $i,j = n,c$ [2], or $S_{ij}(k)$ with $i,j = t,x$, where the $t-x$ pair of dynamical variables corresponds to total density $n_t(k,t)$ and mass-concentration density $n_x(k,t)$ [18,19]. We observed the tendency towards nonzero constants in $S_{\rm cc}(k)$ when $k\to0$, that is the consequence of the absence of long-range Coulomb two-body potentials in

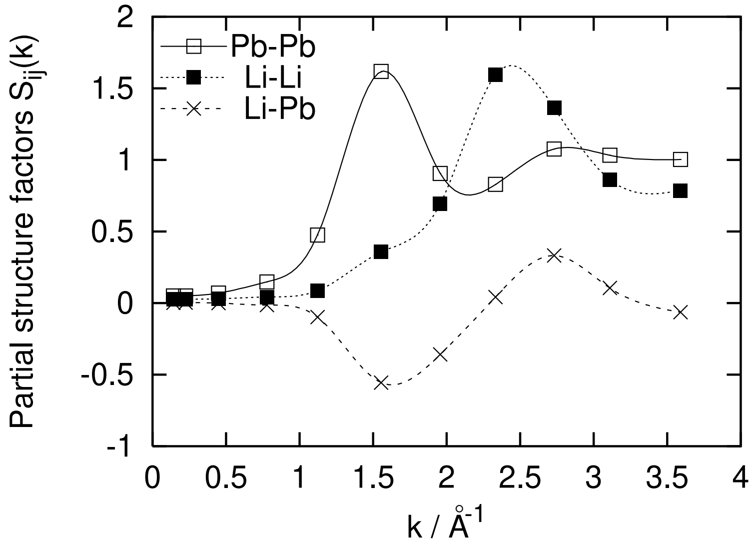

Figure 1. Partial static structure factors of Li_4Pb obtained directly in MD: Pb-Pb (open boxes), Li-Pb (cross symbols) and Li-Li (filled boxes). Lines correspond to cubic spline interpolation.

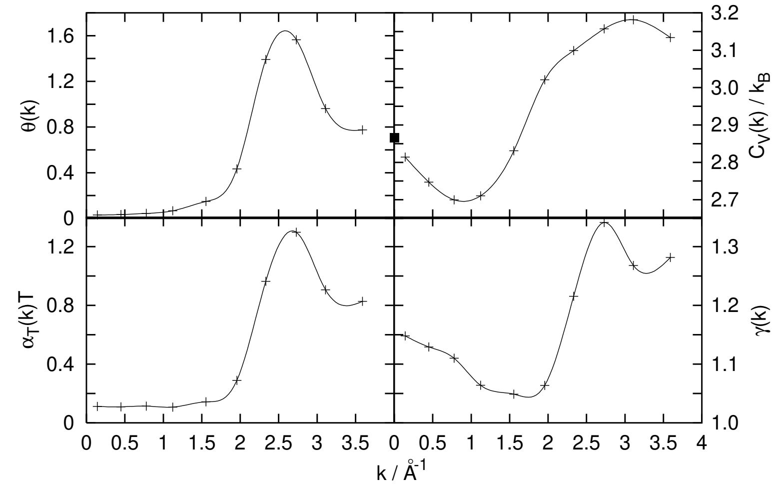

Figure 2. Generalized thermodynamic quantities for molten Li_4Pb at T=1085 K: generalized reduced compressibility $\theta(k)$ (upper left frame), generalized thermal expansion coefficient $\alpha_{\mathrm{T}}(k)$ (lower left frame), generalized specific heat at constant volume $C_{\mathrm{V}}(k)$ (upper right frame), generalized ratio of specific heats $\gamma(k)$ (lower right frame). The filled box at $k = 0$ in the upper right frame denotes the specific heat C_{V} obtained from the temperature fluctuations formula during MD run. Solid lines are the spline interpolation.

molten Li_4Pb due to the screening by electronic density. Otherwise, the structure factor $S_{cc}(k)$ would be $\propto k^2$ in long-wavelength limit as in the case of molten salts.

The isothermal compressibility κ_T in the case of binary liquids is usually expressed via a combination of partial structure factors at $k = 0$ (see [2]). Here we follow the expressions derived in [8] for reduced generalized isothermal compressibility $\theta(k)$

$$\theta(k) = \frac{N}{V} k_B T \kappa_T(k) \ ,$$

which is shown in figure 2 in the upper left frame. It is seen, that $\theta(k)$ behaves almost the same as $S_{LiLi}(k)$. In figure 2 we also show the k-dependence of generalized thermodynamic quantities (see [8] for original expressions): generalized thermal expansion coefficient $\alpha_T(k)$, generalized specific heat at constant volume $C_V(k)$ and generalized ratio of specific heats $\gamma(k)$. Smooth behaviour of $\alpha_T(k)$ at $k \to 0$ made it possible to estimate the thermal expansion coefficient for Li_4Pb at $1085K$ to be $1.03 \cdot 10^{-4} K^{-1}$. The generalized specific heat at a constant volume $C_V(k)$, which is defined via the static value of "heat density-heat density" time correlation function $F_{hh}(k,t)$, tends in the $k \to 0$ limit towards the value of 2.87, obtained from the temperature fluctuations during MD production run. The ratio of specific heats $\gamma(k)$ is a very important quantity, which permits to judge about the static coupling between heat and density fluctuations. It is important to note that $\gamma(k)$ tends in the long-wavelength limit towards the value of ≈ 1.15, which is a quite reasonable value for metallic melts.

3.2. Time correlation functions

Time correlation functions of primary interest are the ones defined on the hydrodynamic variables. We will focus on the analysis of the following six time correlation functions: $F_{ij}(k,t)$, $F_{\varepsilon i}(k,t)$, $F_{\varepsilon\varepsilon}(k,t)$, $i,j =$Li,Pb, which are shown for the smallest wavenumber in figure 3. The most interesting are the functions describing autocorrelations of partial densities $F_{ii}(k,t)$, and energy density $F_{\varepsilon\varepsilon}(k,t)$. It is seen from the behaviour of $F_{LiLi}(k,t)$ and $F_{PbPb}(k,t)$, that even for the smallest wavenumber sampled in MD simulations these functions reflect processes of different time scales: light Li atoms are responsible for damped oscillating behaviour of $F_{LiLi}(k,t)$, which would manifest itself as a side Brillouin peak on the partial structure factor $S_{LiLi}(k,\omega)$. Collective correlations of heavy Pb atoms are of a relaxing form, which, however, cannot be an evidence that Pb atoms do not participate in the oscillating motion. One can expect that for much smaller wavenumbers so far not accessible in MD simulations, both functions $F_{LiLi}(k,t)$ and $F_{PbPb}(k,t)$ will display long-wavelength oscillations with approximately the same frequency reflecting the hydrodynamic sound propagation in the liquid. The energy-energy autocorrelation functions $F_{\varepsilon\varepsilon}(k,t)$ are very similar in shape to the $F_{LiLi}(k,t)$ function, which means that the main contribution to the energy time correlations at small wavenumbers is determined by the light Li subsystem.

In all frames of figure 3 the six GCM replicas $F_{ij}^{(GCM)}(k,t)$ (2) are shown by solid lines. One can see that MD-derived functions (bold symbols "plus") and their GCM replicas are almost identical, which indicates a very good quality of the applied eight-variable approximation and the correct correspondence of the main collective dynamical processes to the dynamical eigenmodes obtained for these wavenumbers, which are beyond the hydrodynamic region considered.

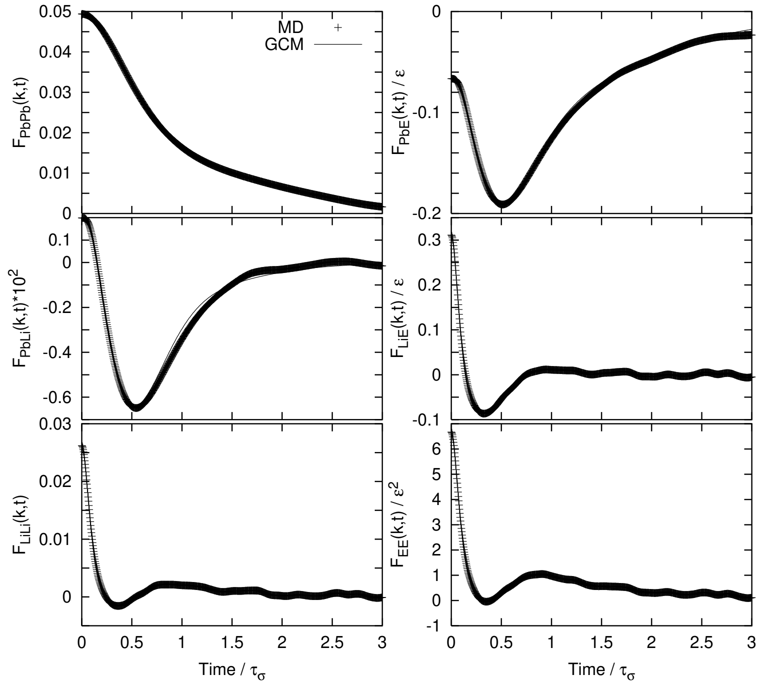

Figure 3. MD-derived time correlation functions at $k = 0.1414$ Å^{-1} (plus symbols) and their GCM replicas (lines).

3.3. Spectrum of collective excitations in molten Li_4Pb

The set of eight complex and purely real eigenvalues at different k points sampled in MD represents the spectrum of collective excitations. For the sake of simplicity we will mark the purely real eigenvalues which correspond to relaxing processes as $d_j(k)$, while the complex eigenvalues

$$z_j(k) = \sigma_j(k) \pm \mathrm{i}\omega_j(k)$$

are represented by pairs of complex conjugated numbers corresponding to the processes propagating in opposide directions with frequency $\omega_j(k)$ and damping $\sigma_j(k)$. For the case of basis set $\mathbf{A}^{(8)}(k,t)$ the spectrum of collective excitations in molten Li_4Pb consisted of two pairs of propagating modes and four relaxing processes in the whole k-region. Note that for the case of Li_4Pb we did not obtain solutions of the heat waves type, which we observed earlier in GCM studies of pure liquids [13], Lennard-Jones binary mixtures [19] and molten salts.

The imaginary and real parts of complex eigenvalues for Li_4Pb are shown in figure 4. An interesting behaviour of dispersion of two branches is observed on the top frame: the branches correspond to the processes well separated in frequency. The high-frequency branch shown by open boxes has a pronounced minimum at the position of the main maximum of partial static structure factor $S_{\mathrm{LiLi}}(k)$ and tends to a nonzero frequency in the long-wavelength region, which is a specific feature of optic-like excitations in binary liquids [19]. The low-frequency branch is even more interesting. It has a similar pronounced minimum at $k \approx 1.45$ Å^{-1}, which is at the main maximum location of $S_{\mathrm{PbPb}}(k)$. However, this branch has another minimum in dispersion law at $k \approx 0.25$ Å^{-1}. Such a minimum is never observed in binary liquid mixtures with comparable masses of species and concentrations. However, it is obvious that for the disparate-mass liquid mixtures there should be a qualitative difference in spectra of collective excitations between two cases of comparable concentrations and an impurity limit of the heavy component. In the latter case, one would expect the absence of low-frequency branch in the spectrum of collective excitations in long-wavelength region, while the high-frequency branch of light subsystem would continuously transform into hydrodynamic sound in the limit $k \to 0$. A more detailed GCM study of mass ratio and concentration dependence of spectra of collective excitations in binary liquids will be reported elsewhere. For the case of $\mathrm{Li_4Pb}$, we see that for $k < 0.25$ Å^{-1} the spectrum of propagating excitations assumes the features of regular binary liquids, where in a long-wavelength region two branches of propagating excitations correspond to hydrodynamic sound and optic-like excitations caused by fast mass-concentration fluctuations. This means that in $\mathrm{Li_4Pb}$, the heavy subsystem plays an important role in the collective dynamics and hence the small-k region, where the dispersion of low-frequency branch displays a minimum, can be treated as a crossover region between partial character of collective dynamics ($k > 0.25$ Å^{-1}) and intrinsic collective behaviour in terms of hydrodynamic sound and optic-like excitations in the region of smaller k.

The real parts of propagating eivenvalues which correspond to the excitation damping (or inversed lifetime) are shown in the lower frame in figure 4. A well pronounced maximum in $\sigma(k)$ for each branch is observed at the main maximum position of the corresponding partial static structure factor $S_{ii}(k), i =$Li,Pb, that again supports the partial character of branches in the region of intermediate and large wavenumbers. For $k < 0.75$ Å^{-1}, the wavenumber dependence of damping coefficients has an opposite tendency for high- and low-frequency branches. The low-frequency branch shows a slow change towards damping of hydrodynamic sound, which should be proportional to k^2 in the long-wavelength limit. Instead, the high-frequency branch becomes more overdamped when $k \to 0$, which is a specific feature of kinetic propagating modes [8,15,18]. The large difference in damping coefficients for high- and low-frequency branches explains why in the numerical approach to the estimation of dispersion of collective excitations via maxima positions of partial spectral functions, a merger of two branches was observed in small-k region for $\mathrm{Li_4Pb}$ [5,6]. It is obvious that the contribution from strongly overdamped high-frequency branch cannot be well observed in spectral functions on the background of a pronounced maximum coming from the low-frequency branch.

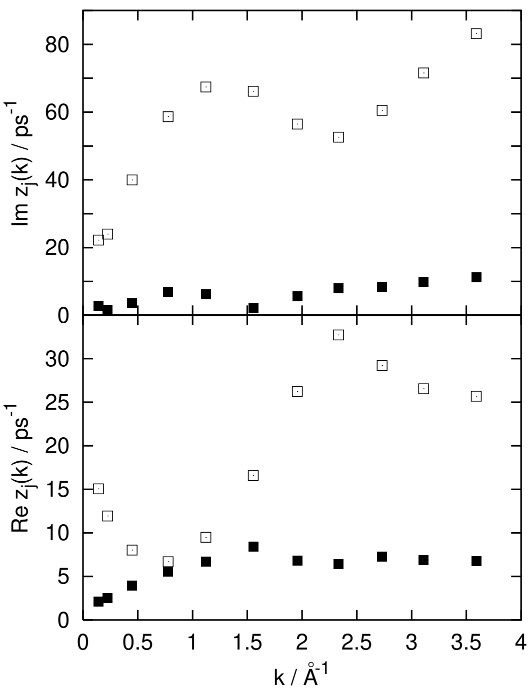

Figure 4. Imaginary and real parts of complex eigenvalues $z_j(k)$ corresponding to frequency and damping of propagating collective excitations, respectively.

The behaviour of relaxation processes existing in the binary liquid on different spatial and time scales is reflected by the wavenumber dependence of purely real eigenvalues $d_j(k)$ shown in figure 5. In the whole k-region studied we observed two pairs of complex conjugated eigenvalues and four purely real (relaxing) modes. The highest relaxing eigenmode corresponds to extremely short-time processes and does not considerably affect the collective dynamics of the studied system. Therefore, in figure 5 we show the k-dependence of three main relaxing processes, which reflect the heat relaxation (filled circles) and relaxing processes in light (filled triangles) and heavy (open triangles) subsystems for $k > 0.25$ Å^{-1}. The way we identified k-dependence of each relaxing process among the four real eigenvalues was the same as we used in our previous study of liquid Lennard-Jones mixture Kr-Ar [19] applying separated subsets of dynamical variables. In figure 5 by dotted and dash-dotted lines there is shown the behaviour of the lowest real eigenvalues, obtained from the 2×2 and 3×3 generalized hydrodynamic matrices generated on the separated sets $\mathbf{A}^{(2h)} = \{h(k,t), \dot{h}(k,t)\}$ and $\mathbf{A}^{(3\mathrm{Pb})} = \{n_{\mathrm{Pb}}(k,t), J^{\mathrm{L}}_{\mathrm{Pb}}(k,t), \dot{J}^{\mathrm{L}}_{\mathrm{Pb}}(k,t)\}$ respectively. It is clearly seen that for $k > 0.25$ Å^{-1} the relaxing process shown by open triangles is completely defined by the heavy subsystem of Pb atoms. For smaller wavenumbers, this relaxing mode continuously changes into a kinetic relaxing process of structural relaxation with the inversed relaxation time, which in the case of pure liquids has the following k-dependence [19]:

$$d_{\mathrm{str}}(k) = \frac{c_\infty^2 - c_s^2}{D_{\mathrm{L}}} - D_{\mathrm{L}} k^2 - (\gamma - 1) A k^2 \ ,$$

where D_{L} is longitudinal viscosity, c_{∞} and c_s are the high-frequency and hydrodynamic speed of sound, respectively, and A is some constant dependent on the coupling between thermal and viscous processes. In figure 5 we show how the k^2

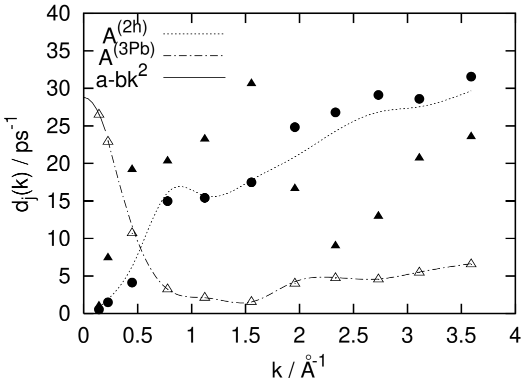

Figure 5. Purely real eigenvalues $d_j(k)$ in molten Li_4Pb corresponding to relaxation processes on different spatial scales. By dotted line is shown the lowest real eigenvalue obtained on the two-variable set $\mathbf{A}^{(2h)}$ for the treatment of heat fluctuations. The dash-dotted line represents the only real eigenvalue from the treatment of solely partial dynamics of the heavy subsystem by the set $\mathbf{A}^{(3\mathrm{Pb})}$.

dependence of $d_{\mathrm{str}}(k)$ matches the relaxing behaviour of a heavy subsystem. The existence of different relaxation processes in light and heavy subsystems is reflected by well pronounced minima in k-dependence of corresponding $d_j(k)$ at the positions of main maxima in partial static structure factors.

In a long-wavelengh region there exist two relaxing hydrodynamic processes: the mutual diffusion and thermal diffusion processes, which must have k^2 dependence. One can see how the relaxing process in the light subsystem of Li atoms (filled triangles) transforms into the mutual diffusion mode when $k \to 0$. Hence, we may conclude that in the disparate-mass molten alloy the mutual diffusion is connected, on the departure from hydrodynamic region, with the light subsystem, while the kinetic process of structural relaxation on the boundary of hydrodynamic region is defined mainly by the subsystem of large and heavy Pb atoms.

3.4. Generalized k-dependent transport coefficients in molten Li_4Pb

The approach of GCM makes it possible to generalize transport coefficients of a liquid onto different spatial and time scales which are reflected in (k, ω)-dependence of the coefficients. For the case of a simple Lennard-Jones fluid, the generalized (k, ω)-dependent transport coefficients obtained within the GCM approach were reported in [20]. The case of binary and multicomponent fluids is much more complicated for the study of generalized transport coefficients. The simplest generalization of mutual diffusion coefficients $D(k, \omega)$ is mainly known in the literature, while even the standard Green-Kubo calculations of thermal conductivity λ or longitudinal viscosity η_{L} are extremely scarce for binary liquids. This is mainly connected

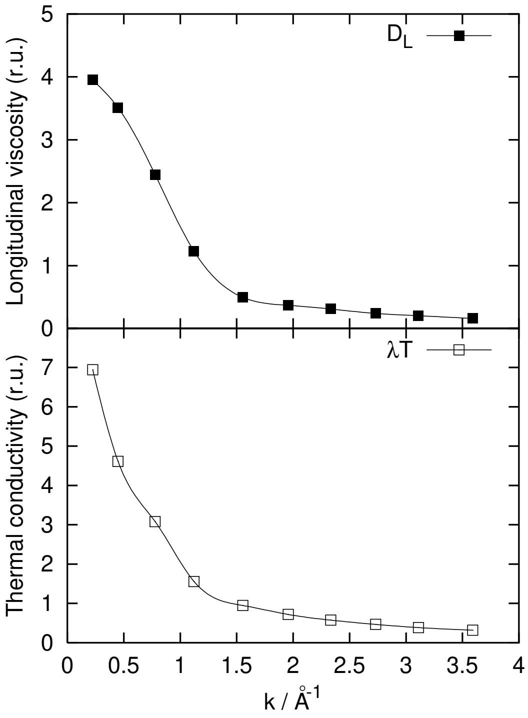

Figure 6. Generalized longitudinal viscosity $D_{\rm L}(k)$ and thermal conductivity $\lambda(k)T$ in molten Li_4Pb.

with the problems of unambiguous definition of generalized transport coefficients in multicomponent systems. The theory of generalized (k,ω)-dependent transport coefficients in multicomponent liquids based on GCM approach was developed in [12]. An advantage of N-variable approach in solving the system of N generalized transport equations was shown in [12] in the form of recurrence relations for the matrix of memory functions of different order. For the case of binary liquids, the final 4×4 hydrodynamic matrix of the lowest memory functions is directly connected with the generalized transport coefficients $\tilde{L}_{ij}(k,\omega)$:

$$\tilde{\phi}(k,\omega) = k^2 V k_{\rm B} T \tilde{\mathbf{L}}(k,\omega)\mathbf{F}(k,t=0)\ , \qquad (3)$$

where the hydrodynamic basis set of four dynamical variables used in defining the transport coefficients consists of two partial densities of particles $n_i(k,t),\ i=1,2,$ total longitudinal momentum density $J_t^{\rm L}(k,t)$ and heat density $h(k,t)$. As it was shown in [12], the matrix of hydrodynamic memory functions defines the following transport coefficients in the limit $\omega \to 0, k \to 0$: longitudinal viscosity $D_{\rm L} = \eta_{\rm L}/\rho$, thermal conductivity λ, mutual diffusion coefficients $D_{ij},\ i,j=1,2$ and thermal diffusion coefficients $K_i,\ i=1,2$. It is important to note that the diffusion and thermal diffusion coefficients derived in such a way within the GCM approach satisfy the following conditions that follow from the momentum conservation law [12]:

$$\sum_{i=1}^{2} m_i D_{ij}(k,\omega) = \sum_{j=1}^{2} D_{ij}(k,\omega) m_j \equiv 0$$

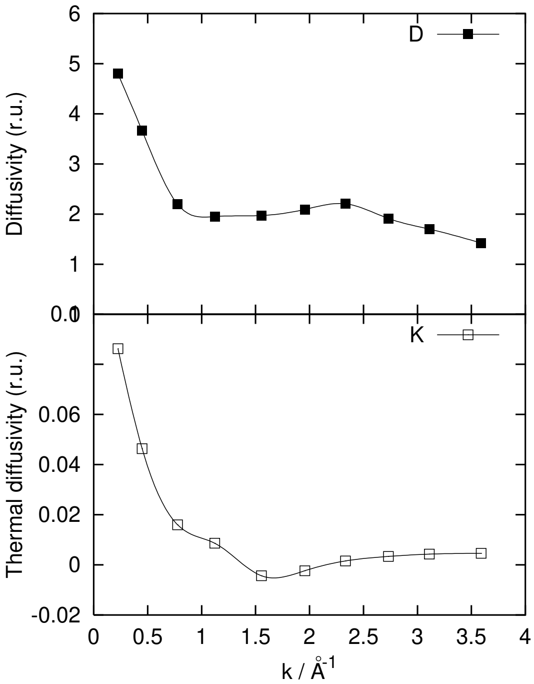

Figure 7. Generalized irreducible coefficients of mutual diffusivity D(k) and thermal diffusivity K(k) in molten Li_4Pb.

and

$$\sum_{i=1}^{2} m_i K_i(k,\omega) \equiv 0 \ .$$

In figures 6-8 we report generalized k-dependent transport coefficients for the disparate-mass metallic molten alloy Li_4Pb. The frequency dependence of generalized transport coefficients in Li_4Pb will be reported elsewhere. In figure 6 the k-dependent generalized longitudinal viscosity $D_{\rm L}(k)$ and thermal conductivity $\lambda(k)$ display similar behaviour. In the large-k region they behave almost like $\propto k^{-1}$, while in the long-wavelength limit, the behaviour resembling $D_{\rm L}(k) = D_{\rm L} - Ak^2$ is expected. The behaviour of wavenumber-dependent diffusion and thermal diffusion is more interesting. Note that in figure 7 we show the irreducible coefficients D(k) and K(k), which are connected to $D_{ij}(k)$ and $K_i(k)$ as follows:

$$D_{ij}(k) = (-1)^{(i+j)} \frac{\mathrm{D}(k)}{m_i m_j}, \qquad K_i(k) = (-1)^{(i+1)} \frac{\mathrm{K}(k)}{m_i} \ .$$

The striking difference of both irreducible transport coefficients from the k-dependence of longitudinal viscosity $D_{\rm L}(k)$ and from thermal conductivity $\lambda(k)$ is the nonmonotonic behaviour in the region of intermediate wavenumbers 0.7 Å$^{-1} < k <$ 3 Å^{-1}, where we observe a maximum at $k \approx 2.3$ Å^{-1} for generalized diffusivity D(k) and a minimum for generalized thermal diffusivity K(k) at $k \approx 1.6$ Å^{-1}. These both features imply the effects of the light Li subsystem on the mutual diffusion and of the heavy Pb subsystem onto the thermal diffusivity on different spatial scales.

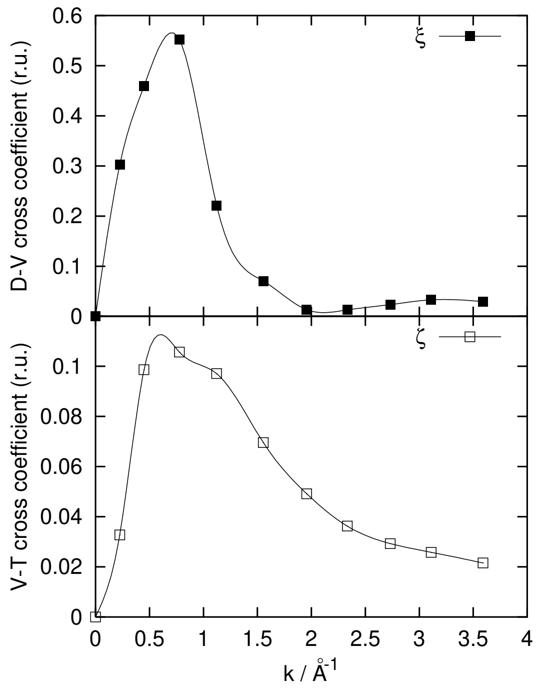

Figure 8. Purely imaginary generalized cross-correlation transport coefficients: cross diffusivity-viscosity coefficient $\xi(k)$ and cross viscosity-heat coefficient $\zeta(k)$ in molten Li_4Pb.

The approach of GCM permits to introduce additional transport coefficients for the case of binary liquids, which for the static case $\omega = 0$ are purely imaginary numbers and describe the dynamical cross-correlations in diffusivity-viscosity $\xi(k)$ and in viscosity-heat $\zeta(k)$ transport properties. Imaginary parts of these cross-coefficients are shown in figure 8. Note that in the $k \to 0$ limit both cross-coefficients should vanish. The behaviour of their k-dependence in a small-wavenumber region shows the right tendency. Both transport cross-coefficients display a well pronounced maximum in their k-dependence at $k \approx 0.6 - 0.7$ Å^{-1} which indicates very strong cross-correlations between microscopic processes describing diffusivity, viscosity and heat transport. Another characteristic is observed on the k-dependence of $\xi(k)$ cross-coefficients which may be connected with the characteristic in mutual diffusivity $\mathrm{D}(k)$ due to the light Li subsystem. We would like to stress that the coefficient $\xi(k)$ does not have an analogy in the case of pure liquids, where only cross-correlation between viscosity and heat transport can be represented via an additional transport coefficient $\zeta(k)$ [20].

4. Conclusions

In this study we focused on the calculations of the spectrum of collective excitations and generalized k-dependent transport coefficients in the disparate-mass metallic molten alloy Li_4Pb using a combination of molecular dynamics simulations and analytical eight-variable generalized collective modes approach. The main conclusions of this study are as follows. Our analytical analysis of different time correlation functions and the obtained dispersion curves for the propagating collective excitations permit us to conclude that in the region $k \approx 0.25$ Å^{-1} there exists a crossover from the "partial" picture of collective dynamics in terms of light and heavy subsystems to the "intrinsic collective" behaviour of the liquid alloy for $k < 0.25$ Å^{-1}. In this long-wavelength limit, two branches of propagating excitations assume the specific features of hydrodynamic sound (low-frequency branch) and optic-like (high-frequency) branch. The damping of high-frequency optic-like branch in a long-wavelength region is much higher than that of hydrodynamic sound excitations, which does not permit one to see the high-frequency excitations as a well-defined maximum on relevant spectral functions on the background of the contribution coming from the hydrodynamic sound. This is perhaps the main reason why the numerical approaches of spectrum estimation reported in [5,6] resulted in a merger of two high- and low-frequency branches in the long-wavelength region. In the case of disparate-mass metallic alloy, the relaxation processes distinctly show a "partial" origin in the region of intermediate wavenumbers, where the structural relaxation can be represented as a combination of relaxations in the light and heavy subsystems in contrast to our recent results for a Lennard-Jones liquid mixture [19], where "intrinsic collective" character of structural relaxation was observed. For the first time we have calculated the generalized k-dependent transport coefficients in molten Li_4Pb. The results show an interesting effect of light and heavy subsystems onto the generalized mutual diffusivity and thermal diffusivity. We also showed for the first time how the cross-correlation transport coefficients behave on different spatial scales in the disparate-mass metallic molten alloy.

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Колективні збудження та узагальнені коефіцієнти переносу в розплавленому металічному сплаві Li_4Pb

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Колективна динаміка в розплавленому металічному сплаві Li_4Pb досліджується комбінацією аналітичного багатозмінного підходу узагальнених колективних мод та комп'ютерних симуляцій методом молекулярної динаміки. Дисперсія та загасання двох віток пропагаторних колективних збуджень аналізується в широкій області хвильових чисел. Обговорюються особливості колективної динаміки, пов'язані з великою різницею у масах компонент сплаву. Подано узагальнені k-залежні коефіцієнти переносу для Li_4Pb.

Ключові слова: *колективна динаміка, бінарна рідина, колективні збудження, узагальнені коефіцієнти переносу*

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