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## Optic-like excitations in binary liquids: transverse dynamics

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**Abstract.** The generalized collective mode approach is applied for the study of transverse dynamics in binary mixtures. The scheme is based on simultaneous treatment of the conserved total mass current and the mutual mass-concentration currents, as well as their time derivatives. The condition for existence of optic-like transverse modes in a binary system is derived. It is shown that high mutual diffusion and a tendency towards demixing prevent the emergence of transverse optic-like modes. Optic-like excitations are found in a Lennard-Jones Kr–Ar fluid and the liquid-metallic alloys Mg<sub>70</sub>Zn<sub>30</sub> and Li<sub>4</sub>Pb, while in the ‘fast-sound’ dense gas mixture He<sub>75</sub>Ar<sub>25</sub> they do not appear for small wavenumbers.

### 1. Introduction

Over the last two decades the dynamical theory of pure liquids has advanced at a rapid pace. With the active use of computer simulations and memory function formalism, the study of dynamics has progressed from a simple investigation of diffusion and dynamical structure factors to a sophisticated theory of hydrodynamic and 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 fairly well, while the mechanism of formation of the collective excitation spectrum and the mode contributions to total spectral functions are not yet finally established.

Collective excitations in binary liquids have been the subject of active research during the last five years (see, e.g., [1–7]). Two branches (low- and high-frequency ones) of collective excitations have been found to contribute to the longitudinal dynamics of binary systems with disparate mass, but their origin is still under study.

In the hydrodynamic limit ( $k \rightarrow 0$ ,  $\omega \rightarrow 0$  with  $k$  and  $\omega$  being the wavevector and frequency, respectively), the collective mode spectrum can be studied analytically [8, 9]. For the transverse dynamics of liquids there exists only one conserved variable (the density of the total transverse current  $\hat{J}_t(k, t)$ ), and in the hydrodynamic limit the corresponding time correlation function  $F_{tt}(k, t)$  has the well-known single-exponential form [8, 9]

$$F_{tt}(k, t) \simeq \frac{M}{N} k_B T \exp\{-\eta k^2 t / \rho\} \quad (1)$$

where  $\rho = M/V$  and  $\eta$  are a mass density and a shear viscosity, respectively. This result is valid within the precision of the zeroth-frequency moment and can be applied in the long-wavelength limit for simple fluids as well as their mixtures. According to (1), a binary liquid is treated in the hydrodynamic limit as an effective ‘averaged’ one-component fluid and all the specific features due to the difference in species are then neglected.

A generalized collective mode (GCM) method was suggested in [10] for investigating dynamical properties of a simple Lennard-Jones liquid over a wide range of wavevectors. The main idea of this new method was to extend the basis set of dynamical variables by taking, in addition to the hydrodynamic ones, their time derivatives, which were supposed to describe short-time processes in liquids. In general, the basis set of  $N_v$  dynamical variables generated an  $N_v \times N_v$  secular equation from generalized Langevin equations, and resulted in  $N_v$  generalized collective modes (eigenvalues). In [11] this method of generalized collective modes was modified into a parameter-free approach and in [12] was advanced to a high-number-of-variables approximation, taking into account the first three time derivatives of the hydrodynamic variables in the basis set.

Beyond the hydrodynamic region, short-time kinetic processes become important and, in the case of transverse dynamics, shear waves emerge in fluid-like systems [8, 9]. Shear waves are in fact *kinetic* modes [11, 13, 14] supported by liquid in the region of intermediate wavenumbers  $k$ , where elastic-like behaviour is dominant over viscous behaviour. Shear waves exist in both pure liquids and their mixtures.

Starting from the 1970s, there have been several reports about the optic-like excitations in ionic binary liquids (see, e.g., [15, 16]). In particular, it was found for LiF that the theoretical results for the spectrum of optic excitations are in good correlation with direct observations of polariton emission in the hot solid phase. However, the general opinion was that optic modes are very specific features of ionic liquids only.

The goal of this study is to investigate within the GCM method the origin of high-frequency branches in spectra of transverse collective modes in binary liquids and to focus our main attention on the role of mass-concentration fluctuations, which cause a dissimilarity to the case of a pure fluid. The transverse dynamics is much easier to investigate than the longitudinal dynamics because of the absence of coupling with energy fluctuations. Some results for high-frequency transverse dynamics can be easily generalized to the longitudinal case when energy fluctuations are neglected. Thus, it is expected that the results of this study will be very useful for understanding the key features of longitudinal dynamics as well.

## 2. Theoretical framework

We define two operators of currents  $\hat{J}_t(k, t)$  and  $\hat{J}_x(k, t)$ :

$$\begin{pmatrix} \hat{J}_x \\ \hat{J}_t \end{pmatrix} = \begin{pmatrix} x_2 & -x_1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} \hat{J}_1 \\ \hat{J}_2 \end{pmatrix} \quad (2)$$

as the linear combinations of partial transverse current operators and

$$\hat{J}_\alpha(k, t) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N_\alpha} m_\alpha v_{\alpha i}^{tr} \exp(i\mathbf{k} \cdot \mathbf{r}_{\alpha i}(t)) \quad \alpha = 1, 2 \quad (3)$$

where  $r_{\alpha i}$  and  $v_{\alpha i}^{tr}$  denote the position and the transverse component of the velocity of the  $i$ th particle in the  $\alpha$ th species, respectively, and  $x_1 = m_1 N_1 / M$  and  $x_2 = m_2 N_2 / M$  are the mass concentrations of particles of that species:  $M = m_1 N_1 + m_2 N_2 = \bar{m} N$ . The time correlation functions of these transverse current operators are defined in the following way:

$$F_{\alpha\beta}(k, t) = \langle \hat{J}_\alpha(k, 0) \hat{J}_\beta^*(k, t) \rangle \quad \alpha, \beta = t, x$$

where the asterisk means complex conjugation.

The operator  $\hat{J}_t(k, t)$  is a conserved dynamical variable and its time autocorrelation function behaves in the hydrodynamic limit as described by (1). A variable complementary to the total current operator  $\hat{J}_t(k, t)$  is the mass-concentration current  $\hat{J}_x(k)$ , which describes

the process that is orthogonal in the sense of the thermodynamic fluctuation theory to those connected with the total current  $\hat{J}_t(k)$ , so  $F_{xt}(k, 0) = F_{tx}(k, 0) = 0$ . It is seen from (2) and (3) that at  $k = 0$  the dynamical variable  $\hat{J}_x(k)$  describes opposite motions of particles of different species. Also, the mutual diffusion coefficient  $D_{12}$  (see, e.g., [17]) is directly related to the function  $F_{xx}(k, t)$  at  $k = 0$ :

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

where  $S_{xx}(0)$  is the value of the ‘mass-concentration–mass-concentration’ static structure factor  $S_{xx}(k)$  [18] at  $k = 0$ . Another important point is that in ionic liquids with  $Q_1N_1 + Q_2N_2 = 0$ , where  $Q_\alpha$  denotes the charge of particles of the  $\alpha$ th species, the transverse charge current density

$$\hat{J}_Q^t(k) = \frac{Q_1}{m_1} \hat{J}_1(k) + \frac{Q_2}{m_2} \hat{J}_2(k) \equiv \left( \frac{Q_1}{m_1} - \frac{Q_2}{m_2} \right) \hat{J}_x(k) \tag{5}$$

is just proportional to the mass-concentration current  $\hat{J}_x(k)$ .

To achieve an understanding of the main features in the dispersion of transverse branches, we performed some analytical analysis of the spectrum for the case where the effects of coupling between different branches was neglected. One can write down the macroscopic equations of motion (a chain for memory functions) for the simplest nontrivial case, when the first-order memory function is taken in the Markovian approximation, in the following form:

$$\begin{aligned} i\omega \langle \hat{J}_\alpha(k) \rangle^\omega - \langle \hat{J}_\alpha(k) \rangle^\omega &= 0 \\ \bar{\omega}_{2,\alpha}(k) \langle \hat{J}_\alpha(k) \rangle^\omega + (i\omega + \tilde{\varphi}_1^\alpha(k, 0)) \langle \hat{J}_\alpha(k) \rangle^\omega &= 0 \end{aligned} \tag{6}$$

where  $\langle \dots \rangle^\omega$  means the Fourier transform of a nonequilibrium averaged dynamical variable [19], the subscript  $\alpha$  denotes either total current  $t$  or mass concentration  $x$ ,  $\bar{\omega}_{2,\alpha}(k)$  is the second-order frequency moment, and the first-order memory function is connected with the  $k$ -dependent Maxwell-like time of relaxation  $\tau_\alpha(k)$ :

$$\bar{\omega}_{2,\alpha}(k) = \frac{\langle \hat{J}_\alpha(k) \hat{J}_\alpha(-k) \rangle}{\langle \hat{J}_\alpha(k) \hat{J}_\alpha(-k) \rangle} \quad \tilde{\varphi}_\alpha(k, 0) = \frac{1}{\tau_\alpha(k)}.$$

In (6), for the case of the total transverse operator ( $\alpha = t$ ) one can immediately estimate that

$$\hat{J}_t(k) = iL_N \hat{J}_t(k) = ik \hat{\sigma}_{tr}(k)$$

where  $\hat{\sigma}_{tr}(k)$  is a transverse component of the microscopic stress tensor  $\hat{\sigma}_{\alpha\beta}(k)$ . For  $\bar{\omega}_{2,t}(k)$  we have

$$\bar{\omega}_{2,t}(k) = \frac{k^2}{\bar{m}k_B T} \langle \hat{\sigma}_{tr}(k) \hat{\sigma}_{tr}(-k) \rangle = \frac{k^2}{\rho} G(k)$$

where  $G(k)$  is the generalized shear modulus (rigidity modulus). For the  $k$ -dependent Maxwell-like time of relaxation, in the hydrodynamic limit one has the well-known result

$$\tau_t(k) \Big|_{k \rightarrow 0} = \eta / G(0).$$

In the case of mass-concentration fluctuations, when  $\alpha = x$  in (6), the quantities  $\bar{\omega}_{2,x}(k)$  and  $\tau_x(k)$  tend to constant values in the limit  $k \rightarrow 0$ .

We derived from the two sets of two macroscopic equations of motion (see (6)) the following analytical expressions for the time correlation functions  $F_{tt}(k, t)$  and  $F_{xx}(k, t)$ ,

which in the approximation accepted were within the precision of second-order frequency moments (details are given in [20]):

$$\frac{F_{\alpha\alpha}(k, t)}{F_{\alpha\alpha}(k)} = -\frac{z_{\alpha}^{-}(k)}{z_{\alpha}^{+}(k) - z_{\alpha}^{-}(k)} e^{-z_{\alpha}^{+}(k)t} + \frac{z_{\alpha}^{+}(k)}{z_{\alpha}^{+}(k) - z_{\alpha}^{-}(k)} e^{-z_{\alpha}^{-}(k)t} \quad \alpha = t, x \quad (7)$$

where the corresponding eigenvalues are

$$z_{\alpha}^{\pm}(k) = \frac{1}{2\tau_{\alpha}(k)} \pm \left[ \frac{1}{4\tau_{\alpha}^2(k)} - \bar{\omega}_{2,\alpha}(k) \right]^{1/2} \quad \alpha = t, x. \quad (8)$$

For the case of eigenvalues  $z_t^{\pm}(k)$ , expression (8) takes the form

$$z_t^{\pm}(k) = \frac{1}{2\tau_t(k)} \pm \left[ \frac{1}{4\tau_t^2(k)} - \frac{k^2}{\rho} G(k) \right]^{1/2}. \quad (9)$$

In the hydrodynamic limit one gets from equation (9) two relaxing modes with the purely real eigenvalues

$$z_t^{+}(k) = z_t^{2R}(k) = \frac{G}{\eta} - \frac{\eta}{\rho} k^2 \quad z_t^{-} = z_t^{1R} = \frac{\eta}{\rho} k^2$$

one of which ( $z_t^{1R}$ ) corresponds to the hydrodynamic viscodiffusive mode well known from standard Navier–Stokes hydrodynamics, while the other is the lowest-lying kinetic mode with fixed damping coefficient in the hydrodynamic limit. We see that the kinetic mode  $z_t^{2R}(k)$  describes the shear relaxation [8,21] known for simple fluids (note that  $\lim_{k \rightarrow 0} z_t^{2R}(k) = 1/\tau_t$ ). The properties of the solutions (9) change significantly when  $k$  increases, namely, for  $k > k_H$ , where the value of  $k_H$  can be estimated from the equation

$$k_H^2 = \frac{\rho}{4\tau_t^2(k)G(k)} \simeq \left[ \frac{\rho G(k)}{4\eta^2(k)} \right]_{k \rightarrow 0} = \frac{\rho G}{4\eta^2} \quad (10)$$

with the  $k$ -dependent shear viscosity  $\eta(k)$ . Hence one gets two propagating collective modes

$$z_t^{\pm} = \pm i\omega_t(k) + \sigma_t(k)$$

when  $k > k_H$ . For large  $k$  the dispersion of these modes is given by

$$\omega_t(k)|_{k \gg k_H} = k [G(k)/\rho]^{1/2} \quad (11)$$

which formally coincides with result known from the theory of elastic media for shear waves.

The condition for the existence of propagating mass-concentration waves (or optic-like collective modes)

$$z_x^{\pm} = \pm i\omega_x(k) + \sigma_x(k) \quad (12)$$

is obtained from (8) in the form

$$\frac{\bar{\omega}_{2,x}(k)\tau_{x0}^2(k)}{4} < 1 \quad (13)$$

where

$$\tau_{x0}(k) = \frac{1}{F_{xx}(k, t=0)} \int_0^{\infty} F_{xx}(k, t) dt = (\bar{\omega}_{2,x}(k)\tau_x(k))^{-1} \quad (14)$$

is the zeroth-order correlation time. It is easy to check out that in the Gaussian approximation for the time correlation function  $F_{xx}(k, t)$  (the limit of large wavenumbers) the condition (13) is always satisfied. In the hydrodynamic limit we can rewrite (13) as follows:

$$\delta \equiv \bar{\omega}_{2,x}(0)D_{12}^2 \frac{S_{xx}^2(0)}{4(x_1x_2k_B T)^2} < 1. \quad (15)$$

It is seen that there are several factors which determine the existence of optic-like excitations in the hydrodynamic limit, namely, the mutual diffusion  $D_{12}$ , the structure factor  $S_{xx}(0)$ , temperature, and the second-order frequency moment of  $F_{xx}(k, t)$ . Thus, the high mutual diffusion and tendency towards demixing in the system (when  $S_{xx}(k=0)$  is large) prevent the emergence of optic-like transverse modes. When condition (15) is valid, the frequency and damping of optic-like modes are given by

$$\begin{aligned}\omega_x(0) &= \text{Im}(z_x^\pm) = \sqrt{(1-\delta)\bar{\omega}_{2,x}(0)} \\ \sigma_x(0) &= \text{Re}(z_x^\pm) = \sqrt{\delta\bar{\omega}_{2,x}(0)}.\end{aligned}\quad (16)$$

The original result is the relationship (16) between the frequency of the optic-like mode at  $k=0$  and its damping. When the damping reaches the value  $\sqrt{\bar{\omega}_{2,x}(0)}$ , the long-wavelength optic-like modes disappear. Hence, when the parameter  $\delta$  is slightly smaller than 1, the optic-like branch in the spectrum can even look like a pseudo-sound one. In this case the overdamped optic-like branch can exhibit rapidly decaying behaviour when  $k \rightarrow 0$ .

### 3. Results and discussion

In order to study the peculiarities of transverse dynamics in binary liquids, discussed in the previous section, we performed molecular dynamics (MD) simulations in the standard microcanonical ensemble with a cubic box for:

- (i) a Lennard-Jones ‘ordinary’ Kr–Ar liquid (at  $T = 116$  K,  $n = 0.0182 \text{ \AA}^{-3}$ ) [22];
- (ii) a Lennard-Jones ‘fast-sound’ mixture He<sub>75</sub>Ar<sub>25</sub> (at  $T = 160$  K,  $n = 0.013 \text{ \AA}^{-3}$ ) [23];
- (iii) another classical ‘fast-sound’ liquid Li<sub>4</sub>Pb (at  $T = 1085$  K,  $n = 0.04558 \text{ \AA}^{-3}$ ) [24], and
- (iv) a glass-forming metallic alloy Mg<sub>70</sub>Zn<sub>30</sub> (at  $T = 833$  K,  $n = 0.0435 \text{ \AA}^{-3}$ ).

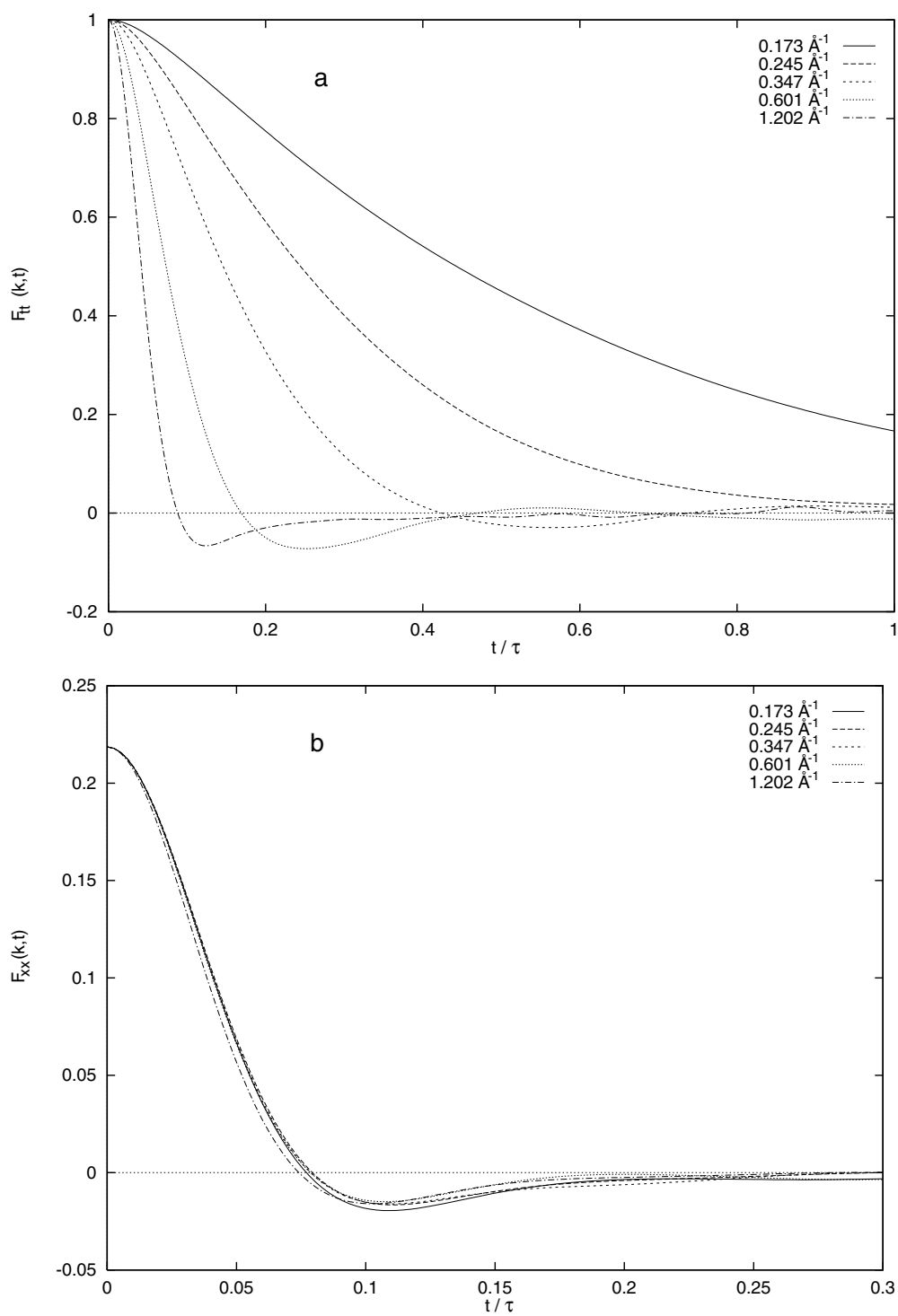
For the case of Kr–Ar and Mg<sub>70</sub>Zn<sub>30</sub>, a system of 864 particles was considered, while for He<sub>75</sub>Ar<sub>25</sub> and Li<sub>4</sub>Pb, 1000 particles were taken. During the production run over  $3 \times 10^5$  time steps, the time evolution of the basis dynamical variables was traced to evaluate relevant static and time correlation functions. Interatomic potentials for Li<sub>4</sub>Pb and Mg<sub>70</sub>Zn<sub>30</sub> were taken from [25] and [26], respectively.

The operators  $\hat{J}_t(k, t)$  and  $\hat{J}_x(k, t)$  in the long-wavelength limit, in fact, describe processes with different timescales. This statement is illustrated in figures 1(a), 1(b), where the time correlation functions  $F_{tt}(k, t)$  and  $F_{xx}(k, t)$  obtained for Kr–Ar are shown. It is seen that in contrast to the function  $F_{tt}(k, t)$ , which is very close to the single-exponential form (1) at  $k \rightarrow 0$ , the function  $F_{xx}(k, t)$  has a minimum at short times for all  $k$ , which usually indicates the existence of propagating modes. This means that even for small  $k$ -values there exist high-frequency propagating transverse waves in a neutral binary liquid, which cannot be described within the standard scheme of linear hydrodynamics.

Two dynamical variables (2) were used to generate a basis set  $A^{(8)}$  of eight operators for calculations of the transverse collective mode spectra:

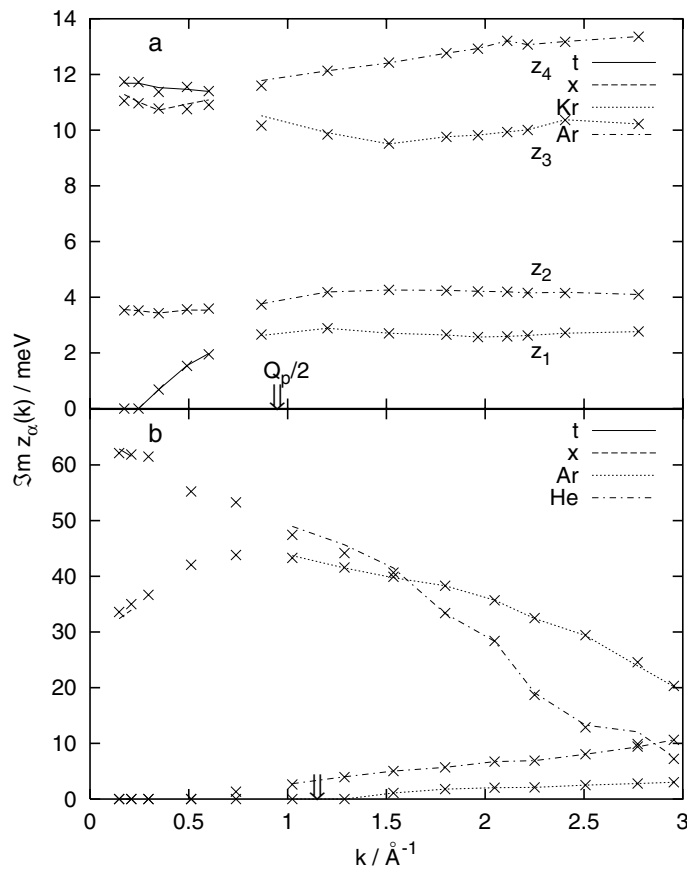
$$A^{(8)}(k, t) = \left\{ J_t(k, t), J_x(k, t), \dot{J}_t(k, t), \dot{J}_x(k, t), \ddot{J}_t(k, t), \ddot{J}_x(k, t), \ddot{J}_t(k, t), \ddot{J}_x(k, t) \right\}. \quad (17)$$

The basis  $A^{(8)}$  contains the first three time derivatives of dynamical variables (2) to take into account short-time effects in the transverse dynamics. The spectra of collective modes were obtained from  $8 \times 8$  secular equations derived from generalized Langevin equations in the Markovian approximation (see, for details, [5, 11, 19]). All matrix elements of the secular equations were evaluated directly in the molecular dynamics simulations.



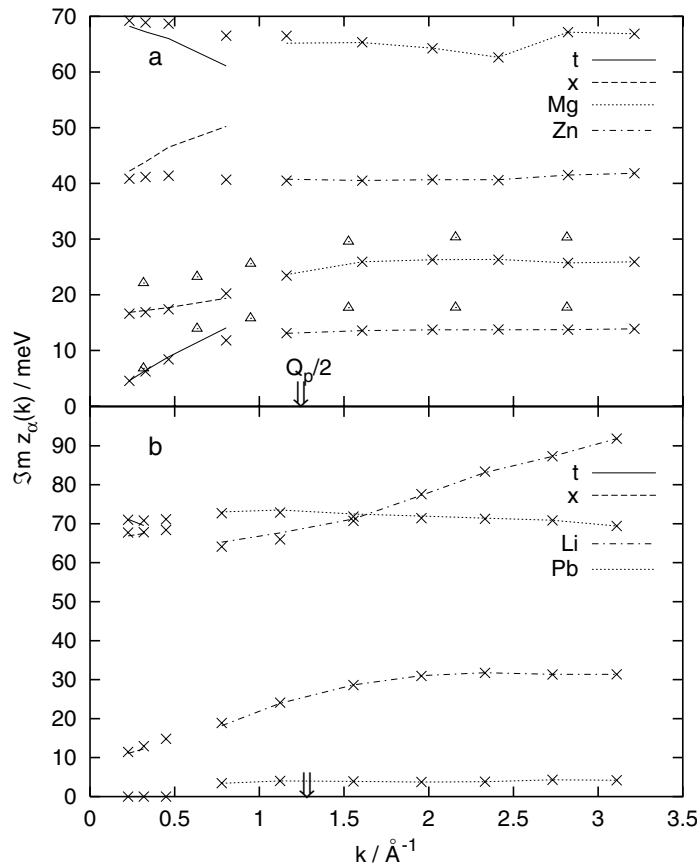
**Figure 1.** Time correlation functions  $F_{tt}(k, t)$  (a) and  $F_{xx}(k, t)$  (b) for the Lennard-Jones liquid Kr-Ar. Timescale:  $\tau = 4.598$  ps.

In figures 2 and 3 the imaginary parts of the eigenvalues (shown by crosses) represent the dispersion of propagating transverse modes in KrAr, He<sub>75</sub>Ar<sub>25</sub>, Mg<sub>70</sub>Zn<sub>30</sub>, and Li<sub>4</sub>Pb. In general four branches of propagating excitations are obtained within the eight-variable approximation of the GCM method. In fact, all these modes are kinetic ones, because they cannot be found within the standard hydrodynamic treatment. The two highest branches  $z_3(k)$  and  $z_4(k)$  are overdamped because of the large damping coefficients (real parts of eigenvalues), and they contribute only to short-time behaviour. Therefore we are mainly interested in the behaviour of the two lower branches  $z_1(k)$  and  $t_2(k)$  with comparable damping coefficients for  $k \gtrsim 1 \text{ \AA}^{-1}$ . In agreement with the hydrodynamic theory, the general feature of the lowest branch  $z_1(k)$  is the existence of a propagating gap at small  $k$ -values ( $k < k_H$ ). The width of the propagation gap for the transverse sound waves  $k_H$  corresponds to a  $k$ -range where the viscous behaviour of the liquid is dominant over the elastic behaviour. The quantities  $k_H$  obtained for KrAr, Mg<sub>70</sub>Zn<sub>30</sub>, Li<sub>4</sub>Pb, and He<sub>75</sub>Ar<sub>25</sub> are  $0.35 \text{ \AA}^{-1}$ ,  $0.05 \text{ \AA}^{-1}$ ,  $0.45 \text{ \AA}^{-1}$ , and  $1.29 \text{ \AA}^{-1}$ , respectively. For Mg<sub>70</sub>Zn<sub>30</sub> the width of the propagation gap was found to be smaller than the smallest wavenumber reached in the molecular dynamics, so an additional



**Figure 2.** Imaginary parts of eigenvalues for Lennard-Jones mixtures: (a) liquid KrAr; (b) a dense gas system He<sub>75</sub>Ar<sub>25</sub>. Results obtained for the ‘coupled’ set  $A^{(8)}$  and for the separated sets  $A^{(4t)}$ ,  $A^{(4x)}$ ,  $A^{(4a)}$ , and  $A^{(4b)}$  are shown by symbols ( $\times$ ) and different lines, respectively. The lines are given only in restricted regions, where the coupling is not significant and the spectra obtained for eight- and four-variable sets correlate well. The double arrows show the positions of  $Q_p/2$ .





**Figure 3.** Imaginary parts of eigenvalues for liquid-metallic alloys: (a)  $\text{Mg}_{70}\text{Zn}_{30}$ ; (b)  $\text{Li}_4\text{Pb}$ . Triangles show the spectrum of transverse collective excitations found for amorphous  $\text{Mg}_{70}\text{Zn}_{30}$  at room temperature (from reference [26]). All other notation is as in figure 2.

extrapolation procedure [13] for the matrix elements of the secular equation was used for small wavenumbers  $k$  in order to estimate the value of  $k_H$ . Such an extrapolation procedure can be very easily performed by setting the known hydrodynamic asymptotes for each matrix element, and its application to the investigation of transverse dynamics as well as the generalized  $(k, \omega)$ -dependent shear viscosity of liquid Cs near the melting point showed very good agreement with experimental data (see [13] for details).

More interesting for analysis is the behaviour of the second branch  $z_2(k)$ . It is clearly seen for  $\text{KrAr}$  and  $\text{Mg}_{70}\text{Zn}_{30}$  that the imaginary parts of these eigenvalues tend to certain nonzero frequencies when  $k \rightarrow 0$ . For  $\text{Li}_4\text{Pb}$  the same result is still valid, while for  $\text{He}_{75}\text{Ar}_{25}$  the propagating modes  $z_2(k)$  disappear inside the propagation gap for  $k \lesssim 0.6 \text{ \AA}^{-1}$ .

The GCM method allows one also to study the spectra of collective excitations for separated subsets of the basis set  $\mathbf{A}^{(8)}$ . Let us consider the separated sets of dynamic variables:

$$\mathbf{A}^{(4\alpha)} = \left\{ J_\alpha(k, t), j_\alpha(k, t), \ddot{J}_\alpha(k, t), \ddot{j}_\alpha(k, t) \right\} \quad \alpha = t, x.$$

In this case one can obtain the spectra of eigenvalues when the coupling between the total current and mass-concentration fluctuations is neglected. In a similar way, an analysis of the

separated ‘partial’ sets

$$\mathbf{A}^{(4i)} = \left\{ J_i(k, t), \dot{J}_i(k, t), \ddot{J}_i(k, t), \ddot{\ddot{J}}_i(k, t) \right\} \quad i = 1, 2$$

allows one to exclude direct coupling between particles in the different species. If the coupling effects are small, then the eigenvalues obtained for the separated sets and the ‘coupled’ set  $\mathbf{A}^{(8)}$  have to be very close, and vice versa if the coupling is strong, one would find a significant difference between the corresponding eigenvalues. The results obtained for the separated sets are shown in figures 2, 3 by different lines (see the descriptions in the figure captions). It is seen that at small  $k$  the appropriate explanation of transverse dynamics can be given in terms of the total and mass-concentration currents, while for  $k \gtrsim Q_p/2$  ( $Q_p$  is the position of the main peak of the static structure factor  $S_{NN}(k)$ ) all four branches are well described within the ‘partial’ sets  $\mathbf{A}^{(4i)}$ . Hence one can conclude that for large  $k$ , the collective modes  $z_1(k)$  and  $z_2(k)$  reflect the dynamics of heavy and light components, respectively. Therefore, there is an analogy with the crystalline state, for which it is known [27] that the frequencies of optic (high-frequency) and acoustic (low-frequency) phonon excitations on the boundary of the Brillouin zone depend on  $1/\sqrt{m_l}$  and  $1/\sqrt{m_h}$ , respectively, where  $m_h$  and  $m_l$  are the masses of heavy and light particles in a binary system. The analogy is straightforward, since  $Q_p \sim 2\pi/\langle a \rangle$  with  $\langle a \rangle$  the average interparticle distance in liquid. Hence, the value  $Q_p/2$  is like the boundary of the first pseudo-Brillouin zone. It is easy to show that within the precision of second-frequency moments, the ratio of the imaginary parts of the branches  $z_2(k)$  and  $z_1(k)$  in the limit  $k \rightarrow \infty$  for a binary liquid will be  $\sqrt{m_h/m_l}$ , i.e. the same as is expected for the ratio of the frequencies of the optic and acoustic branches at the boundary of the Brillouin zone for a two-component solid, obtained in the harmonic approximation.

For small  $k$  the propagating modes  $z_2(k)$  in the dense binary liquids KrAr, Mg<sub>70</sub>Zn<sub>30</sub>, and Li<sub>4</sub>Pb appear due to the mass-concentration current fluctuations only. Taking into account that these fluctuations are caused by opposite motions of particles of the different species, and recalling equation (5), we can conclude that the propagating modes  $z_2(k)$  correspond to optic-like transverse excitations. This conclusion is supported by comparing our results found for Mg<sub>70</sub>Zn<sub>30</sub> with the data obtained for amorphous Mg<sub>70</sub>Zn<sub>30</sub> (shown by triangles in figure 3) at room temperature [26, 28]. The high-frequency modes identified in the amorphous state as ‘optic phonon excitations’ are just slightly above our results. Taking into account the higher density and the lower temperature of the amorphous state considered [26, 28], this seems to be quite reasonable.

The study of crossover from the ‘collective’ behaviour (at small  $k$ -values) to the ‘partial’ one (for  $k > Q_p/2$ ) can be completed by the discussion of the mode contributions to different time correlation functions or spectral functions. Within the  $N_v$ -variable approximation of the method of GCM, the solution for time correlation functions can be written in the form

$$F_{ij}(k, t) = \sum_{\alpha=1}^{N_v} G_{ij}^{\alpha}(k) e^{-z_{\alpha}(k)t} \quad (18)$$

where  $G_{ij}^{\alpha}(k)$  are the complex weighting coefficients of the mode contributions. They are expressed [11] via eigenvectors associated with an eigenvalue  $z_{\alpha}(k)$ . Taking into account the symmetry properties of the weighting coefficients and assuming that among the  $N_v$  eigenvalues there are  $N_p$  pairs of complex conjugate eigenvalues (propagating modes):

$$z_{\alpha}(k) = \pm i\omega_{\alpha}(k) + \sigma_{\alpha}(k)$$

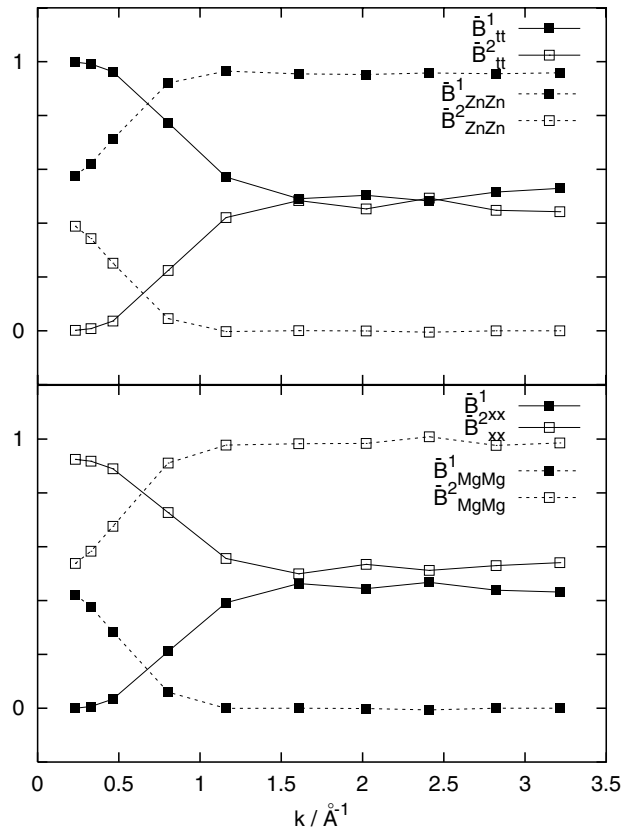
and  $N_r$  purely real ones (relaxing modes), one can rewrite (18) in a widely accepted form [8, 18]:

$$F_{ij}(k, t) = \sum_{r=1}^{N_r} A_{ij}^r e^{-\sigma_r t} + \sum_{p=1}^{N_p} [B_{ij}^p \cos(\omega_p t) + C_{ij}^p \sin(\omega_p t)] e^{-\sigma_p t}. \quad (19)$$

It is obvious that

$$\sum_{r=1}^{N_r} A_{ij}^r(k) + \sum_{p=1}^{N_p} B_{ij}^p(k) = F_{ij}(k, 0)$$

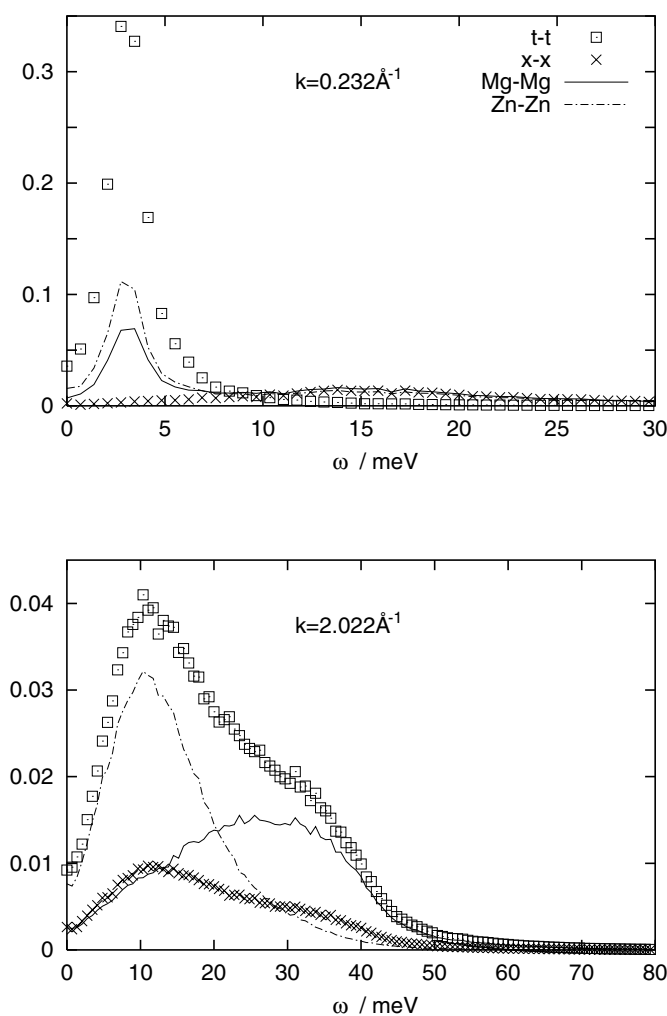
which gives in fact the zeroth-order sum rules. By taking the Fourier transform of expression (19), one obtains the mode contributions to the spectral function  $C_{ij}(k, \omega)$ , which include:  $N_r$  central Lorentzians with amplitudes  $A_{ij}^r(k)$ ;  $N_p$  noncentral Lorentzians with amplitudes  $B_{ij}^p(k)$ ; and  $N_p$  so-called ‘non-Lorentzian’ corrections with the amplitudes  $C_{ij}^p(k)$ . In figure 4 we show the normalized amplitudes  $\bar{B}_{ii}^p(k) = B_{ii}^p(k)/F_{ii}(k, 0)$  with  $i = t, x, 1, 2$  for the lowest two propagating modes (shear waves and optic-like excitations) in the case of  $\text{Mg}_{70}\text{Zn}_{30}$ . For  $k > k_H$  within the eight-variable approximation, there are four branches of propagating modes, i.e.  $N_r = 0$  and  $N_p = 4$ . One can see in figure 4 that for large  $k$ -values the branches  $z_1(k)$  and  $z_2(k)$  define almost completely the partial autocorrelation functions  $F_{\text{ZnZn}}(k, t)$  and  $F_{\text{MgMg}}(k, t)$ , respectively. The same can be said about the contributions of these modes at small  $k$ -values to the autocorrelation functions  $F_{tt}(k, t)$  and  $F_{xx}(k, t)$ . Thus, the results obtained are in agreement with our analysis of the collective mode spectrum given above.



**Figure 4.** Normalized weighting coefficients  $\bar{B}_{ij}^p(k)$  of  $\text{Mg}_{70}\text{Zn}_{30}$  found for the lowest two propagating excitations  $z_1(k)$  (closed boxes) and  $z_2(k)$  (open boxes) for four different time correlation functions. Solid and dashed lines in the upper frame correspond to the contributions to the autocorrelation functions  $F_{tt}(k, t)$  and  $F_{\text{ZnZn}}(k, t)$ , respectively. In the lower frame the solid and dashed lines correspond to the cases of functions  $F_{xx}(k, t)$  and  $F_{\text{MgMg}}(k, t)$ , respectively.

One remark should be added here about the definition of collective excitations. Within the method of GCM the collective modes are associated with the eigenvalues of the generalized hydrodynamic matrix [19]. These eigenvalues give the poles of relevant correlation Green functions, which is the generally accepted definition of collective excitations in statistical physics. Sometimes another definition is used to obtain the dispersion of collective excitations from partial spectral functions via the positions of the maxima of the partial spectral functions. This approach is, in fact, taken over from the case of pure liquids, where it works reasonably well. However, when the contributions of different propagating modes to partial spectral functions are comparable, it can cause substantial problems with the estimation of the collective mode spectrum.

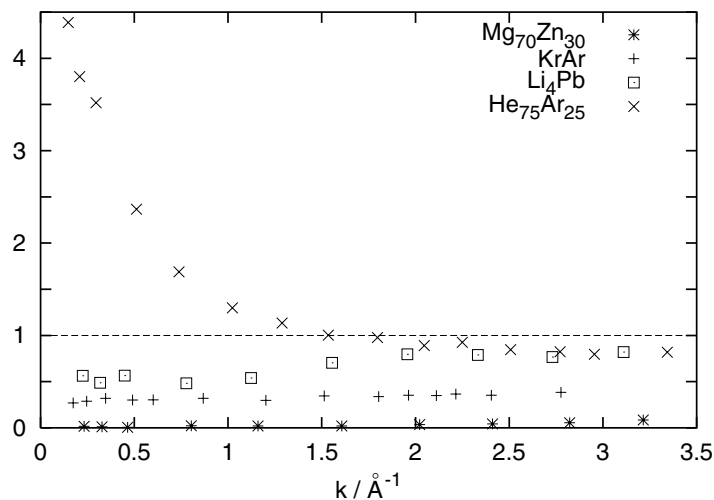
In figure 5 the transverse spectral functions  $C_{tt}^t(k, \omega)$ ,  $C_{xx}^t(k, \omega)$ ,  $C_{11}^t(k, \omega)$ , and  $C_{22}^t(k, \omega)$  for  $\text{Mg}_{70}\text{Zn}_{30}$ , obtained as the numerical Fourier transforms of the relevant MD-derived time



**Figure 5.** Spectral functions  $C_{tt}^t(k, \omega)$  (open boxes),  $C_{xx}^t(k, \omega)$  (crosses),  $C_{\text{MgMg}}^t(k, \omega)$  (solid line), and  $C_{\text{ZnZn}}^t(k, \omega)$  (dashed-dotted line) for  $\text{Mg}_{70}\text{Zn}_{30}$  at two  $k$ -values. The spectral functions are obtained numerically as Fourier transforms of the relevant MD time correlation functions.

correlation functions, are shown for two  $k$ -values. One can see that the spectral functions of dynamical variables  $J_t$  and  $J_x$  for  $k = 0.232 \text{ \AA}^{-1}$  have well-defined maxima, the positions of which correspond closely to the frequencies of collective excitations obtained in this study by the GCM method. Spectral functions of partial dynamical variables for the smallest  $k$ -value have the first peak located nearly at the frequency of the shear wave branch, which is much more pronounced in both partial spectral functions than the shoulder (or heavily smeared peak) connected with the optic-like excitations. For the case of large  $k$ -values, the situation is quite the opposite. One can see in figure 5 that for  $k = 2.022 \text{ \AA}^{-1}$  the partial spectral functions have a one-peak structure, while the functions  $C_{tt}^t(k, \omega)$  and  $C_{xx}^t(k, \omega)$  each exhibit a main peak (nearly at the position of the maximum for  $C_{22}^t(k, \omega)$ ) and a shoulder (close to the position of the maximum for  $C_{11}^t(k, \omega)$ ). This is consistent with our discussion on the mode contributions: at small  $k$ -values the spectrum of the lowest two eigenvalues correlates with positions of maxima of the spectral functions  $C_{tt}^t(k, \omega)$  and  $C_{xx}^t(k, \omega)$ , while for  $k > Q_p/2$  the maxima of the partial spectral functions correspond to the relevant eigenvalues. We note that estimating the collective excitations from just the peak positions of the partial spectral functions can lead potentially to incorrect results for small  $k$ -values, where instead of two branches of collective excitations their merger would be observed. This problem will be discussed in more detail elsewhere, together with results for the longitudinal dynamics.

In figure 6 one can see how the condition (13) is fulfilled for the binary systems investigated. It is seen that only for  $\text{He}_{75}\text{Ar}_{25}$  are the mass-concentration waves not supported in the long-wavelength limit (for  $k < 1.7 \text{ \AA}^{-1}$ ). This explains why the optic-like transverse modes have not been found in the spectrum of  $\text{He}_{75}\text{Ar}_{25}$  (see figure 2). Another general feature is seen from figure 6: for the smaller width of the propagation gap  $k_H$  (which corresponds to the case of higher viscosity), the left-hand side of condition (13) is fulfilled better and the long-wavelength optic-like excitations are supported by a liquid. This can be understood quite easily from the expression for the width of the propagation gap (10). If the viscosity of the system increases, the diffusive motion of particles will decrease, and the liquid will



**Figure 6.** The left-hand side of condition (13) as a function of  $k$  for:  $\text{Mg}_{70}\text{Zn}_{30}$ ,  $\text{Kr-Ar}$ ,  $\text{Li}_4\text{Pb}$ , and  $\text{He}_{75}\text{Ar}_{25}$ . Reduced units:  $k_B T = 1$ ,  $\bar{m} = 1$ , and  $k_{\min} = 1$  are used, where  $k_{\min}$  is the smallest  $k$ -value reached in molecular dynamics.

become more rigid, which favours optic-like excitations. For the case of very large viscosity, as one has in the amorphous phase, the width of the propagation gap tends to zero, and optic-like modes along with transverse sound excitations become well-defined collective excitations.

#### 4. Conclusions

We conclude with the following remarks:

- (i) Transverse optic-like excitations can exist in dense binary mixtures of simple liquids and they arise as a result of mass-concentration fluctuations.
- (ii) The condition for existence of these excitations is derived. In particular, it is shown that the high mutual diffusion and tendency towards demixing in the system prevent the emergence of optic-like modes in the long-wavelength limit.
- (iii) The general feature of transverse collective excitations is their ‘partial’ character beyond the first pseudo-Brillouin zone when  $k \gtrsim Q_p/2$ . For small  $k$  the collective modes reflect the collective properties of the system being described correctly in terms of total and mass-concentration currents.
- (iv) Optic-like transverse excitations are found to be supported in  $\text{Li}_4\text{Pb}$ , while in  $\text{He}_{75}\text{Ar}_{25}$  they are suppressed. On the basis of this result we can assume that two different mechanisms of the ‘fast-sound’ phenomenon in binary liquids exist: the kinetic one found by Campa and Cohen [29] and the mechanism of optic-like excitations discussed in this study.

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