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Generalized hydrodynamics of binary liquids: Transverse collective modes

Taras Bryk and Ihor Mryglod
Institute for Condensed Matter Physics, National Academy of Sciences of Ukraine, 1 Svientsitskii Street, UA-79011 Lviv, Ukraine

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The parameter-free generalized collective modes approach in eight-variable approximation is applied for investigation of transverse dynamics of Lennard-Jones liquid Kr-Ar beyond the hydrodynamic region. We find four branches of propagating eigenmodes in the spectrum of transverse collective excitations. Different basis sets of dynamical variables are applied to estimate the origin of different branches in the spectrum. It is shown that for large wave numbers the general feature of transverse collective excitations is their ''partial'' character, while in hydrodynamic limit they are formed by collective behavior of liquid. A detailed analysis of the separated contributions from different collective modes into time correlation functions and spectral functions is performed. The condition of existence of high-frequency mass-concentration waves is derived. It is shown that high-frequency collective excitations, caused by the mass-concentration fluctuations, reflect some properties of optic phonon modes in solids.

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I. INTRODUCTION

Over the last two decades the theory of dynamics in pure liquids has advanced at a rapid pace. With the active use of computer simulations and memory function theory the study of dynamics has progressed from a simple investigation of diffusion and dynamical structure factors to a sophisticated generalization of hydrodynamics, which takes into account short-time kinetic processes. For the dynamics of binary liquids the situation is quite different. Only the simplest dynamic properties such as self- diffusion and mutual diffusion are understood pretty well, while the mechanism of formation of collective excitations and their contributions into total spectral functions are not yet established.

The transverse dynamics of binary liquids is much less investigated even than the longitudinal one. Since transverse excitations are not visible in scattering experiments, only computer simulations can give some information about spectra of transverse modes. However, this information can be very valuable both for the interpretation of computer experiments and for understanding in more details the main specific features in the dynamics of a binary fluid, which appear due to the coupling between partial currents. The longitudinal dynamics is much more complicated because of additional coupling between the density and energy fluctuations. Nevertheless, one can expect that the results obtained for the transverse dynamics could also be useful for understanding some features of the longitudinal case.

In the last few years there were just a few reports [1–4] on transverse dynamics of binary liquid and amorphous systems, in which the problem of transverse excitations was considered. Typically, the spectra of transverse (as well as longitudinal) excitations are obtained from the analysis of Fourier-spectra of ''current-current'' time correlation functions (TCFs), so that the intuitive definition for collective modes prevails. Within such a scheme the dispersion and damping coefficient of particular modes are directly related to the position and width of corresponding maxima in partial or total ''current-current'' spectral functions (see also Ref. [5,6]). It is evident that such an approach is not satisfactory from the theoretical point of view and cannot be considered as a rigorous one. Hence, the first problem is to define collective modes in an appropriate way and to study their role in dynamics of fluids.

Within the generalized collective mode (GCM) approach, proposed originally in Ref. [7] and developed then in Ref. [8–10], the collective excitations in fluids are directly associated with eigenvalues of so-called generalized hydrodynamic matrix, which determines the time evolution of a system. Such a definition of collective modes is in agreement with the generally accepted principle of statistical physics, when collective modes are identified with the poles of corresponding Green function or generalized susceptibility. The GCM approach was developed with the purpose of theoretical analysis of TCFs obtained in molecular dynamics (MD). MD-derived functions contain in their shape the information about all possible long- and short-time processes in liquid (diffusivelike, propagating, and kinetic collective modes), and mode-coupling effects. The analysis based on hydrodynamic set of equations fails to explain the shape of MD functions, because such a method can only describe the most long-time processes in fluid. The GCM method, which is the most consistent approach of generalization of hydrodynamics, treats on the same footing the long- and short-time processes: the generalized Langevin equation for time correlation functions is solved in matrix form using the basis set of dynamical variables, which in addition to hydrodynamic variables contains their time derivatives. The time evolution of these ''extended'' variables, which describe processes of shorter time scale than hydrodynamic one, is obtained in computer experiments to evaluate relevant time correlation functions and static averages. In general, the basis set of N_v dynamical variables generates a $N_v \times N_v$ secular equation and results in N_v generalized collective modes (eigenvalues). Among N_v eigenvalues the lowest ones always correspond to the hydrodynamic modes, which have the right asymptotics at $k \rightarrow 0$ predicted by linear hydrodynamics. All other eigenvalues are called *kinetic* modes, which correspond to the processes of short-time scale and cannot be obtained within the standard hydrodynamic treatment.

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For transverse dynamics the GCM approach has been applied for the study of a simple Lennard-Jones liquid [8,11] and a liquid metallic Cs [12], where the collective mode spectra, time correlation functions and the generalized (k,ω)-dependent (k and ω being wave vector and frequency, respectively) shear viscosities were calculated. The obtained results within the Markovian approximation were in good agreement with molecular dynamics data over the whole range of wave numbers and frequencies considered. One of the main findings herein was the dispersion of the lowest branch of propagating modes, which was able to explain all the peculiarities of crossover from viscous to elastic behavior in simple fluids. The main feature of this crossover is the existence of propagating gap with the width depending on temperature. In Ref. [3] the temperature dependence of propagating gap was studied for a metallic binary glass-forming system $Mg_{70}Zn_{30}$.

Comparing the transverse dynamics of binary fluids with the case of a simple liquid one can expect some specific features due to the coupling of different components. In the hydrodynamic limit there is no qualitative difference in the time behavior of hydrodynamic ‘‘current-current’’ TCFs in the both cases. This is because the only conserved quantity is the density of total transverse current, so that the corresponding hydrodynamic equation has the same form. Hence, in hydrodynamic limit a binary liquid is treated as an effective ‘‘averaged’’ one-component fluid and all the specific features due to difference in species are then neglected. However, beyond the hydrodynamic region, for finite values of k and ω the transverse dynamics of a binary mixture can have its own specific properties, which are not observed in simple fluids. As an example we may refer to Brownian particles in a liquid, which can be considered as a binary mixture in the limit of very large mass ratio of heavy and light particles. Another specific feature in dynamics of a binary system has been observed in ionic fluids. In particular, in the dynamic ‘‘charge-charge’’ structure factor of liquid LiF (just above the melting point) it was found (besides the central peak, due to dissipative processes) two side peaks due to propagating charge waves, which were, in fact, opticlike high-frequency excitations. Moreover, it was found that the spectrum of phonon excitations for crystalline LiF at high temperatures correlates well with the data for liquid state, and the effect of melting is a comparatively minor one. However, in neutral binary liquids there was neither experimental nor theoretical information about the existence of opticlike excitations. Hence, we aimed in this paper to show how to take into account in a consistent way two kind of processes in the transverse dynamics: fluctuations of total transverse current and mass-concentration fluctuations. This will result in appearence of several branches in the spectrum of collective modes. Hence, another goal of this study is to investigate the origin of each branch of transverse collective excitations of binary liquids.

The paper is organized as follows. In Sec. II an application of the method of generalized collective modes to a Lennard-Jones liquid Kr-Ar is reported. We give the simplest analytical treatment of transverse mass-concentration fluctuations in Sec. III and Sec. IV contains conclusions of this study.

II. ANALYSIS OF TRANSVERSE DYNAMICS IN A BINARY LIQUID

We applied the parameter-free GCM approach to investigation of transverse time correlation functions and spectrum of transverse collective excitations of a Lennard-Jones equimolar Kr-Ar liquid at temperature $T=116$ K and density $n=0.0182$ Å^{-3} [13]. The standard molecular dynamics simulations within microcanonical ensemble for the system of 864 particles were performed over 3×10^5 time steps to obtain the time evolution of basis dynamical variables, relevant static averages and time correlation functions. Fourteen k points were considered. The smallest wave number reached in MD was $k_{\min}=0.1735$ Å^{-1}. For each k point the shape of MD-derived time correlation functions and the spectrum of eigenvalues were analyzed within the high-variable approach [10] of the GCM method. Although the main features of the spectrum of collective excitations can be reproduced within two-variable approximation, the high-variable basis set allows to obtain branches of high-frequency kinetic modes, which due to mode-coupling effects correct locations of low-frequency branches. It was shown in Ref. [10], that the nine-variable approximation for longitudinal dynamics of a simple liquid (first three time derivatives of hydrodynamic variables were taken into account) allowed to obtain relatively good converged low-frequency branches in spectrum of collective excitations. The situation with dynamical eigenvalues in the GCM method is quite similar with the standard electronic structure methods, when the more orthogonal basis functions are taken in expansion of wave functions, the better converged are the energies of lower bands. The following energy, mass, spatial and time scales were used to reduce the dimension of relevant quantities: $\varepsilon=k_BT$, $\mu=\overline{m}$, $\sigma=k_{\min}^{-1}$, $\tau=\sigma(\mu/\varepsilon)^{1/2}=4.598$ ps.

A. Time correlation functions

The standard hydrodynamic treatment of transverse dynamics [14] of binary liquids is based on the only dynamical variable $J_t(k)$

$$J_t(k)=J_1(k)+J_2(k)=\frac{1}{\sqrt{N}}\sum_{\alpha=1}^{2}\sum_{i=1}^{N_\alpha} m_\alpha v_{\alpha i}^{t}\exp(i\mathbf{k}\cdot\mathbf{r}_{\alpha i}), \tag{1}$$

where $J_t(k)$ is the total transverse current operator, $N=N_1+N_2$ is the total number of particles and $\mathbf{r}_{\alpha i}$, $v_{\alpha i}^{t}$ denote a position and a transverse component of velocity of the ith particle in the αth species. In that approach the single-exponential expression is obtained for transverse ‘‘current-current’’ time correlation function $F_{JJ}^{(t)}(k,t)$ [15,14]

$$F_{JJ}^{(t)}(k,t)\simeq\frac{M}{N}k_BT\exp\{-\eta k^2t/\rho\}=\overline{m}k_BT\exp\{-t/\tau_{JJ}^{h}\}, \tag{2}$$

where $\rho=M/V$ and η are a mass density and shear viscosity, respectively. Note that $M=\overline{m}N=m_1N_1+m_2N_2$. This result is valid within the precision of zeroth frequency moment and can be applied in long length limit for simple fluids as well as their mixtures. Hence, in this limit a binary liquid is treated as an effective ''averaged'' one-component fluid and all the specific features due to difference in species are then neglected.

We start from the definition of a dynamical variable, which is the complementary one to the total current operator (1). Such a variable is the transverse mutual mass-concentration current $J_x(k)$, which is also the linear combination of partial currents $J_1(k)$ and $J_2(k)$:

$$J_x(k)=x_2J_1(k)-x_1J_2(k), \tag{3}$$

where $x_\alpha=m_\alpha N_\alpha/N\overline{m}=m_\alpha c_\alpha/\overline{m}$ are the mass concentrations $x_1+x_2=1$. Note that the dynamic variable $J_x(k)$ is orthogonal to the transverse total current $J_t(k)$ in the sense of thermodynamic theory of fluctuations. This means that $F_{xt}(k)=F_{tx}(k)=0$. It should be mentioned also that at $k=0$ the variable $J_x(k)$ describes, in fact, the opposite motion of particles of different species. Another important point is, that the mutual diffusion coefficient D_{12} (see, e.g., Ref. [16]) is directly related to the function $F_{xx}(k,t)$ at $k=0$

$$D_{12}=\frac{1}{\overline{m}S_{xx}(0)}\int_0^\infty F_{xx}(0,t)\ \ dt, \tag{4}$$

where $S_{xx}(0)$ is the value of the ''mass concentration-mass concentration'' static structure factor $S_{xx}(k)$ [17] at $k=0$.

Thus, we are interested in three transverse time correlation functions. (i) Total current autocorrelation function:

$$F_{tt}(k,t)=\langle J_1(k,t)J_1(k,0)\rangle+2\langle J_1(k,t)J_2(k,0)\rangle$$
$$+\langle J_2(k,t)J_2(k,0)\rangle. \tag{5}$$

(ii) Total current–mass-concentration current function:

$$F_{tx}(k,t)=x_2\langle J_1(k,t)J_1(k,0)\rangle+(x_2-x_1)\langle J_1(k,t)J_2(k,0)\rangle$$
$$-x_1\langle J_2(k,t)J_2(k,0)\rangle. \tag{6}$$

(iii) Mass-concentration current autocorrelation function:

$$F_{xx}(k,t)=x_2^2\langle J_1(k,t)J_1(k,0)\rangle-2x_1x_2\langle J_1(k,t)J_2(k,0)\rangle$$
$$+x_1^2\langle J_2(k,t)J_2(k,0)\rangle. \tag{7}$$

Corresponding zeroth frequency moments are

$$F_{tt}(k,t=0)=\overline{m}k_BT,$$
$$F_{tx}(k,t=0)=0, \tag{8}$$
$$F_{xx}(k,t=0)=x_1x_2\overline{m}k_BT.$$

Normalized time correlation functions $F_{tt}(k,t)$ (5) and $F_{xx}(k,t)$ (7) for five k values in the range $0.1735-1.2023$ Å^{-1} are shown in Figs. 1 and 2, respectively. Functions $F_{tt}(k,t)$ display in general the same behavior as transverse current autocorrelation functions in the case of simple liquids [11,12]: at small k values $F_{tt}(k,t)$ behave in agreement with (2) having long-range exponential tail, while by increasing k the negative minimum appears at short times, that is the consequence of existence of propagating modes in the system. The position of minimum in $F_{tt}(k,t)$ is changing towards smaller times by increasing k. One can see in Fig 1, that at the smallest k value reached in our computer experiment, the short-time behavior of MD-derived functions $F_{tt}(k,t)$ is in agreement with general properties of time correlation functions (odd frequency moments are equal to zero), while the tail of $F_{tt}(k,t)$ can be fitted to the single-exponential form (2). Here we note, that the hydrodynamic expression (2) is obtained in the limit $k\rightarrow 0$ and does not reflect the right short-time behavior (for example, the first time derivative at $t=0$ has nonzero value).

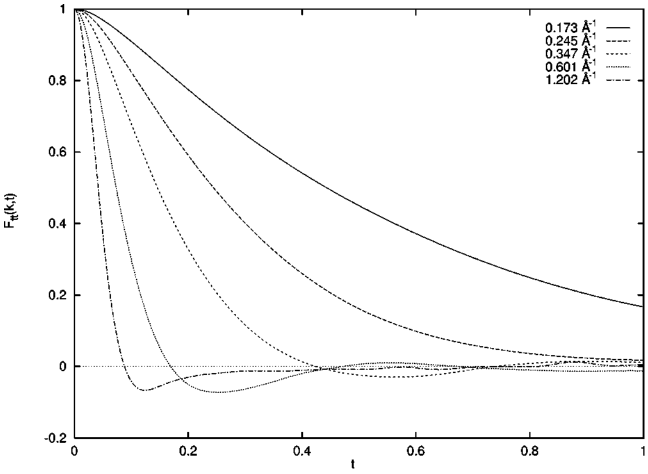

FIG. 1. Transverse total current autocorrelation functions $Ftt(k,t)$ for five k values for an equimolar liquid Kr-Ar.

It is seen in Fig. 2, that the functions $F_{xx}(k,t)$ exhibit completely different behavior than total current autocorrelation functions $F_{tt}(k,t)$. For the smallest k value the function $F_{xx}(k,t)$ already has a minimum at $\sim 0.11\tau$, which remains nearly in the same region for all k values shown. In contrast to $F_{tt}(k,t)$ these functions at very small k are rapidly decaying and do not have long tails. This means, that mass-concentration fluctuations, which are not taken into accout within the standard hydrodynamic treatment and which describe the processes of shorter time scale than the hydrodynamic one, can cause propagating modes.

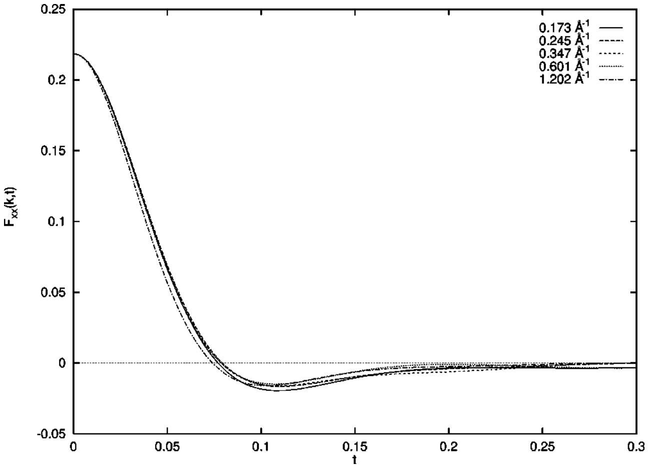

FIG. 2. Transverse mass-concentration current autocorrelation functions $Fxx(k,t)$ for five k values for an equimolar liquid Kr-Ar.

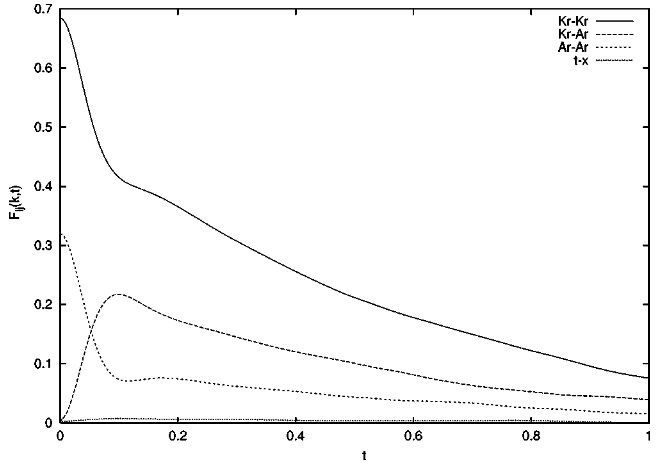

FIG. 3. Partial transverse current time correlation functions $F_{ij}(k,t)(i,j=\mathrm{Kr,Ar})$ for $k=0.1735\ \text{Å}^{-1}$. The cross-correlation function $F_{tx}(k,t)$ (total current–mass-concentration current) is shown for comparison by dotted line.

One can compare the behavior of partial transverse current time correlation functions $F_{ij}(k,t)$, $i,j=\mathrm{Kr,Ar}$, shown for $k=0.1735\ \text{Å}^{-1}$ in Fig. 3, with functions $F_{tt}(k,t)$ and $F_{xx}(k,t)$. All three partial time correlation functions have a long-time tail and nonmonotonic behavior at $t\sim 0.1\tau$. Comparing cross-correlation functions $F_{\mathrm{KrAr}}(k,t)$ and $F_{tx}(k,t)$ in Fig. 3 one can estimate, that partial dynamic cross correlations for small k-values are nearly one order of magnitude stronger than the t-x ones. Thus, we can conclude, that the representation of transverse time correlation functions on the basis of total current (1) and mass-concentration current (3) operators is more appropriate for small wave numbers than a treatment within the basis set of partial operators.

B. Models of transverse dynamics

Basis set of operators in the method of GCM defines dynamical variables, which are used to generate an eigenvalue problem from the generalized Langevin equation [9,18]. The number of dynamical variables N_v determines the order of the eigenvalue problem and the number of single-exponential mode contributions into any GCM time correlation functions

$$\mathrm{F}_{ij}^{(m)}(k,t)=\sum_{\alpha=1}^{N_v} G_{\alpha}^{ij}(k)e^{-z_{\alpha}(k)t}, \tag{9}$$

where the weight coefficients $G_{\alpha}^{ij}(k)$ are expressed via eigenvectors associated with a dynamical eigenvalue $z_{\alpha}(k)$ [9]. The time evolution of dynamical variables of the basis set can be obtained in molecular dynamics. One has to note here, that within the Newton dynamics any operator of the basis set is expessed in an analytical form via positions of particles, their velocities, and spatial derivatives of interatomic potential (see Ref. [9]). Hence, one can evaluate directly in MD any static average between basis variables within the same precision.

Since the dynamical variables of transverse total current (1) and mass-concentration current (3) define completely the transverse dynamics of binary liquids, the basis set of operators within the method of GCM for the theoretical analysis of transverse dynamics consists of these two variables and their first s time derivatives. One obtains the better agreement between MD-derived time correlation functions and their GCM functions (9), when the higher number of time derivatives of dynamical variables are included into the basis set (this means that $2s+1$ frequency moments are identical for MD-derived TCFs and GMC functions). In this study we used the basis set of eight operators, which included $J_t(k)$, $J_x(k)$ and their first time derivatives up to the third order including

$$\mathbf{A}^{(8)}(k)=\{\mathbf{A}_0,i\hat{L}_N\mathbf{A}_0,(i\hat{L}_N)^2\mathbf{A}_0,(i\hat{L}_N)^3\mathbf{A}_0\}, \tag{10}$$

where $i\hat{L}_N$ is the Liouville operator, and $\mathbf{A}_0=\mathbf{A}_0(k)=\{\hat{J}_t(k),\hat{J}_x(k)\}$. This basis set will provide for the GMC functions $F_{i,j}^{(m)}(k,t)$ with $i,j=t,x$ the precision within the sixth frequency moments. For comparison, the ''current-current'' TCFs are usually studied within the approximation of the second frequency moments in memory function approach. It was shown in Ref. [8], that the high-variable approximation with first three time derivatives of hydrodynamic variables produced GCM functions in perfect agreement with MD data.

To calculate the generalized collective mode spectrum within the method of GCM we generate the eigenvalue problem (see Ref. [9,18]) for the generalized hydrodynamic matrix

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

using the basis set (10). For this basis set one obtains 8×8 secular equation with the real symmetric matrix of static correlation functions $\mathbf{F}(k)=\mathbf{F}(k,t=0)$

$$\mathbf{F}(k)=\begin{pmatrix} F_{00}(k) & 0 & -F_{11}(k) & 0 \\ 0 & F_{11}(k) & 0 & -F_{22}(k) \\ -F_{11}(k) & 0 & F_{22}(k) & 0 \\ 0 & -F_{22}(k) & 0 & F_{33}(k) \end{pmatrix}, \tag{11}$$

and antisymmetric matrix $\tilde{\mathbf{F}}(k)=\tilde{\mathbf{F}}(k,z=0)$,

$$\tilde{\mathbf{F}}(k)=\begin{pmatrix} I(k) & F_{00}(k) & 0 & -F_{11}(k) \\ -F_{00}(k) & 0 & F_{11}(k) & 0 \\ 0 & -F_{11}(k) & 0 & F_{22}(k) \\ F_{11}(k) & 0 & -F_{22}(k) & 0 \end{pmatrix}. \tag{12}$$

Each matrix element in (11) and (12) is a 2×2 matrix evaluated on relevant t-x operators. The subindex denotes the order of time derivatives of current operators, for example,

$$F_{11}(k)=\begin{pmatrix} \langle \dot{J}_t\dot{J}_t\rangle & \langle \dot{J}_t\dot{J}_x\rangle \\ \langle \dot{J}_x\dot{J}_t\rangle & \langle \dot{J}_x\dot{J}_x\rangle \end{pmatrix}. \tag{13}$$

Similarly, $I(k)$ is the 2×2 matrix with elements

$$I_{\alpha\beta}(k)=\int_0^{\infty} F_{\alpha\beta}(k,t)dt, \quad \alpha,\beta=J_t,J_x. \tag{14}$$

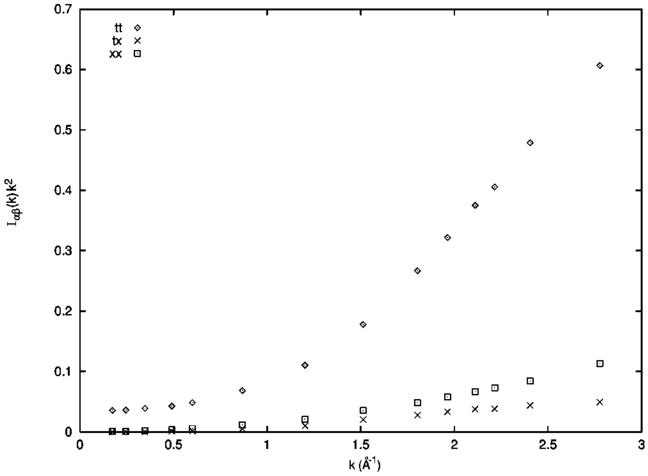

FIG. 4. Functions $f_{\alpha\beta}(k)=k^2 I_{\alpha\beta}$, $\alpha,\beta=J_t,J_x$, calculated from Eq. (14) on the basis of MD-derived time correlation functions.

It is worth mentioning that almost all matrix elements of $\mathbf{F}(k)$ and $\tilde{\mathbf{F}}(k)$ are static correlation functions, which can be directly evaluated in molecular dynamics. Only the quantities $I(k)$ (14) contain information about time-dependent properties of the system but they can be also estimated from computer experiments. Using $I_{\alpha\beta}(k)$ one can obtain expressions for correlation times relevant for transverse dynamics of a binary liquid

$$\tau_{tt}(k)=\frac{I_{J_tJ_t}}{F_{tt}(k,t=0)}, \qquad \tau_{xx}(k)=\frac{I_{J_xJ_x}}{F_{xx}(k,t=0)}. \tag{15}$$

From the expression (2) one can evaluate the small-k asymptotics for the correlation time $\tau_{tt}(k)\propto k^{-2}$. We show in Fig. 4 the behavior of functions $f_{\alpha\beta}(k)=k^2 I_{\alpha\beta}$, $\alpha,\beta=J_t,J_x$. Since we included the nonhydrodynamic variable $J_x(k)$ into the basis set (10) with the purpose to take into account mass-concentration fluctuations in transverse dynamics of a binary liquid, one can expect different behavior of correlation times (15) at small k values. One can see from the Fig. 4 that the correlation time $\tau_{tt}(k)$ behaves in complete agreement with hydrodynamics having asymptotics $\propto k^{-2}$ for small k values. For large k values the function $k^2\tau_{tt}(k)$ behaves $\propto k$, that is consistent with the behavior of generalized static shear viscosity as the function of k^{-1} in Gaussian limit. For small k the functions $f_{tx}(k)$ and $f_{xx}(k)$ are weakly dependent on k and tend to zero in the limit $k\to 0$. This means, that contrary to $\tau_{tt}(k)$ other correlation times do not have the hydrodynamic asymptotics.

It is possible to consider separated subsets of dynamical variables with the purpose to establish the origin of different branches in the spectrum of eigenvalues. Let us construct two separated subsets

$$\mathbf{A}^{(4\alpha)}=\{\hat{J}_\alpha, i\hat{L}_N\hat{J}_\alpha, (i\hat{L}_N)^2\hat{J}_\alpha, (i\hat{L}_N)^3\hat{J}_\alpha\}, \qquad \alpha=t,x. \tag{16}$$

In this case two separated subsets form the "coupled" eight-variable basis set $\mathbf{A}^{(8)}(k)$ and it is obvious, that for separated subsets the t-x cross correlations are neglected. As it was shown in previous section, the t-x dynamic cross correlations for small k values are much smaller, than the partial ones. In this case, one can expect that the solutions of two 4×4 secular equations generated for basis sets (16) will be very close to the eigenvalues obtained for the "coupled" eight-variable basis set (10). This would permit to identify the origin of different branches in the spectrum of transverse collective excitations and to estimate the mode-coupling effects between them. Similarly, an analysis of spectra can be performed using another kind of separated partial subsets:

$$\mathbf{A}^{(4j)}=\{\hat{J}_j, i\hat{L}_N\hat{J}_j, (i\hat{L}_N)^2\hat{J}_j, (i\hat{L}_N)^3\hat{J}_j\}, \qquad j=\text{Kr,Ar}. \tag{17}$$

In this case each subset would allow to analyze separately partial dynamics of components when cross correlation of different species is neglected.

Similar analysis of the spectrum using separated subsets of dynamical variables was used in Ref. [19] for investigation of longitudinal collective modes in liquid bismuth. This allowed to find a branch of heat waves in the spectrum of collective excitations of a liquid semimetal.

C. Spectra of transverse excitations

One of the predictions of hydrodynamics is the absence of transverse sound waves in the limit $k\to 0$, what means that the liquid does not support long-wave transverse sound excitations. A width of hydrodynamic region, where the acoustic transverse excitations cannot propagate depends on the thermodynamic point considered. It is interesting that this width decreases by cooling and vanishes in amorphous systems, where transverse sound waves are well defined even at $k\to 0$. In Ref. [3] the temperature dependence of propagation gap for transverse sound was investigated for liquid and undercooled metallic alloy $\mathrm{Mg_{70}Zn_{30}}$ within the method of GCM. In the case of the liquid mixture Kr-Ar at 116 K we find in contrast to $\mathrm{Mg_{70}Zn_{30}}$ a very wide propagation gap. In Fig. 5 the imaginary and real parts of eigenvalues obtained within the four-variable basis $\mathbf{A}^{(\mathbf{4t})}$ are shown. One can see in Fig. 5 that there exists a small k region where the lowest collective mode is purely diffusive and acousticlike transverse modes cannot propagate. This propagation gap determines, in fact, the range of hydrodynamic viscous behavior in a fluid [20]. Beyond the propagation gap, two pairs of propagating modes $z_j^{\pm}(k)$ are obtained for the four-variable set $\mathbf{A}^{(\mathbf{4t})}$ (shown by symbols in Fig. 5):

$$z_{t,j}^{\pm}(k)=\pm i\omega_j(k)+\sigma_j(k), \qquad \sigma_j=\mathrm{Re}\, z_j^{\pm}(k)>0, \qquad j=1,2. \tag{18}$$

Inside the propagation gap the lowest pair of propagation modes $z_{t,1}^{\pm}(k)$, which is well defined for $k>k_H$ and associated with shear (or transverse acousic-like) waves, disappears and transforms into two relaxing modes with purely real eigenvalues $z_{\pm,R}(k)$,

$$\mathrm{Im}\, z_t^{j,R}(k)=0, \qquad j=1,2. \tag{19}$$

For a binary Kr-Ar mixture we obtained a rather wide propagating gap with $k_H\sim 0.35$ Å^{-1}. When k is small, one of these modes $z_t^{1,R}(k)$ behaves as

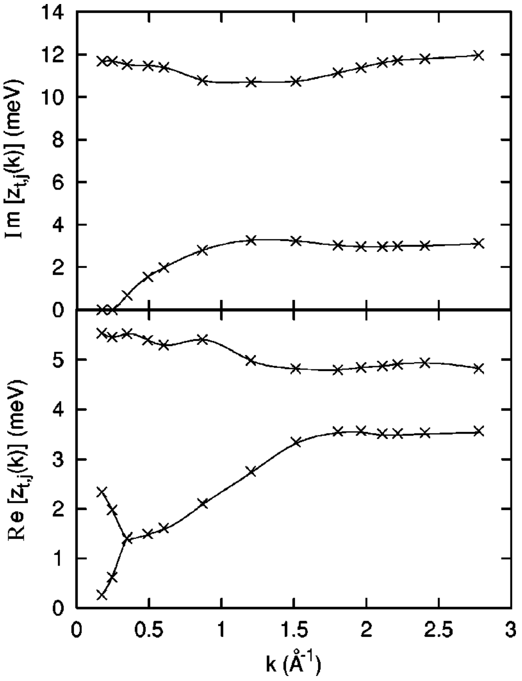

FIG. 5. Imaginary and real parts of eigenvalues obtained for the four-variable set $\mathbf{A}^{(4t)}$ (16). Spline interpolation of eigenvalues is shown by solid line.

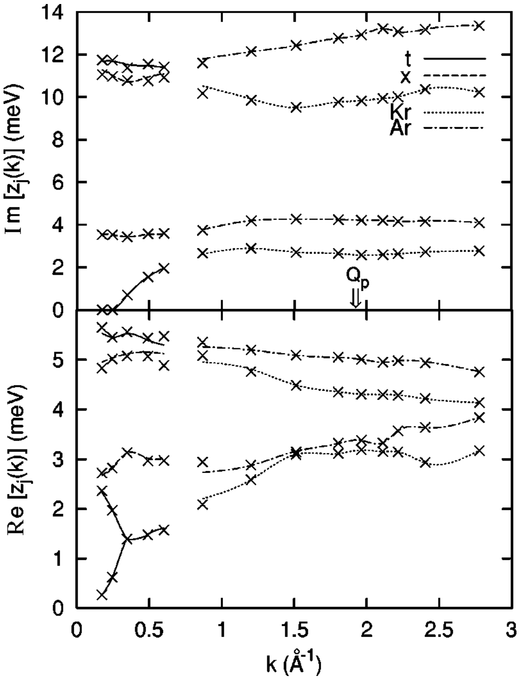

FIG. 6. Spectrum of collective excitations for a liquid KrAr, obtained for the ''coupled'' basis set $\mathbf{A}^{(8)}(k,t)$ (10) shown by symbols. The eigenvalues obtained on the separated basis sets are shown by spline-interpolated lines: solid, dashed, dotted, and dashed-dotted lines correspond to results on the four-variable sets $\mathbf{A}^{(4t)}$, $\mathbf{A}^{(4x)}$, $\mathbf{A}^{(4,\mathrm{Kr})}$, and $\mathbf{A}^{(4,\mathrm{Ar})}$. Q_p denotes the position of main peak for the ''number-number'' static structure factor $S_{NN}(k)$.

$$\mathrm{Re}\, z_t^{1,R}(k) \simeq Dk^2 \tag{20}$$

with D being a kinematic viscosity $(D=\eta/\rho)$ known from the standard hydrodynamic treatment [15,14]. By analogy, this mode can be called viscodiffusive one because D is proportional to the shear viscosity η of the system. The second relaxing mode $z_t^{2,R}(k)$ is a kinetic one because in the hydrodynamic limit $z_t^{2,R}(k)$ it tends to the nonzero value, which gives a finite damping coefficient. This means, that the kinetic mode $z_t^{2,R}(k)$ is irrelevant in hydrodynamic limit. The same can be said about all kinetic modes, which have finite damping coefficient in the limit $k \to 0$. However, these kinetic modes contribute significantly into dynamics beyond the hydrodynamic region. The spectrum, obtained within the basis $\mathbf{A}^{(4t)}$ and shown in Fig. 5, has the same number of modes and the same features as those obtained for simple LJ liquid [8,11] and metallic Cs [12].

The difference between spectra of transverse excitations in a binary system and simple liquid appears when we apply the ''coupled'' basis set $\mathbf{A}^{(8)}$ (10) for the solution of the generalized Langevin equation. We obtained four pairs of propagating modes beyond the propagating gap for $k \geqslant 0.357$ Å^{-1} (Fig. 6):

$$z_j^{\pm}(k) = \pm i\omega_j(k) + \sigma_j(k), \qquad \sigma_j = \mathrm{Re}\, z_j^{\pm}(k) > 0, \qquad j=1,2,3,4. \tag{21}$$

The same splitting of the lowest pair of propagating modes into relaxing ones inside the propagating gap was obtained. Comparing Figs. 5 and 6 one can conclude, that the main difference is the appearence of two additional branches of propagating excitations with intermediate frequencies between propagating modes obtained on the basis set constructed of total operators. Thus, taking into account mass-concentration fluctuations we obtained two additional branches of propagating transverse excitations $z_2^{\pm}(k)$ and $z_3^{\pm}(k)$. The most interesting is the lower branch $z_2^{\pm}(k)$, which has very flat dispersion $\omega_2(k)$ and for $k > 0.8$ Å^{-1} it is just above the generalized acoustic branch $z_1^{\pm}(k)$. We have to stress, that the basis set (10) results in spectrum of collective excitations, where the mode coupling effects between mass concentration and total current fluctuations are already taken into account. Therefore, the branches $z_1^{\pm}(k)$ and $z_4^{\pm}(k)$ get some shift due to ''hybridization'' with branches $z_2^{\pm}(k)$ and $z_3^{\pm}(k)$ in comparison with the ''bare'' branches $z_{t,1}^{\pm}(k)$ and $z_{t,2}^{\pm}(k)$ (Fig. 5), obtained without taking into account mass-concentration fluctuations.

The origin of branches is clearly understood, when we apply for analysis of ''coupled'' spectrum the separated subsets (16) and (17). In Fig. 6 we show by different four lines results obtained for the separated basis sets. The interesting result for the eight-mode spectrum is the ''partial'' characther of branches beyond $Q_p/2$, where Q_p is the position of main peak of the structure factor $S_{NN}(k)$. One can see from the Fig. 6, that the branch $z_2^{\pm}(k)$ at large values of k is defined only by the light component (Ar) of the binary system, while the lowest branch $z_1^{\pm}(k)$ reflects the dynamics of heavy component (Kr). Interesting, that for $k \to \infty$ the ratio of frequencies of branches $z_2^{\pm}(k)$ and $z_1^{\pm}(k)$ taken at the largest k value considered in this study is ~ 1.482 that is close to $\sqrt{m_{\mathrm{Kr}}/m_{\mathrm{Ar}}} = 1.448$. This has some analogy with the crystalline state. In binary solids within the harmonic approximation it is known [21], that the frequencies of optic (high-frequency) and acoustic (low-frequency) phonon branches on the Brillouin zone boundary depend on the masses of particles as $C/\sqrt{m_{\mathrm{light}}}$ and $C/\sqrt{m_{\mathrm{heavy}}}$, where C is some elastic constant, respectively. This analogy between dynamics of liquid and solid states becomes strightforward when we consider $Q_p/2$ as the boundary of the first pseudo-Brillouin zone in a binary liquid, because $Q_p \sim 2\pi/\langle a\rangle$, where $\langle a\rangle$ is the average interparticle distance.

One can obtain within two-variable approximation in Gaussian limit

$$\frac{z_2^{\pm}(k)}{z_1^{\pm}(k)} = \sqrt{\frac{m_{\mathrm{heavy}}}{m_{\mathrm{light}}}}. \tag{22}$$

In high-variable approximations the deviation from the value (22) is caused by coupling effects with higher branches.

At $k < Q_p/2$ one can see in Fig. 6, that the ''partial'' charachter of the spectrum changes to ''collective'' one, which becomes dominant for $k \to 0$. The branch $z_2^{\pm}(k)$ in that limit is completely defined by mass-concentration fluctuations. For the liquid Kr-Ar the condition (25) for existence of mass-concentration waves, derived in Sec. II, is fulfilled in the whole k region investigated. Taking into account the fact, that these fluctuations are caused by opposite motion of particles in different species, we can conclude, that the propagating modes $z_2^{\pm}(k)$ correspond to optic like transverse excitations in the binary liquid. However, in contrast to crystalline state, in a binary fluid these optic like collective excitations have finite time of life $\tau_2(k)$ defined by their damping coefficients (real parts of eigenvalues). We estimated that the opticlike collective excitations in the Kr-Ar mixture are characterized by $\tau_2(k) \sim 0.2$ ps (see Fig. 6). The branches $z_3^{\pm}(k)$ and $z_4^{\pm}(k)$ correspond to excitations with extremely small time of life, which are caused by mass concentration and total current fluctuations, respectively. Due to mode coupling effects these extremely high-frequency branches renormalize the position of ''bare'' acoustilike and opticlike modes, wich can be obtained within precision of the second frequency moments (two-variable separated basis sets).

In the case of Kr-Ar mixture the smallest k point, reached in MD experiment, was located, in fact, in the hydrodynamic region ($k_{\mathrm{min}} < k_H$), so we could use (20) and estimated the value of the shear viscosity η. In such a way it was found that $\eta = 2.517 \times 10^{-4}$ Pa s. This correlates well with the value 2.36×10^{-4} Pa s obtained from the Green-Kubo formulas by integrating the relevant time correlation function. Both our results are in good agreement with the experimental and MD data known previously [13] for the Kr-Ar liquid at 116 K.

D. Mode contibutions into time correlation functions

The method of GCM makes possible to represent any time correlation function between basis dynamical variables as the sum of mode contributions (9). Since in previous section we identified the branch $z_2^{\pm}(k)$ as the opticlike modes, it is interesing to estimate how these excitations contribute into different time correlation functions.

In Figs. 7(a), 7(b) one can see how the different branches contribute into time correlation functions $F_{tt}(k,t)$ and $F_{xx}(k,t)$ for two k values. By asterisks the MD-derived time correlation functions are shown. GCM functions (9), shown by solid lines, are in good agreement with MD functions. In general, for both k values the behavior of $F_{xx}(k,t)$ is defined by the opticlike branch $z_2^{\pm}(k)$. Only short-time behavior has some mixing of other branches. The function $F_{tt}(k,t)$ has for $k = k_{\mathrm{min}}$ two main contributions: long-time tail is determined exclusively by the viscodiffusive mode $z_t^{1,R}(k)$, while the

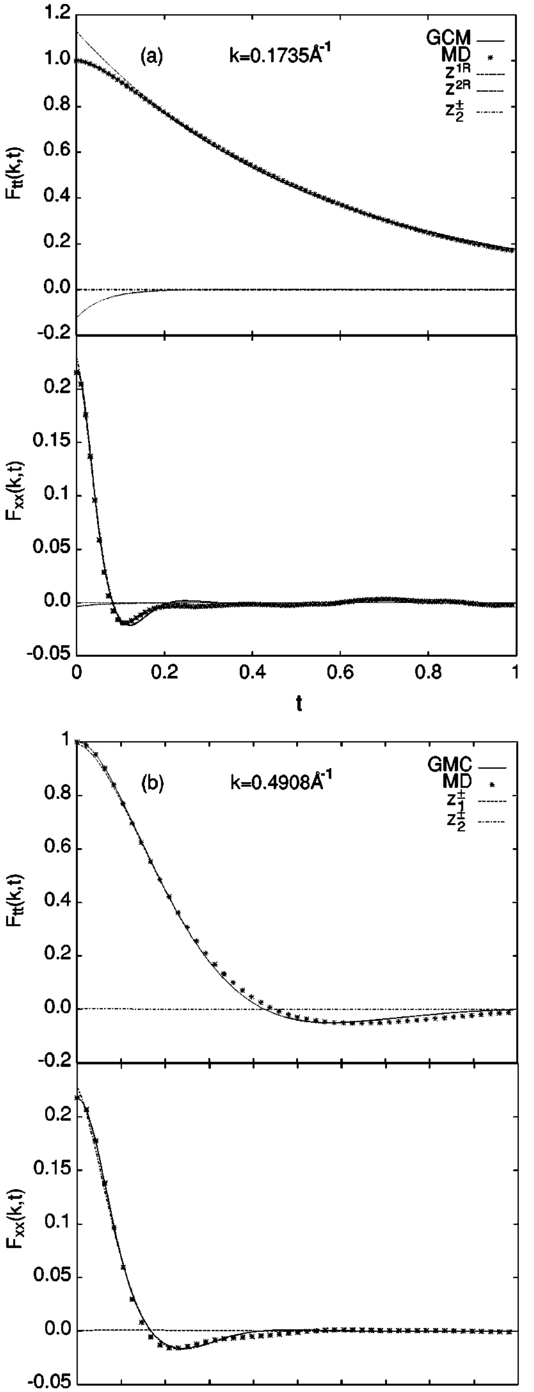

FIG. 7. The separated mode contributions into $F_{tt}(k,t)$ and $F_{xx}(k,t)$ time correlation functions for two k values. MD-derived function and the result of GCM study (9) are shown by symbols and solid lines, respectively. Mode contributions from kinetic optic-like waves, generalized shear excitations are given by dashed and dashed-dotted lines, respectively.

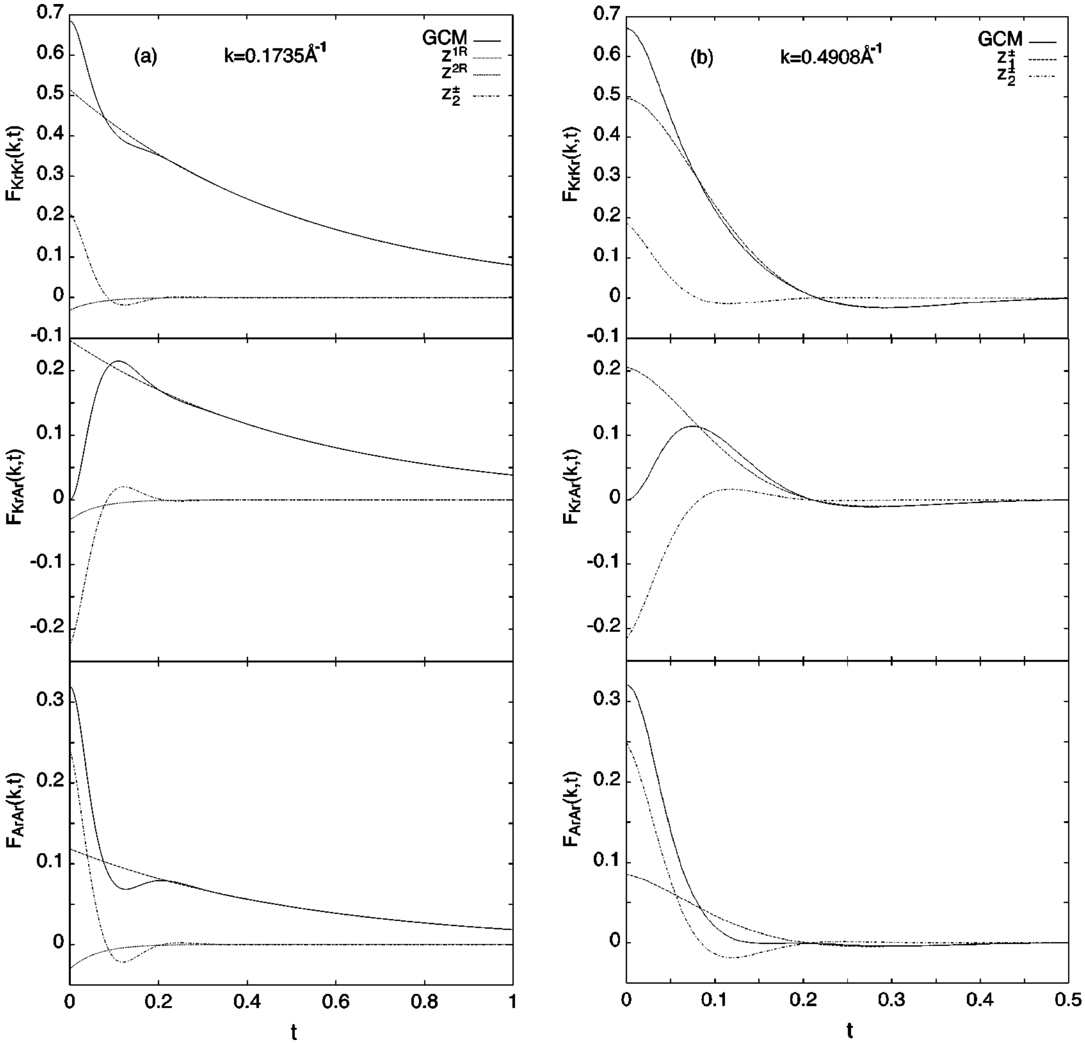

FIG. 8. The separated mode contributions into partial $F_{ij}(k,t)$, $(i,j=\mathrm{Kr,Ar})$ time correlation functions for four k values. All settings are as in previous figure.

short-time behavior has rather strong negative contribution of the second relaxing kinetic mode $z_t^{2,R}(k)$. This contribution makes the deviation from the asymptotic hydrodynamic single-exponential form, defined by the contribution of viscodiffusive mode $z_t^{1,R}(k)$ even in hydrodynamic region. For higher k values, $k_H<k<Q_p/2$ the function $F_{tt}(k,t)$ is nearly almost due to contribution of the propagating branch $z_1^{\pm}(k)$. Very week contributions of higher branches $z_3^{\pm}(k)$ and $z_4^{\pm}(k)$ correct slightly the short-time behavior of time correlation functions.

According to our analysis of spectrum for $k<0.7$ Å^{-1} the transverse dynamics of binary liquid is described well in terms of mass concentration and total-current fluctuations. For $k>Q_p/2$ the description is correct in terms of partial current fluctuations. We show in Figs. 8(a)–8(d) contributions of different branches into partial time correlation functions for different k values within the investigated k region. In agreement with the analysis of spectra the partial time correlation functions $F_{\mathrm{KrKr}}(k,t)$ and $F_{\mathrm{ArAr}}(k,t)$ are mainly described by contributions from the branches $z_1^{\pm}(k)$ and $z_2^{\pm}(k)$, respectively. For the smallest k value [Fig. 8(a)] all three partial time correlation functions $F_{\mathrm{KrKr}}(k,t)$, $F_{\mathrm{KrAr}}(k,t)$, and $F_{\mathrm{ArAr}}(k,t)$ have very long tail, which is defined by viscodiffusive mode $z_t^{1,R}(k)$. The short-time part of all three partial functions has rather big contributions of kinetic relaxing mode $z_t^{2,R}(k)$ and opticlike modes $z_2^{\pm}(k)$. This is rather surprising, that opticlike modes contribute so significantly into the short-time behavior of partial time correlation even in hydrodynamic region. For $k=0.4908$ Å^{-1} [Fig. 8(b)] the situation with contributions is a little bit different. Only week tails of all three functions for $t>0.25\tau$ are defined by the lowest branch of shear waves (acoustic transverse excitations), while for smaller times the contributions from opticlike branch are comparable with those from the generalized acoustic branch. Even, there appears the tendency for functions $F_{\mathrm{KrKr}}(k,t)$ to be described for intermediate times mainly by contributions from $z_1^{\pm}(k)$ and the functions $F_{\mathrm{ArAr}}(k,t)$ by $z_2^{\pm}(k)$. This tendency becomes the rule for large k values: autocorrelation partial current functions of light-heavy species in a mixture are determined almost completely (except very short-time part) by the modes of higher-lower branch [see Fig. 8(c), 8(d)]. For all k values beyond the propagation gap the contributions from acousticlike and opticlike branches $z_1^{\pm}(k)$ and $z_2^{\pm}(k)$ into cross-correlation function $F_{\mathrm{KrAr}}(k,t)$ are in opposite phases. For large k-values cross-correlation partial functions become extremely small

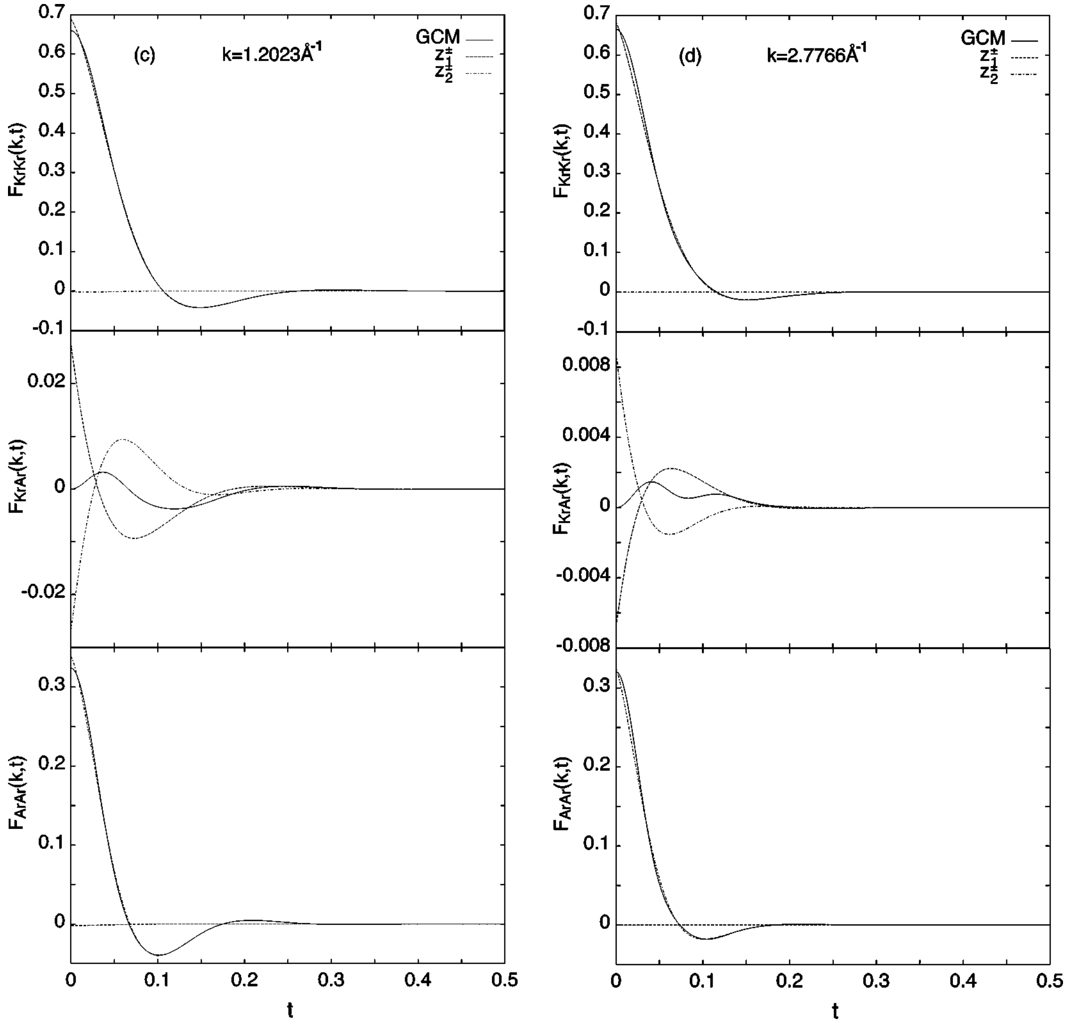

FIG. 8 (*Continued*).

and irrelevant for consideration of collective effects.

All this treatment of mode contributions into different time correlation functions is in agreement with our result for the spectrum of transverse collective excitations: at small k values all dynamical properties are described well in terms of mass concentration and total current fluctuations, while for large k the ''partial'' picture in dynamics prevails.

E. Total spectral function

We can define different spectral functions as the Fourier transform of time correlation functions $F_{tt}(k,t)$ and $F_{xx}(k,t)$. Using the expression

$$\tilde{F}_{ij}^{(m)}(z)=\sum_{\alpha=1}^{N_v}\frac{G_{\alpha}^{ij}(k)}{z+z_{\alpha}(k)}, \quad z=i\omega, \tag{23}$$

we are able to investigate mode contributions into any spectral function of interest. However, in scattering experiments one can explore only longitudinal processes in dynamics of liquids. And the longitudinal total ''current-current'' spectral function, expressed via total dynamic structure factor of a binary liquid as

$$C^{l}(k,\omega)=\frac{\omega^2}{k^2}S(k,\omega),$$

does not contain mass factors, which we used for definition of current operators. It follows, that the total spectral function defined as the Fourier-transform of $F_{tt}(k,t)$ (5) has other weights for partial contribution, than longitudinal one measured in scattering experiments. Therefore, to keep some analogy with longitudinal case we report here the parameter-free analysis of mode contributions into the total transverse spectral function $C^{t}(k,\omega)$,

$$C^{t}(k,\omega)=F_{uu}(k,\omega),$$

where $\hat{u}(k,t)=\hat{J}_1(k,t)/m_1+\hat{J}_2(k,t)/m_2$ is defined in usual way as the weighted sum of partial spectral functions. Note that $\hat{J}_1=x_1\hat{J}_t+\hat{J}_x$ and $\hat{J}_2=x_2\hat{J}_t-\hat{J}_x$. In contrast to longitudinal case the transverse spectral function $C^{t}(k,\omega)$ has nonzero value at $\omega=0$, which is connected with the value of generalized shear viscosity $\eta(k)$, namely, $C^{t}(k,\omega=0)\sim\eta^{-1}(k)$. In Fig. 9 the function $C^{t}(k,\omega)$ for a Kr-Ar mixture as well as the separated contributions from the low-frequency collective modes, calculated for the ''coupled'' set of dynamic variables $\mathbf{A}^{(8)}$, are displayed for several values of k. It is seen that in complete agreement with the standard hydrodynamics for small k ($k=0.1735$ Å^{-1} is within the propagating gap) the total spectral function is nearly completely defined by the viscodiffusive hydrodynamic mode

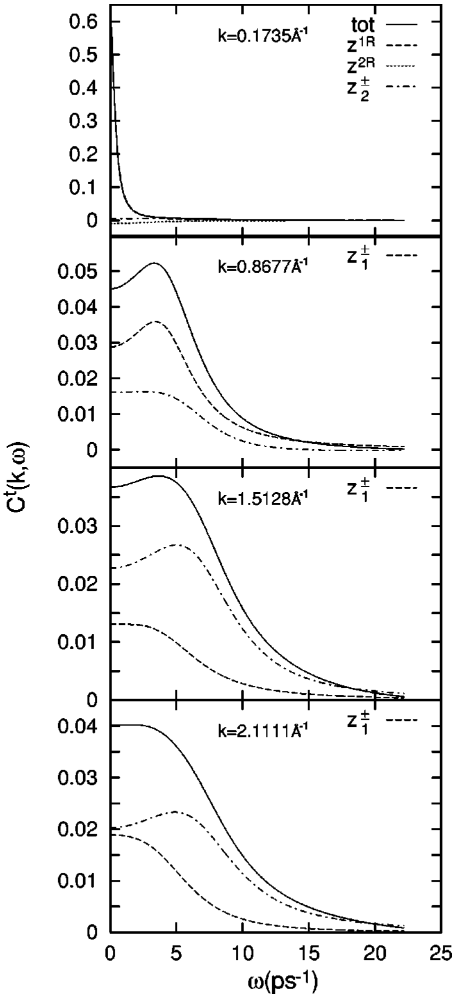

FIG. 9. Separated contributions to $C^t(k,\omega)$ from the opticlike $z_2^{\pm}(k)$ (solid line with dots) and acoustilike modes $z_1^{\pm}(k)$ (bold dots) for liquid Kr-Ar. The total spectral function $C^t(k,\omega)$ is shown by a solid line. At $k=0.1735$ Å^{-1} the contributions from the viscodiffusive mode $z_t^{1,R}(k)$ and the relaxing kinetic mode $z_t^{2,R}(k)$ are shown by bold dots and dots, respectively.

$z_t^{1,R}(k)$. The total contributions from the other high-frequency modes for the smallest k are practically equal to zero (note that the second relaxing mode $z_t^{2,R}(k)$ has very small negative weight). We emphasize that for intermediate k-values the contribution from the opticlike collective modes $z_2^{\pm}(k)$ increases and becomes even dominant for $k > 1$ Å^{-1}. For all the k values considered beyond the propagation gap we find that the function $C^t(k,\omega)$ displays a maximum at $\omega \neq 0$. However, one may expect that in a binary system with a large difference in location of opticlike and acousticlike excitations two maximum structure of the total spectral function can also be observed.

III. CONDITION FOR EXISTENCE OF LONGWAVE OPTICLIKE EXCITATIONS

The study of opticlike (mass-concentration) modes and their role in transverse dynamics of binary liquids can be completed by a simple analytical treatment of mass-concentration current fluctuations. The task is to take into account the damping of kinetic opticlike modes, which in contrast to the case of hydrodynamic modes remains a nonzero one in the limit $k \to 0$.

The simplest set of memory function equations [or macroscopic equations of motion for a nonequilibrium averaged dynamical variable $\langle J_x(k)\rangle^{\omega}$] [22,23,20] can be written in the form

$$i\omega\langle J_x(k)\rangle^{\omega} - \langle \dot{J}_x(k)\rangle^{\omega} = 0,$$

$$\Gamma_0^x\langle J_x(k)\rangle^{\omega} + (i\omega + \tilde{\varphi}_1^x(k,\omega=0))\langle \dot{J}_x(k)\rangle^{\omega} = 0,$$

where $\Gamma_0^x(k)$ and $\tilde{\varphi}_1^x(k,\omega=0)$ are the second frequency moment and first order memory function in Markovian approximation, respectively,

$$\Gamma_0^x(k) = \frac{\langle \dot{J}_x(k)\dot{J}_x(-k)\rangle}{\langle J_x(k)J_x(-k)\rangle} = \overline{\omega}_{2,x}(k), \quad \tilde{\varphi}_1^x(k,\omega=0) = \frac{1}{\tau_{x1}(k)}.$$

Here $\tau_{x1}(k)$ is a k-dependent Maxwell-like time of relaxation. Hence, the solutions of the system of two equations for the collective modes are given by

$$z_x^{\pm}(k) = \frac{1}{2\tau_{x1}(k)} \pm \left[\frac{1}{[2\tau_{x1}(k)]^2} - \overline{\omega}_{2,x}(k)\right]^{1/2}, \tag{24}$$

and, depending on the relation between the Maxwell-like relaxation time $\tau_{x1}(k)$ and the second order frequency moment $\overline{\omega}_{2,x}(k)$ of TCF $F_{xx}^t(k,t)$, one has two different kinds of collective modes: (i) two purely relaxing modes for the case when $\overline{\omega}_{2,x}(k)[\tau_{x1}(k)]^2 < 0.25$ and (ii) two complex-conjugated propagating modes for $\overline{\omega}_{2,x}(k)[\tau_{x1}(k)]^2 > 0.25$. It is easily checked that in Gaussian approximation for the TCF $F_{xx}^t(k,t)$ the condition (ii) is always valid. Using the expression for the zeroth-order correlation time $\tau_{x0}(k)$, which is connected via Green-Kubo-like equation with time correlation function $F_{xx}(k,t)$

$$\tau_{x0}(k) = \frac{1}{F_{xx}(k)}\int_0^{\infty} F_{xx}(k,t)\,dt = [\overline{\omega}_{2,x}(k)\tau_{x1}(k)]^{-1},$$

the condition of existence of propagating mass-concentration waves (or opticlike collective modes) $z_x^{\pm} = \pm i\omega_x(k) + \sigma_x(k)$ can be obtained from (24) in the form

$$\overline{\omega}_{2,x}(k)\tau_{x0}^2(k)/4 < 1. \tag{25}$$

In the hydrodynamic limit we can rewrite (25) as

$$\delta \equiv \overline{\omega}_{2,x}(0)D_{ab}^2 S_{xx}^2(0)/4(x_a x_b k_B T)^2 < 1. \tag{26}$$

It is seen, that there are several factors, which determine the existence of opticlike excitations in the limit $k \to 0$, namely, the mutual diffusion D_{ab}, structure factor $S_{xx}(k=0)$, temperature T, and the second order frequency moment of $F_{xx}(k,t)$. In particular, the high mutual diffusion and tendency to demixing in the system [when $S_{xx}(0)$ is large] prevent the emergence of opticlike transverse modes. When condition (26) is valid, the frequency $\omega_x(0) = \mathrm{Im}\, z_x^+$ and damping $\sigma_x(0) = \mathrm{Re}\, z_x^{\pm}$ of opticlike modes at $k=0$ are

$$\omega_x(0)=\sqrt{\overline{\omega}_{2,x}(0)(1-\delta)}, \quad \sigma_x(0)=\sqrt{\overline{\omega}_{2,x}(0)\delta}. \quad (27)$$

We see in (26) and (27) an interesting connection between the frequency and damping coefficient of opticlike transverse excitations in longwave limit. In particular, for small δ an opticlike branch becomes very ‘‘soft’’ and can look even like a pseudosound one.

It is seen from the results presented in this section that the opticlike propagating excitations, which are caused by mutual mass-concentration fluctuations, can exist in a binary fluid. Such excitations were found previously for ionic liquids with charged particles in the species (see, e.g., Refs. [24,25]). However, the general opinion was, that they are the specific feature of charged binary liquids only, and cannot be observed in a mixture of neutral fluids. One can easily verify, that the charge current $\mathbf{J}_Q(\mathbf{k})$,

$$\hat{\mathbf{J}}_Q(\mathbf{k})=\frac{Q_1}{m_1}\hat{\mathbf{J}}_1(\mathbf{k})+\frac{Q_2}{m_2}\hat{\mathbf{J}}_2(\mathbf{k}),$$

when an ionic liquid is totally neutral, is simply related to the mass-concentration current $\mathbf{J_x}(\mathbf{k})$, namely,

$$\mathbf{J}_Q(\mathbf{k})=\left(\frac{Q_1}{m_1}-\frac{Q_2}{m_2}\right)\mathbf{J_x}(\mathbf{k}).$$

Hence, the opticlike excitations, observed in an ionic liquid, are in fact the mutual mass-concentration waves discussed in this paper. The main difference between the cases of ionic and neutral liquids is the following: the oppositely charged particles in different species create in their relative motion an electric field, which can be detected in optic experiments. In a neutral binary liquid the concentration fluctuations properties cannot be directly determined experimentally. Only computer simulations and special analysis of mode contributions can shed light on the physics of high-frequency excitations and their manifestation in experimental data.

IV. CONCLUSIONS

(i) In this study the parameter-free method of generalized collective modes is extended for investigation of transverse dynamics of a binary liquid taking into account simultaneously total- and mass-concentration current fluctuations.

(ii) A condition of existence of mass-concentration waves (opticlike excitations) is derived, and it follows that high mutual diffusion and tendency to demixing in a binary system prevent the emergence of opticlike modes in longwave limit.

(iii) The high number of dynamical variables in basis set used in numerical study enables to obtain transverse GCM functions within the precision of the sixth frequency moment. For comparison, the memory function approach for transverse dynamics is usually applied within the precision of the second frequency moment. Such a high-variable approach in the case of transverse dynamics allows to obtain up to four branches of propagating excitations in the spectrum.

(iv) The original analysis of spectra using separated subsets of dynamical variables makes it possible to conclude, that the branch of propagating transverse modes with intermediate frequencies is caused mainly by mass-concentration current fluctuations. This branch of transverse excitations is just above the transverse ‘‘acoustic’’ branch and corresponds to opticlike modes in the binary liquid.

(v) The feature of branches of transverse collective excitations is their ‘‘partial’’ character beyond the first pseudo-Brillouin zone, for $k>Q_p/2$. For small k values the collective modes reflect collective properties of the system being described correctly in terms of total- and mass-concentration current fluctuations.

(vi) We found the propagation gap for transverse sound for $k<0.35$ Å^{-1}. In this region two relaxing modes appear instead of the lowest pair of transverse sound modes. One of them is the viscodiffusive hydrodynamic mode with real eigenvalue $\sim\eta k^2$. The value of shear viscosity, obtained from this eigenvalue, is 2.517×10^{-4} Pa s, that is in good agreement with experiments and computer simulation results [13].

(vii) We were able within the GCM method to separate contributions from different modes into time correlation functions and their Fourier spectra. We found, that immediately beyond the propagation gap the contribution of the opticlike branch is comparable with the contribution of transverse sound modes and is much bigger, than one from the other kinetic modes. If the similar picture of mode contributions exists in longitudinal case, there should exist binary liquids for which the opticlike modes would be visible on dynamical structure factors.

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