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Collective excitations in dynamics of liquids: a «toy» dynamical model for binary mixtures

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We propose a new «toy» dynamical model that permits us to derive analytical expressions for dispersion of two branches of «bare» propagating collective excitations in binary disordered systems in the whole range of wavenumbers. These expressions are used for the analysis of dependence of dispersion curves on mass ratio and concentration at fixed density of the system. An effect of hybridization of two branches is discussed in terms of mode contributions to time correlation functions. This allows us to estimate the regions with dominant types of coherent or partial dynamics.

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1. Introduction

Neutron and x-ray scattering experiments [1,2] are main experimental techniques that along with molecular dynamics (MD) simulations are intensively used for exploration of dynamical processes of crystals, glasses and liquids. With a subsequent use of mainly oversimplified models like damped harmonic oscillator (DHO) the experimental and MD data on spectral functions can be used for estimation of dispersion law and damping of collective excitations. Collective excitations in liquids and glass-forming systems are extremely difficult for theoretical treatment, when the system is considered on spatial and time scales comparable with specific atomic scales, i.e beyond the hydrodynamic description of the system as a continuum media. Therefore any analytical results that can shed light on dispersion law of propagating modes in disordered systems are of great interest. For binary systems the situation is even more sophisticated — in some studies [3,4] it was stressed, that for binary liquids there exist regions of wavenumbers with different types of collective dynamics: «coherent» type in long-wavelength region and «partial» one in the region of intermediate and large wavenumbers. The existence of two types of collective dynamics follows from the shape of current spectral functions $C^{L,T}_{\alpha\alpha}(k,\omega)$ with sub-index α representing either total mass current t, or mass-concentration current x, or partial currents A, B. It appears [3,4], that in long-wavelength region the spectral functions $C_{tt}(k,\omega)$ and $C_{xx}(k,\omega)$ represent two distinct collective excitations, while $C_{AA}(k,\omega)$ and $C_{BB}(k,\omega)$ are very similar and usually have a single-peak shape.

In this study we will focus on a theoretical treatment of dispersion law for two types of propagating collective excitations in binary liquids. The current status of theory in this field is far from being satisfactory. Up to the date there do not exist *analytica1* solutions for theoretical models with simultaneous treatment of two branches of collective excitations — only numerical calculations within the GCM approach [4], memory function formalism [5,6] and numerical analysis of MD data [3,7,8] were reported for dispersion and damping of two branches of collective excitations in binary liquids and glasses. The problems in theoretical treatment are connected with different origin of the two branches of collective excitations:

hydrodynamic acoustic excitations and kinetic high-frequency excitations. The absence of consistent analytical solutions for the two branches of collective excitations causes many confusions in analysis of MD or experimental data — hence there were reports of existence of exotic «fast sound» excitations [9] or a hypothetical merger of dispersion laws of two branches of collective excitations into a hydrodynamic sound branch by approaching the hydrodynamic region [10–12]. All these results were based on some assumptions of absence of coupling between the two types of collective modes and did not take into account different asymptotics in long-wavelength region of contributions from low- and high-frequency excitations, because of absence of relevant analytical results, which would be a basis for analysis of experimental and MD data.

There exist in the literature analytical results for a separated treatment of high-frequency collective excitations in binary liquids. Based on a three-variable dynamical model of mass-concentration fluctuations [13] and two-variable dynamical model of transverse mass-concentration current fluctuations [4] it was revealed some mechanisms of damping of optic-like excitations in liquids. In comparison with the hydrodynamic relaxation process of mutual diffusion the contribution from optic-like excitations to the mass-concentration time autocorrelation function contained a pre-factor k^2 and in long-wavelength limit such a time correlation function was in complete agreement with hydrodynamic expression [14].

However, the separated treatment of low- or high-frequency branches in long-wavelength limit cannot explain many features of dynamics of binary liquids, in particular a crossover from «coherent» to «partial» types of collective dynamics by increasing of wavenumbers from hydrodynamic region towards the Gaussian regime. Therefore, the main aim of this study is to propose a simple toy dynamical model, which would permit simultaneous analysis of two branches of collective excitations. This allows us to derive analytical expressions for dispersion laws, to use them for the study of systems with different mass ratio and composition, and to analyze on such a basis the crossover from «coherent» to «partial» types of dynamics in dependence on mass ratio of components.

The paper is organized as follows: in the next Section we discuss our choice of dynamical model and construct a generalized kinetic matrix needed for subsequent calculations. In Sec. 3 both analytical and numerical results for dispersion laws of two branches of propagating collective excitations are presented and the mass-ratio and concentration dependence of dispersion curves is discussed. Conclusions of this study are collected in the last Section.

2. Elastic four-variable model for binary disordered systems

2.1. General definitions

Collective dynamics of binary liquids in a wide range of wavenumbers is much less studied that in the case of pure single-component fluids. Partially this is connected with a fact, that hydrodynamic expressions [15] cannot be applied for the analysis of MD simulation results, which clearly indicate the presence of two branches of collective excitations [4,7]. In order to match hydrodynamic and MD results Bosse and coauthors [9] proposed existence of a «fast sound» excitations with a linear dispersion law in long-wavelength limit, but with propagation speed in several times higher than for the hydrodynamic acoustic excitations. Here we are studying the collective propagating excitations in binary liquids within an approach of generalized collective modes, based on an eigenmode analysis of collective processes in a wide region of spatial and temporal scales.

Let us consider a binary liquid as a mixture of N_A particles with a mass m_A and N_B particles with mass m_B, $N_A + N_B = N$, which are confined in a volume V and interacting via two-body potentials $\Phi_{\alpha\beta}(r_{ij})$, $\alpha,\beta = A, B$. Instantaneous positions and velocities of particles $\mathbf{r}_{i,\alpha}(t)$ and $\mathbf{v}_{i,\alpha}(t)$ have additional species subindex α. Dynamical variables of partial densities of particles, defined as

$$n_\alpha(k,t) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N_\alpha} \exp(i\mathbf{k}\mathbf{r}_{i,\alpha}(t)), \quad \alpha = A, B, \tag{1}$$

are connected by continuity equations with longitudinal components of partial mass-current densities:

$$\frac{dn_\alpha(k,t)}{dt} = \frac{ik}{m_\alpha} J^L_\alpha(k,t), \quad \alpha = A, B,$$

where

$$J^L_\alpha(k,t) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N_\alpha} m_\alpha \frac{\mathbf{k}\mathbf{v}_{i,\alpha}}{k} \exp(i\mathbf{k}\mathbf{r}_{i,\alpha}(t)), \ \alpha = A, B \tag{2}$$

are the longitudinal components of partial mass-currents.

The hydrodynamic set of variables $\mathbf{A}^{(4\mathrm{hyd})}(k,t)$ for binary liquids contains along with total density, total longitudinal current and heat density also an additional dynamical variable $n_c(k,t)$ in comparison with the case of simple fluids,

$$n_c(k,t) = c_B n_A(k,t) - c_A n_B(k,t), \tag{3}$$

that describes the concentration fluctuations in the mixture and is expressed via partial densities (1), so that

$$\mathbf{A}^{(4\mathrm{hyd})}(k,t) = \{n_t(k,t), n_c(k,t), J^L_t(k,t), h(k,t)\}. \tag{4}$$

Analytical expressions for time correlation functions and dynamical structure factors of binary liquids valid in the hydrodynamic limit were obtained in [15,16]. An important feature of binary liquids in hydrodynamic limit is a purely relaxation behavior of time autocorrelation functions of concentration density, that corresponds to absence of any side peaks on the shape of concentration dynamical structure factor $S_{cc}(k,\omega)$, i.e. hydrodynamic approach points out the absence of effects of propagating modes on concentration fluctuations.

A simplest extension of the hydrodynamic model for binary liquids $\mathbf{A}^{(4\mathrm{hyd})}(k,t)$ within the GCM approach is a seven-variable dynamical model (1), that contains among basis variables the first time derivatives of hydrodynamic variables:

$$\mathbf{A}^{(7)}(k,t)= \\ =\{n_t(k,t), n_c(k,t), J_t^L(k,t), h(k,t), J_c^L(k,t), \dot{J}_t^L(k,t), \dot{h}(k,t)\}. \quad (5)$$

Note, that this model takes into account fast longitudinal current fluctuations only via the first time derivative of total current fluctuations. However, one can consider more general dynamical model, that allows us to treat both species on the same footing and therefore it requires the same order of time derivatives of partial currents

$$\mathbf{A}^{(8)}(k,t)=\{n_A(k,t), n_B(k,t), J_A^L(k,t), J_B^L(k,t), h(k,t), \\ \dot{J}_A^L(k,t), \dot{J}_B^L(k,t), \dot{h}(k,t)\}. \quad (6)$$

If the coupling with the thermal fluctuations could be neglected one derives from the eight-variable dynamical model (6) a viscoelastic model [5] of binary liquids

$$\mathbf{A}^{(6)}(k,t)= \\ =\{n_A(k,t), n_B(k,t), J_A^L(k,t), J_B^L(k,t), \dot{J}_A^L(k,t), \dot{J}_B^L(k,t)\}, \quad (7)$$

in framework of which one can correctly treat cross-correlations between partial dynamical variables.

2.2. Elastic approximation

The eight-variable generalized hydrodynamic (6) and six-variable viscoelastic (7) dynamical models are still too complicate for an analytical analysis. That is why we consider a simplified model of collective dynamics in a binary liquid, that can be called «elastic» one because it does not take into account explicitly the slow thermal and mutual diffusion processes in liquid, however microscopic quantities connected with the forces acting on particles (and therefore reflecting elastic properties) are present in this model. In this case the basis set of dynamical variables for longitudinal dynamics includes four variables

$$\mathbf{A}^{(4)}(k,t)=\left\{J_\alpha^L(k,t), J_\beta^L(k,t), \dot{J}_\alpha^L(k,t), \dot{J}_\beta^L(k,t)\right\}, \quad (8)$$

where the pair of indexes α,β corresponds to two orthogonal currents, so that $\langle \mathbf{J}_\alpha \mathbf{J}_\beta \rangle = 0$. In particular, it is convenient to consider as such pairs of orthogonal currents the partial mass currents

$$\mathbf{J}_\alpha = \frac{1}{\sqrt{N}} \sum_{i=1}^{N_\alpha} m_\alpha \mathbf{v}_{i,\alpha}(t) \exp(i\mathbf{k}r_{i,\alpha}(t)), \alpha = A, B, \quad (9)$$

or the linear combinations of partial currents that describe the total mass $\mathbf{J}_t(k,t)$ and mass-concentration $\mathbf{J}_x(k,t)$ currents and are simply related with the partial currents via relation

$$\begin{pmatrix} \mathbf{J}_x \\ \mathbf{J}_t \end{pmatrix} = \begin{pmatrix} x_B & -x_A \\ 1 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{J}_A \\ \mathbf{J}_B \end{pmatrix}, \quad (10)$$

where $x_\alpha = m_\alpha N_\alpha / M$ is a mass-concentration, and $M = m_A N_A + m_B N_B = \overline{m} N$. Since $x_A + x_B = 1$, the determinant of transformation matrix to new variables $\{\mathbf{J}_t, \mathbf{J}_x\}$ is equal to unity.

The basis set of four variables (8) contains only the dynamical variables connected with faster processes, which are defined by velocities and accelerations of particles, that makes close analogy with the treatment of phonon excitations in solids, where acceleration of particles is defined by effective elastic interactions.

Let us construct a generalized kinetic matrix $\mathbf{T}^{(4)}(k)$, constructed on the basis set $\mathbf{A}^{(4)}(k,t)$ for particular pairs of currents $\{A,B\}$ and $\{T,X\}$ introduced above. The matrices of static correlation functions $\mathbf{F}(k,t=0)$ and zeroth Laplace-component of time correlation functions $\tilde{\mathbf{F}}(k,z=0)$ have the following form:

$$\mathbf{F}(k,t=0) = \begin{pmatrix} f_{J_\alpha J_\alpha} & 0 & 0 & 0 \\ 0 & f_{J_\beta J_\beta} & 0 & 0 \\ 0 & 0 & f_{\dot{J}_\alpha \dot{J}_\alpha} & f_{\dot{J}_\alpha \dot{J}_\beta} \\ 0 & 0 & f_{\dot{J}_\beta \dot{J}_\alpha} & f_{\dot{J}_\beta \dot{J}_\beta} \end{pmatrix} \quad (11)$$

and

$$\tilde{\mathbf{F}}(k,z=0) = \begin{pmatrix} 0 & 0 & f_{J_\alpha J_\alpha} & 0 \\ 0 & 0 & 0 & f_{J_\beta J_\beta} \\ -f_{J_\alpha J_\alpha} & 0 & 0 & 0 \\ 0 & -f_{J_\beta J_\beta} & 0 & 0 \end{pmatrix}. \quad (12)$$

By the definition [18,19] the generalized kinetic matrix can be obtained via expression

$$\mathbf{T}^{(4)}(k) = \mathbf{F}(k,t=0)\tilde{\mathbf{F}}^{-1}(k,z=0),$$

so that one has

$$\mathbf{T}^{(4)}(k)=\begin{pmatrix}0 & 0 & -1 & 0\\ 0 & 0 & 0 & -1\\ T_{31}(k) & T_{32}(k) & 0 & 0\\ T_{41}(k) & T_{42}(k) & 0 & 0\end{pmatrix}, \qquad (13)$$

with the matrix elements

$$T_{31}(k)=\frac{f_{\dot{J}_\alpha \dot{J}_\alpha}}{f_{J_\alpha J_\alpha}}, \quad T_{32}(k)=\frac{f_{\dot{J}_\alpha \dot{J}_\beta}}{f_{J_\beta J_\beta}}, \quad T_{41}(k)=\frac{f_{\dot{J}_\beta \dot{J}_\alpha}}{f_{J_\alpha J_\alpha}},$$

$$T_{42}(k)=\frac{f_{\dot{J}_\beta \dot{J}_\beta}}{f_{J_\beta J_\beta}}.$$

The structure of $\mathbf{T}^{(4)}(k)$ is rather simple for an analytical treatment.

3. Results and discussion

3.1. Dispersion laws

For the generalized kinetic matrix (13) it is straightforward to obtain the dynamical eigenmodes, which can propagate in the system:

$$z_1^0=\pm i\left[\frac{1}{2}(T_{31}+T_{42})-\frac{1}{2}\sqrt{(T_{31}-T_{42})^2+4T_{32}T_{41}}\right]^{\frac{1}{2}}\equiv$$

$$\equiv \pm i\omega_1^0(k),$$

$$z_2^0=\pm i\left[\frac{1}{2}(T_{31}+T_{42})+\frac{1}{2}\sqrt{(T_{31}-T_{42})^2+4T_{32}T_{41}}\right]^{\frac{1}{2}}\equiv$$

$$\equiv \pm i\omega_2^0(k). \qquad (14)$$

Note that these eigenvalues are purely imaginary, because all the dissipation mechanisms are neglected in the adopted elastic approximation. For instance, nonzero damping coefficients (real parts of eigenvalues) can appear if one includes in addition the coupling of these «bare» propagating modes with slow relaxation processes in liquids, being connected with structural disorder.

The expressions (14) describe the dispersion of two branches of collective excitations and can be used for both cases of orthogonal currents considered, namely for the partial $\{A,B\}$ and total with mass-concentration $\{T,X\}$. It is also important that in the whole range of wavenumbers such a «toy» dynamical model takes into account in appropriate way the effects of cross-correlations between two propagating processes. Let us consider now in more detail the k-dependence of frequencies (14). To do so we need to know the explicit dependence of the matrix elements $T_{31}(k)$, $T_{32}(k)$, $T_{41}(k)$, $T_{42}(k)$ on wavenumber k. By the definition for small k one has

$$\frac{\langle \dot{J}_t^L \dot{J}_t^L\rangle}{\langle J_t^L J_t^L\rangle}\Big|_{k\to 0}\simeq c_\infty^2 k^2, \qquad (15)$$

where c_∞ is a high-frequency sound velocity. The static cross-correlations $\langle \dot{J}_t^L \dot{J}_x^L\rangle$ are also functions of k^2 in the limit $k\to 0$, while the matrix element $T_{42}(k)$ defined on the pair of orthogonal currents $\{T,X\}$, tends [20] in long-wavelength limit to a nonzero value ω_0^2 that has a sense of square of «bare» frequency for optic-like excitations [13]. Let us look at the behavior of eigenvalues $z_1(k)$ and $z_2(k)$ when $k\to 0$ retaining under the square root terms within the precision $O(k^2)$. One gets for small k the expressions:

$$z_1^0\simeq \pm ic_\infty k, \quad z_2^0\simeq \pm i\omega_0. \qquad (16)$$

This means that in the hydrodynamic limit the elastic approximation leads to two propagating collective modes with different dispersion laws, namely: one branch of collective excitations has the linear dispersion law with a coefficient being the high-frequency (elastic) speed of sound and the second branch describes the propagating optic-like modes with finite frequency.

In the opposite limit $k\to\infty$ the cross-correlations between the partial currents in different species can be neglected and one has from (14) the following solutions:

$$z_1^0=\pm i\left[\frac{\langle \dot{J}_A^L \dot{J}_A^L\rangle}{\langle J_A^L J_A^L\rangle}\right]^{1/2}=\pm i\omega_1^0(k),$$

$$z_2^0=\pm i\left[\frac{\langle \dot{J}_B^L \dot{J}_B^L\rangle}{\langle J_B^L J_B^L\rangle}\right]^{1/2}=\pm i\omega_2^0(k), \qquad (17)$$

i.e. two branches in the limit $k\to\infty$ reflect the dynamics of non-interacting partial densities. One can estimate the mutual location of two branches in the limit $k\to\infty$. From expressions for ratio of fourth and second frequency moments [1,20] it follows, that in this limit

$$\frac{\langle \dot{J}_i^L \dot{J}_i^L\rangle}{\langle J_i^L J_i^L\rangle}\simeq \frac{3k_BT}{m_i}k^2, \quad i=A,B. \qquad (18)$$

so that the ratio of «bare» frequencies is given by

$$\frac{\omega_1^0(k)}{\omega_2^0(k)}\simeq\left[\frac{m_B}{m_A}\right]^{1/2}, \qquad (19)$$

and is the same as the ratio of phonon frequencies of optic and acoustic branches at the first Brillouin zone boundary in binary A–B crystals within a harmonic approximation. The high-frequency branch corresponds to a light particles in the liquid mixture and low-frequency one to the heavy particles.

The elastic approximation has several advantages. First of all, it allows us to estimate the role of coupling to

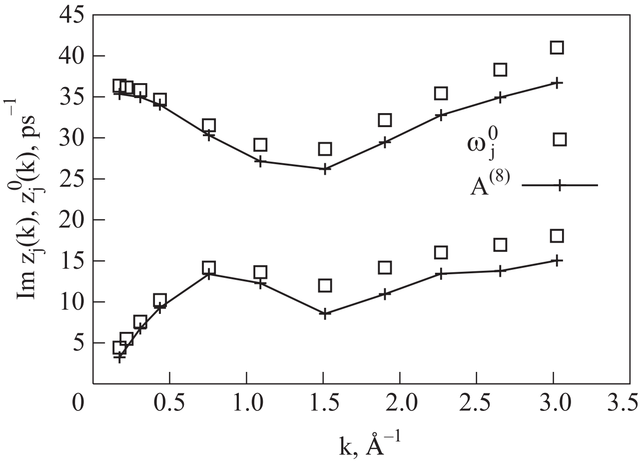

Fig. 1. Imaginary parts (dispersion) of propagating eigenmodes, obtained by the 8-variable treatment of collective dynamics in molten NaI at T = 1080 K (symbols «+» connected by interpolation line) and as analytical solutions (14) within the «elastic» four-variable model (open boxes).

the relaxation processes in different regions of wavenumbers. Second, the analytical expressions obtained are valid in the whole region of wavenumbers, i.e. the «bare» frequencies (14) include already the hybridization effects between the both branches. Third, as a toy model, the elastic approximation can be applied for understanding the tendencies of dispersion law formation in binary systems with different mass ratio of particles in both species.

Now the question arises how good is the elastic approximation in comparison with a complete picture of the collective dynamics of a binary liquid. In Fig. 1 the results of our study, performed within the generalized collective mode approach with the set of eight-variable (6), are presented for molten NaI at T = 1080 K. Eigenfrequencies, calculated within the full treatment of coupling with thermal fluctuations and other slow relaxation processes [21], are shown by symbols «+» connected by lines. Open boxes correspond to the actual analytic elastic approximation. One can see in Fig. 1 that in the whole range of wavenumbers considered the frequencies, obtained within the elastic approximation, have a little bit higher frequencies comparing to the result of full treatment, but correctly describe all the main features in the dispersion laws. This difference can be easily explained and is mainly caused by the coupling of «bare» propagating modes with relaxation processes that results usually to appearance of nonzero damping and reduction of the «bare» frequencies. It is also seen in Fig. 1 that in the region $k > 2.2$ Å^{-1} both branches behave almost linearly with k, and the ratio of their slopes for $k \to \infty$ can be evaluated as 2.57, while the square root of mass ratio $\sqrt{m_{\rm I} / m_{\rm Na}} = 2.35$, that supports the analytical result (19).

3.2. Dispersion laws: dependence on mass ratio and concentration

Let us consider the dependence of dispersion laws for both branches of propagating collective excitations on mass ratio of particles at constant mass-density of the system. In Fig. 2 we show results obtained for the dispersion laws of «bare» collective modes (14) for five systems with identical static properties. A single distinct parameter, used in our calculations, was the mass ratio R that is responsible for solely dynamic response of the system. Lennard–Jones systems with different R were sampled in our previous molecular dynamics study [22], here we use only relevant static averages $T_{ij}(k)$, calculated directly in molecular dynamics simulations. Our task now is to use the analytical model developed for the explanation of the general tendencies in spectra behavior when the mass ratio R is changed.

For the short-wavelength limit we can immediately use the expressions (18) and (19), showing that the frequencies are inversely proportional to the masses and the ratio of frequencies scales as $R^{-1/2}$, where $R = m_h / m_l$, and m_h, m_l are masses of heavy and light atoms, respectively.

In the long-wavelength region one can see in Fig. 3, that the square of «bare» frequency of optic-like excitations $\omega^2_{J_xJ_x}(k)$ is a linear function of R, while the square of «bare» frequency of acoustic-like excitations $\omega^2_{J_tJ_t}(k)$ is independent on R, because it depends only on total density of the system. Now, let us look at the cross-correlation effects between low- and high-frequency branches in long-wavelength region as a function of R. Such a cross-correlation is reflected by the ratio

$$\omega^2_{J_xJ_t} = \frac{\langle \dot{J}_x(k)\dot{J}_t(-k)\rangle}{\langle J_x(k)J_x(-k)\rangle},$$

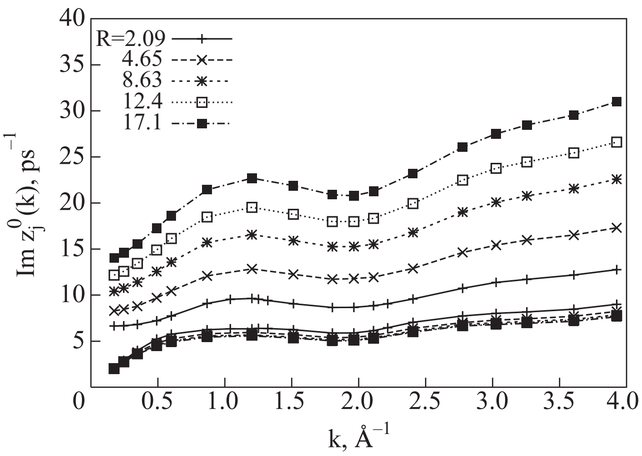

Fig. 2. Frequencies of «bare» propagating collective modes in dependence on the mass ratio R for Lennard–Jones equimolar systems with identical mass-density [22]. The dispersion lines, corresponding to the same mass ratio, are shown by the same line-connected symbols.

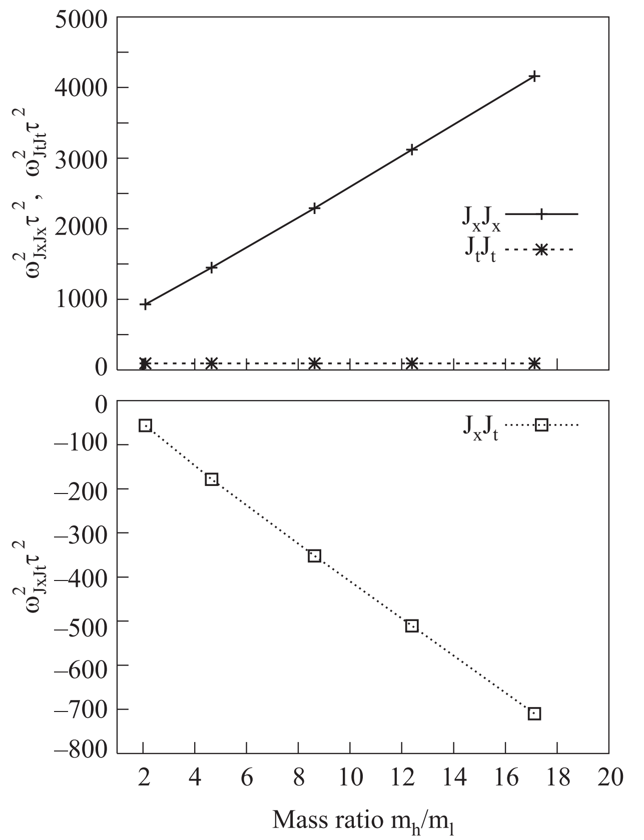

Fig. 3. Dependence of matrix elements of generalized kinetic matrix on the mass ratio for small wavenumbers. The mass ratio values were sampled for the same systems as in previous Figure.

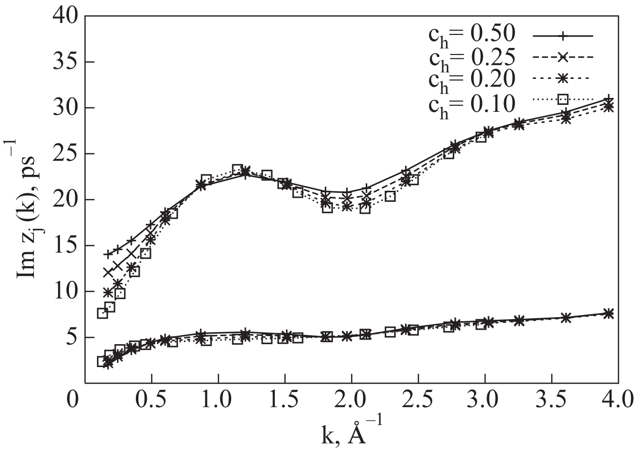

Fig. 4. Frequencies of «bare» propagating collective modes in dependence on the composition for Lennard–Jones systems with the same density for the mass ratio $R = 17.1$. Dispersion lines, corresponding to the same concentration, are shown by the same line-connected symbols. Labels c_h denote the molar concentration of heavy component.

which is shown in the lower frame of Fig. 3 and decrease linearly with increasing of R. Since $\omega^2_{J_tJ_t}(k)$ and $\omega^2_{J_xJ_t}(k)$ are functions of k^2 and $\omega^2_{J_xJ_x}(k)$ tends to a constant in small k limit, one can rewrite the expressions (14) for «bare» frequencies as follows

$$z_1^0(k) \approx \pm i \left[\omega^2_{J_tJ_t}(k) - \frac{\omega^2_{J_tJ_x}(k)\omega^2_{J_xJ_t}(k)}{\omega^2_{J_xJ_x}(k)} \right]^{1/2},$$

$$z_2^0(k) \approx \pm i \left[\omega^2_{J_xJ_x}(k) + \frac{\omega^2_{J_tJ_x}(k)\omega^2_{J_xJ_t}(k)}{\omega^2_{J_xJ_x}(k)} \right]^{1/2}. \qquad (20)$$

It is seen, that due to the coupling with acoustic branch the square of «bare» frequency of optic-like modes gets positive correction $\sim k^4$, which is proportional to the mass ratio R. Similar correction, but with opposite sign gets the dispersion of acoustic-like branch. Hence, one may expect, that just beyond the hydrodynamic region in the systems with large R the high-frequency branch should have a «positive dispersion», while for the low-frequency branch a «negative dispersion» has to be observed. In Fig. 2 the dispersion curves, calculated for Lennard–Jones systems with identical static properties but different mass ratio R, are shown. At small wavenumbers one observes an increase of «bare» frequencies of optic excitations. It is seen also that the effects of «positive dispersion» become more pronounced in this case as it was predicted above. The low-frequency branch in complete agreement with the analytical treatment displays «negative dispersion» effects. For large wavenumbers the distance between two branches scales as $R^{1/2}$ in full agreement with our predictions. Note that the low-frequency branch shows a convergence tendency with R due to a constraint on the constant mass density of systems considered.

About the effect of concentration c_h of heavy particles on the «bare» frequencies one can conclude from Fig. 4. It is clearly observed a gradually shifting down of the high-frequency branch when the concentration c_h decreases. Moreover, the shape of this branch becomes more similar to the k-dependence of acoustic-like branch in small k domain.

3.3. Crossover from «coherent» to «partial» type of dynamics in binary liquids

There is still a lack in simple analytical theory, describing a crossover from «coherent» to «partial» dynamics in binary disordered systems [3,4], in particular in dependence on mass ratio R. Since our «toy» dynamical model is rather simple and quite correct in description of dispersion of two branches in the whole region of wavenumbers, let us consider the contributions from both «bare» excitations to different current-current time correlation functions within the model proposed.

Since the «bare» excitations represent free oscillations in the system, it seems that their contributions to different spectral functions do not have much sense, because the damping effects are not taken into account. In the time-domain the corresponding diagonal current-current time correlation functions, found analytically within the elastic dynamical model for the set $\mathbf{A}^{(4)}(k,t)$, have the form:

$$F_{J_\alpha J_\alpha}(k,t)/F_{J_\alpha J_\alpha}(k,0)= \\ = B^1_{\alpha\alpha}(k)\cos\{\omega^0_1 t\} + B^2_{\alpha\alpha}(k)\cos\{\omega^0_2 t\}\,. \quad (21)$$

The pre-factors or mode amplitudes $B^j_{\alpha\beta}(k)$, describing the harmonic contributions, reflect all the hybridization effects between two branches of «bare» excitations and can be very helpful for understanding of crossover between «coherent» and «partial» regions of collective dynamics in real binary liquid systems [3,4]. These amplitudes correspond to solely symmetric contributions, defined in Ref. 23, and are given by the expressions:

$$B^1_{\alpha\alpha}(k)=\frac{(\omega^0_2)^2 - T^{\alpha\alpha}_{31}(k)}{(\omega^0_2)^2-(\omega^0_1)^2},\; B^2_{\alpha\alpha}(k)=\frac{T^{\alpha\alpha}_{31}(k)-(\omega^0_1)^2}{(\omega^0_2)^2-(\omega^0_1)^2}, \quad (22)$$

so that the sum of both amplitudes is equal to unity as it should be. The upper indices in the matrix elements $T^{\alpha\alpha}_{31}(k)$ correspond to the different choices of currents from the sets $\{A,B\}$ or $\{T,X\}$, used previously for estimation of the matrix element. For the case of a KrAr Lennard–Jones fluid with the mass ratio $R = 2.09$ the calculated values of both amplitudes, describing the mode contributions to the spectral functions $C_{tt}(k,\omega)$ and $C_{\text{ArAr}}(k,\omega)$, are shown in Figs. 5 and 6, respectively. One can see in Fig. 5 that in the long-wavelength region the contribution to the total current autocorrelation function comes completely from the low-frequency acoustic-like branch — its mode amplitude $B^l_{tt}(k)$ is almost equal to unity, while the contribution from the high-frequency branch is very small. For larger k the contributions from both branches become comparable (see Fig. 5). The same tendency was also observed for the mass-current autocorrelation function with the only difference, that in the long-wavelength region the high-frequency branch determines almost completely its shape. From the other side, an opposite situation is observed in the case of partial currents autocorrelation functions. For instance, as it is seen in Fig. 6, for the light subsystem (Ar particles) at $k > 0.5$ Å^{-1} this function can be reasonably described by the contribution from high-frequency branch only, and for $k > 2.5$ Å^{-1} this is exactly correct. Hence, the crossover from «coherent» to «partial» type of dynamics in binary disordered systems can be explained in terms of the mode contributions from «bare» eigenmodes of our «toy» elastic model. In order to rationalize the mass ratio of components affects the region of this crossover we show in Fig. 7 the amplitudes of all contributions $B^j_{\alpha\alpha}(k)$ with $\alpha = t, x, A, B$ calculated at two values of mass ratio $R = 2.09$ (solid lines) and $R = 17.1$ (dashed lines). It is seen that for the larger mass ratio the cross-point of amplitudes $B^h_{tt}(k_{\text{cross}}) = B^h_{AA}(k_{\text{cross}})$, where A denotes a light component of the mixture, is at the same wavenumber as the cross-point of the amplitudes $B^l_{tt}(k_{\text{cross}}) = B^l_{BB}(k_{\text{cross}})$ and in this case the value k_{cross} is smaller, than similar cross-point for the mass ratio $R = 2.09$. For $k > k_{\text{cross}}$ one can accept, that the «partial» type of collective dynamics prevails, while for $k < k_{\text{cross}}$ collective dynamics can be well decsribed in terms of acoustic- and optic-like «bare» collective excitations, representing the «coherent» type of dynamics [3,24]. Note also that for lager k, as it was shown above, the main mechanism responsible for mode formation is connected with the properties of partial currents (see (17)). Hence, we may use the condition for a

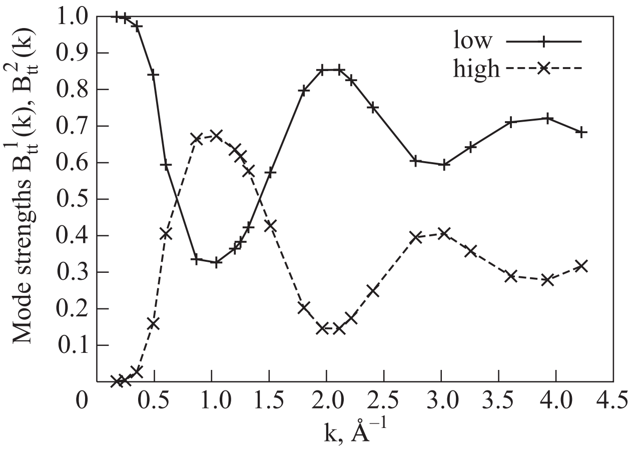

Fig. 5. Mode contributions from the low- and high-frequency branches of «bare» propagating collective modes to the spectral function $C_{tt}(k,\omega)$.

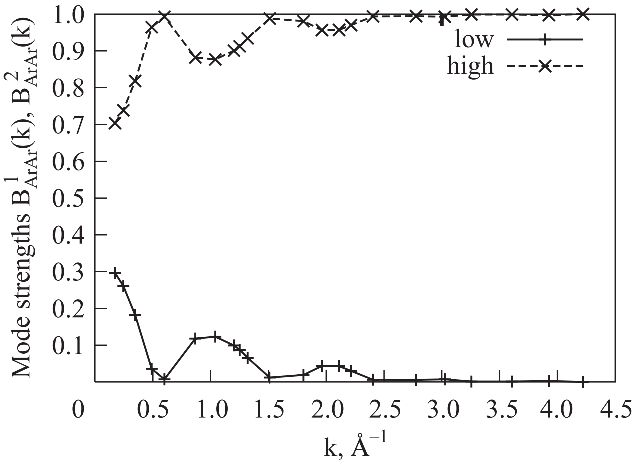

Fig. 6. Mode contributions from the low- and high-frequency branches of «bare» propagating collective modes to the spectral function $C_{\text{ArAr}}(k,\omega)$.

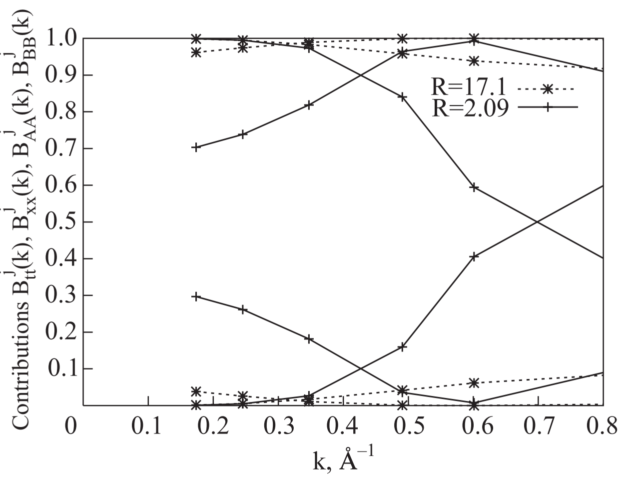

Fig. 7. Crossover region between the «coherent» and «partial» dynamics for two values of the mass ratio.

cross-point of corresponding mode amplitudes and to derive an analytical expression for k_{cross} taking into account the long-wavelength asymptotes of relevant frequency moments. One gets

$$k_{\text{cross}} = \sqrt{\frac{\omega^2_{J_xJ_x}(0)}{c^2_\infty - 2x_1 a_{tx}}}, \tag{23}$$

where x_1 is the mass-concentration of heavy particles and a_{tx} is a constant taken from long-wavelength asymptote of $\omega^2_{J_xJ_t}(k) \simeq a_{tx}k^2$. We have calculated the dependence of k_{cross} on the mass ratio, and the results are shown in Fig. 8. As it follows from Fig. 8, one can conclude that the region of «coherent» dynamics reduces with the increasing mass ratio R. Note, however, that k_{cross} tends to a nonzero value even in the limit $R \to \infty$, because of the constraint put on the total mass density of the systems considered in our study.

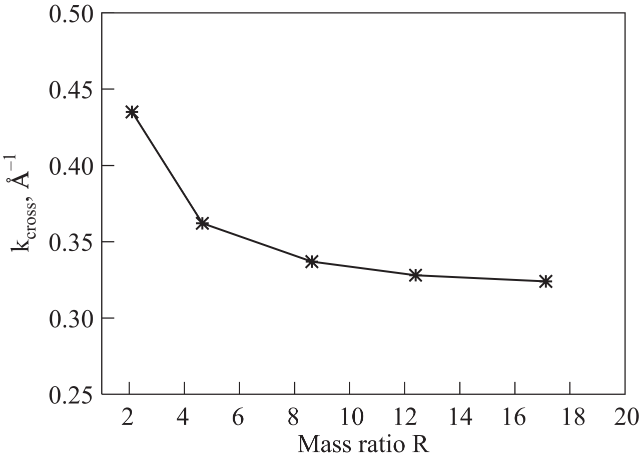

Fig. 8. Dependence of crossover region k_{cross} on the mass ratio R.

4. Conclusions

Within the generalized collective mode approach, for description of dispersion of propagating collective excitations in binary disordered systems, we have proposed and solved analytically in the whole range of wavenumbers a new four-variable «toy» dynamical model. The most important results obtained are the following:

(i) we have obtained analytical expressions for the «bare» frequencies of propagating collective excitations in binary systems that can be applied in the whole range of wavenumbers;

(ii) short-wavelength asymptote of the ratio of «bare» frequencies scales as square root of mass ratio, similarly as it is on the Brillouin zone boundary in a binary A–B crystal. In small k limit the «bare» low-frequency eigenvalues follow linear dispersion law $c_\infty k$ with a coefficient being high-frequency (elastic) sound velocity c_∞, while the high-frequency branch tends to a nonzero frequency ω_0 in complete analogy with optic-like phonon excitations in solids;

(iii) the proposed model allows us to describe the crossover from «coherent» to «partial» dynamics in binary liquids in terms of mode contributions to different current autocorrelation functions;

(iv) it is shown that the crossover region between the «coherent» and «partial» types of dynamics reduces when the mass ratio R of particles in different species increases. This supports, in particular, our recent numerical results [22].

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