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Optic-like Excitations in Binary Liquids: Transverse Dynamics

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Збудження оптичного типу в бінарних рідинах: поперечна динаміка

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Анотація. Підхід узагальнених колективних мод застосовується для дослідження поперечної динаміки в бінарних сумішах. Схема ґрунтується на одночасному розгляді консервативного масового потоку, взаємного мас-концентраційного потоку та їхніх часових похідних. Отримано умову існування поперечних мод оптичного типу в бінарній системі. Показано, що висока взаємна дифузія та тенденція до розшарування запобігають появі поперечних оптичних мод. Збудження оптичного типу знайдено в Леннард-Джонсівській рідині KrAr, рідких металічних сплавах $Mg_{70}Zn_{30}$ та Li_4Pb , тоді як в густій газовій суміші $He_{75}Ar_{25}$ вони не існують для малих хвильових чисел.

Optic-like Excitations in Binary Liquids: Transverse Dynamics

T.Bryk, I.Mryglod

Abstract. Generalized collective mode approach is applied for the study of transverse dynamics in binary mixtures. The scheme is based on simultaneous treatment of conserved total mass current and mutual mass-concentration current, as well as their time derivatives. A condition of existence of optic-like transverse modes in a binary system is derived. It is shown, that high mutual diffusion and tendency to demixing prevent the emergence of transverse optic-like modes. The optic-like excitations are found in a Lennard-Jones KrAr fluid, liquid metallic alloys $Mg_{70}Zn_{30}$ and Li_4Pb , while in 'fast-sound' dense gas mixture $He_{75}Ar_{25}$ they do not appear for small wavenumbers.

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Collective excitations in binary liquids were the subject of active research during last five years (see, e.g., [1–5]). However, there is still no clear understanding of mechanisms responsible for spectra formation beyond the hydrodynamic region. Two branches (low- and high-frequency) of collective excitations have been found to contribute to the longitudinal dynamics of binary systems with disparate masses, but their origin is not finally established.

In the hydrodynamic limit ($\mathbf{k} \rightarrow 0$, $\omega \rightarrow 0$ with \mathbf{k} and ω being wavevector and frequency, respectively) the collective mode spectrum can be studied analytically [6,7]. For transverse dynamics of liquids there exists only one conserved variable (the density of the total 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 [6,7] ($F_{tt}(k, t) \simeq k_B T \rho \exp\{-\eta k^2 t / \rho\}$, where $\rho = M/V$ and η are a mass density and shear viscosity, respectively). This result is valid within the precision of zeroth frequency moment and can be applied in longlength 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.

Beyond the hydrodynamic region short-time kinetic processes become important, and in the case of transverse dynamics the shear waves emerge in fluid-like systems [6–8]. Shear waves are, in fact, kinetic modes [8,9] supported by liquid in the region of intermediate wave numbers k , where elastic-like behaviour is dominant over viscous one. Shear waves exist in both pure liquids and their mixtures. Since the 70’s, there were several reports about the optic-like excitations in ionic binary liquids (see, e.g., [10]). In particular, it was found for LiF, that the theoretical results for spectrum of optic excitations in the liquid state correlate well with direct observations of polariton emission in the hot solid [10]. However, a general opinion was that optic modes are very specific feature of ionic liquids only.

The goal of this study is to investigate the origin of high-frequency branches in spectra of transverse collective modes in binary liquids and to focus on the role of mass-concentration fluctuations, which cause a dissimilarity in comparison with a pure fluid. Transverse dynamics is much easier to investigate than the longitudinal one because of absence of coupling with energy fluctuations. Nevertheless, it is expected, that the results of this study could be very useful for understanding the key features of longitudinal dynamics as well. We report in this paper the spectra of collective transverse excitations obtained for a Lennard-Jones ‘ordinary’ KrAr liquid (at $T = 116\text{K}$, $n = 0.0182\text{\AA}^{-3}$), a Lennard-Jones ‘fast-sound’

mixture $\text{He}_{75}\text{Ar}_{25}$ (at $T = 160\text{K}$, $n = 0.013\text{\AA}^{-3}$) [11], another classical ‘fast-sound’ liquid Li_4Pb (at $T = 1085\text{K}$, $n = 0.04558\text{\AA}^{-3}$) [12] and a glassforming metallic alloy $\text{Mg}_{70}\text{Zn}_{30}$ (at $T = 833\text{K}$, $n = 0.0435\text{\AA}^{-3}$). Interatomic potentials for Li_4Pb and $\text{Mg}_{70}\text{Zn}_{30}$ were taken from [12] and [13], respectively. The spectra were obtained within the high-mode approximations of the parameter-free method of generalized collective modes (GCM) [14,8,15].

We define two dynamic variables $\hat{J}_t(k)$ and $\hat{J}_x(k)$,

$$\hat{J}_t(k) = \hat{J}_a(k) + \hat{J}_b(k), \quad \hat{J}_x(k) = x_b \hat{J}_a(k) - x_a \hat{J}_b(k), \quad (1)$$

as the linear combinations of partial current operators

$$\hat{J}_g(k) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N_g} m_g v_{gi}^t \exp(i\mathbf{k}\mathbf{r}_{gi}t), \quad g = a, b, \quad (2)$$

where \mathbf{r}_{gi} and v_{gi}^t denote a position and a transverse component of velocity of the i th particle for the g th species, respectively, and $x_a = m_a N_a / M$ and $x_b = m_b N_b / M$ are the mass-concentrations of particles in the species, $M = m_a N_a + m_b N_b = \bar{m}N$.

The mass-concentration current $\hat{J}_x(k)$ is a complementary variable to the total current operator $\hat{J}_t(k)$ and describes the process orthogonal in the sense of thermodynamic fluctuation theory to those connected with the total current $\hat{J}_t(k)$, so that $F_{xt}(k, 0) = F_{tx}(k, 0) = 0$. It is seen from (1) and (2), that at $k = 0$ the dynamical variable $\hat{J}_x(k)$ describes opposite motion of particles of different species. Also, the mutual diffusion coefficient D_{ab} (see, e.g., [16]) is directly related to the function $F_{xx}(k, t)$ at $k = 0$

$$D_{ab} = \frac{1}{\bar{m}S_{xx}(0)} \int_0^\infty F_{xx}(0, t) dt, \quad (3)$$

where $S_{xx}(0)$ is the value of the ‘mass concentration-mass concentration’ static structure factor $S_{xx}(k)$ [17] at $k = 0$. Another important point is that in ionic liquids with $Q_a N_a + Q_b N_b = 0$, where Q_g denotes the charge of particles in the g th species, the transverse charge current density $\hat{J}_Q^t(k) = Q_a \hat{J}_a(k) / m_a + Q_b \hat{J}_b(k) / m_b$ is just proportional to the mass-concentration current $\hat{J}_x(k)$,

$$\hat{J}_Q^t(k) \equiv \{Q_a / (2m_a) - Q_b / (2m_b)\} \hat{J}_x(k). \quad (4)$$

Two dynamical variables (1) are used to generate a basis set $\mathbf{A}^{(8)}(k)$ of eight operators for calculation of transverse collective mode spectra [8,15],

$$\mathbf{A}^{(8)}(k) = \left\{ \mathbf{A}_0, i\hat{L}\mathbf{A}_0, (i\hat{L})^2\mathbf{A}_0, (i\hat{L})^3\mathbf{A}_0 \right\}, \quad (5)$$

where $i\hat{L}$ is a Liouville operator and $\mathbf{A}_0 = \mathbf{A}_0(k) = \{\hat{J}_t(k), \hat{J}_x(k)\}$. The basis $\mathbf{A}^{(8)}$ contains three first time derivatives of dynamical variables (1) to take into account short-time effects in the transverse dynamics.

In Figures 1 and 2 the imaginary parts of eigenvalues (shown by crosses) represent dispersion of propagating transverse modes in KrAr, He₇₅Ar₂₅, Mg₇₀Zn₃₀ and Li₄Pb, respectively. The spectra of collective modes were obtained from the 8×8 secular equation derived from generalized Langevin equation in Markovian approximation (see [8,3,15]). All the matrix elements of this equation were evaluated directly in molecular dynamics simulations. In general, four branches of propagating excitations are obtained. In fact, all these modes are kinetic ones, because they cannot be found within standard hydrodynamic treatment. Two highest branches $z_3(k)$ and $z_4(k)$ are overdamped (the real parts of these eigenvalues are large). Therefore we are mainly interested in behaviour of two lower branches $z_1(k)$ and $z_2(k)$ with comparable damping coefficients for $k \gtrsim 1\text{\AA}^{-1}$. In agreement with hydrodynamic theory, the general feature of the lowest branch $z_1(k)$ is the existence of propagating gap at small k -values ($k < k_H$). The width of propagation gap for the transverse sound waves k_H gives the quasihydrodynamic k -range, where viscous behaviour of a liquid is dominant over elastic one. The values k_H obtained for KrAr, Mg₇₀Zn₃₀, Li₄Pb and He₇₅Ar₂₅ are 0.35\AA^{-1} , 0.05\AA^{-1} , 0.45\AA^{-1} and 1.29\AA^{-1} , respectively. More interesting for analysis is the behaviour of the second branch $z_2(k)$. It is clearly seen for KrAr, Mg₇₀Zn₃₀, and Li₄Pb that the imaginary parts of these eigenvalues tend to certain nonzero frequencies when $k \rightarrow 0$. For He₇₅Ar₂₅ the propagating modes $z_2(k)$ disappear inside the propagation gap for $k \lesssim 0.6\text{\AA}^{-1}$.

The GCM method makes also possible to investigate the spectra of collective excitations using separated subsets of the basis set $\mathbf{A}^{(8)}$. Let us consider two groups of separated sets

$$\mathbf{A}^{(4f)} = \left\{ \hat{J}_f, i\hat{L}\hat{J}_f, (i\hat{L})^2\hat{J}_f, (i\hat{L})^3\hat{J}_f \right\},$$

with $f = \alpha = t, x$ and $f = g = a, b$. In the first case of $\mathbf{A}^{(4\alpha)}$ one can obtain the spectra of eigenvalues where the coupling between the total current and mass-concentration fluctuations is neglected. Similarly, an analysis on the separated ‘partial’ sets $\mathbf{A}^{(4g)}$ allows us to exclude the direct coupling between partial currents. If the coupling effects are small then the eigenvalues obtained for the separated sets and the ‘coupled’ set $\mathbf{A}^{(8)}$ are to be very close. And vice versa, if the coupling is strong enough one would find a big difference between the corresponding eigenvalues. The results obtained for the separated four-variable sets

are shown in Figures 1 and 2 by different lines. It is seen that at small k the appropriate description of transverse dynamics can be given in terms of total- and mass-concentration currents, while for $k \gtrsim Q_p/2$ (Q_p is a position of the main peak of the structure factor $S_{NN}(k)$) all four branches are well described by the ‘partial’ sets $\mathbf{A}^{(4g)}$. Hence, one can conclude that for large k the collective modes $z_1(k)$ and $z_2(k)$ reflect the specific features of partial dynamics of heavy and light components, respectively. An analogy with the crystalline state arises herein. For a solid binary system it is known that the frequencies of optic (high-frequency) and acoustic (low-frequency) phonon excitations on the boundary of the Brillouin zone depend on the masses of particles as $1/\sqrt{m_a}$ and $1/\sqrt{m_b}$, respectively, with m_a being the mass of light particles. This analogy becomes straightforward when we consider $Q_p/2$ as the boundary of the first pseudo-Brillouin zone in a binary liquid. Note that $Q_p \sim 2\pi/\langle a \rangle$, where $\langle a \rangle$ is the average interparticle distance.

For small k the propagating modes $z_2(k)$ in binary mixtures KrAr, Mg₇₀Zn₃₀ and Li₄Pb appear due to the mass-concentration fluctuations only (this branch is reproduced perfectly for small k by the separated set $\mathbf{A}^{(4x)}$). Taking into account that these fluctuations are caused by opposite motion of particles in different species and recalling the equation (4), 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 Mg₇₀Zn₃₀ with the data obtained [13] for amorphous Mg₇₀Zn₃₀ (shown by triangles in Figure 2a) at room temperature and a higher density. The high-frequency modes identified in the amorphous state as ‘optic phonon excitations’ are just slightly above our results.

For understanding the obvious difference in high-frequency dynamics of He₇₅Ar₂₅ and the other dense binary liquids considered we derive from the macroscopic transport equations analytical expressions for time correlation functions $F_{tt}(k, t)$ and $F_{xx}(k, t)$ within the precision of second order frequency moments (two-variable approximation). The corresponding eigenvalues are then given by

$$z_\alpha^\pm(k) = \frac{1}{2\tau_\alpha(k)} \pm \left[\frac{1}{4\tau_\alpha^2(k)} - \bar{\omega}_{2,\alpha}(k) \right]^{1/2}, \quad (6)$$

where $\tau_\alpha(k)$ is the k -dependent Maxwell-like relaxation time (connected with the first-order memory function), $\bar{\omega}_{2,\alpha}(k)$ is the second-order frequency moment, and $\alpha = t, x$. The condition of existence of propagating mass-concentration waves (or optic-like collective modes) $z_x^\pm =$

$\pm i\omega_x(k) + \sigma_x(k)$ can be obtained from (6) in the form:

$$\bar{\omega}_{2,x}(k)\tau_{x0}^2(k)/4 < 1, \quad (7)$$

where

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

is the zeroth-order correlation time. It is easily to verify, that in Gaussian approximation for the time correlation function $F_{xx}(k,t)$ (the limit of large wave numbers) the condition (7) is always valid. In the hydrodynamic limit we can rewrite (7) as follows

$$\delta \equiv \bar{\omega}_{2,x}(0)D_{ab}^2S_{xx}^2(0)/4(x_ax_bk_B T)^2 < 1. \quad (8)$$

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_{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 optic-like transverse modes. When condition (8) is valid, the frequency $\omega_x(0) = \text{Im } z_x^+$ and damping $\sigma_x(0) = \text{Re } z_x^\pm$ of optic-like modes at $k=0$ are:

$$\omega_x(0) = \sqrt{\bar{\omega}_{2,x}(0)(1-\delta)}, \quad \sigma_x(0) = \sqrt{\bar{\omega}_{2,x}(0)\delta}. \quad (9)$$

We see in (8) and (9) an interesting connection between the frequency and damping coefficient of optic-like transverse excitations in longwave limit. In particular, for small δ an optic-like branch becomes very ‘soft’ and can look like a pseudo-sound one.

In Figure 3 the left hand side of condition (7) as a function of k is shown for the binary systems considered. It is seen, that only for $\text{He}_{75}\text{Ar}_{25}$ this condition is not fulfilled when $k < 1.7\text{\AA}^{-1}$. This explains why the optic-like modes have not been found for $\text{He}_{75}\text{Ar}_{25}$ mixture (see Figure 1b).

We conclude with the following remarks: (i) It is shown that transverse optic-like excitations can exist in a dense binary mixture of simple liquids and arise due to mass-concentration fluctuations; (ii) The condition of existence of these excitations is derived, and it follows that high mutual diffusion and a tendency to demixing in a binary system prevent the emergence of optic-like modes in longwave limit; (iii) The general feature of transverse collective excitations is their ‘partial’ character beyond the first pseudo-Brillouin zone. For small k the collective modes

reflect collective properties of the system being described correctly in terms of total- and mass-concentration current fluctuations; (iv) Optic-like transverse excitations are found to be supported in KrAr , $\text{Mg}_{70}\text{Zn}_{30}$ and Li_4Pb , while in $\text{He}_{75}\text{Ar}_{25}$ they are suppressed. Our results support the opinion that there exist two different mechanisms of the ‘fast-sound’ phenomenon in binary liquids, namely, the kinetic one found by Campa and Cohen [18] and the mechanism of optic-like excitations discussed in this study (see also [12,11]).

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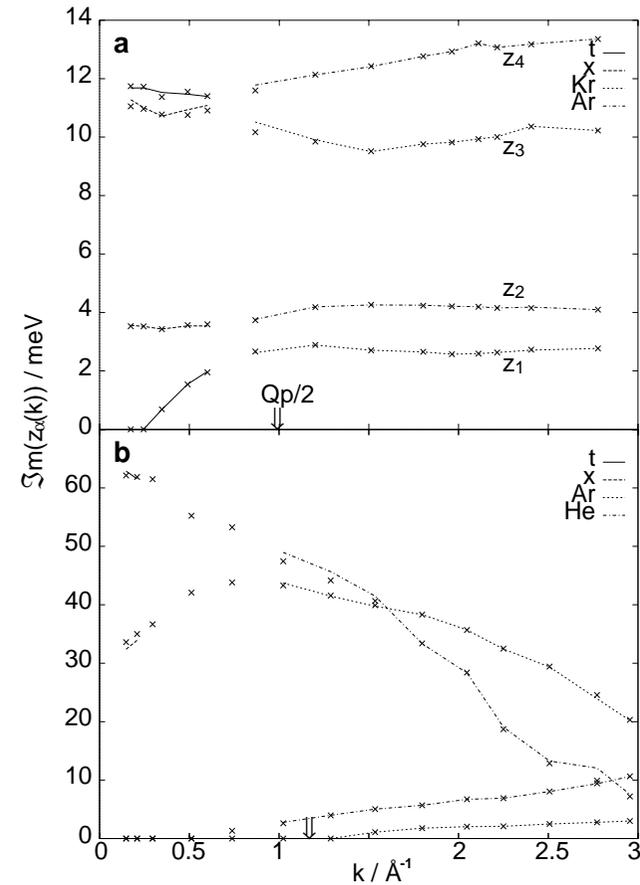


Figure 1. The imaginary parts of eigenvalues for Lennard- Jones mixtures: (a) liquid KrAr; (b) a dense gas system He₇₅Ar₂₅. Results obtained for the 'coupled' set $\mathbf{A}^{(8)}$ and for the separated sets $\mathbf{A}^{(4t)}$, $\mathbf{A}^{(4x)}$, $\mathbf{A}^{(4a)}$, and $\mathbf{A}^{(4b)}$ are shown 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 8- and 4-variable sets correlate well. The double arrows show positions of $Q_p/2$.

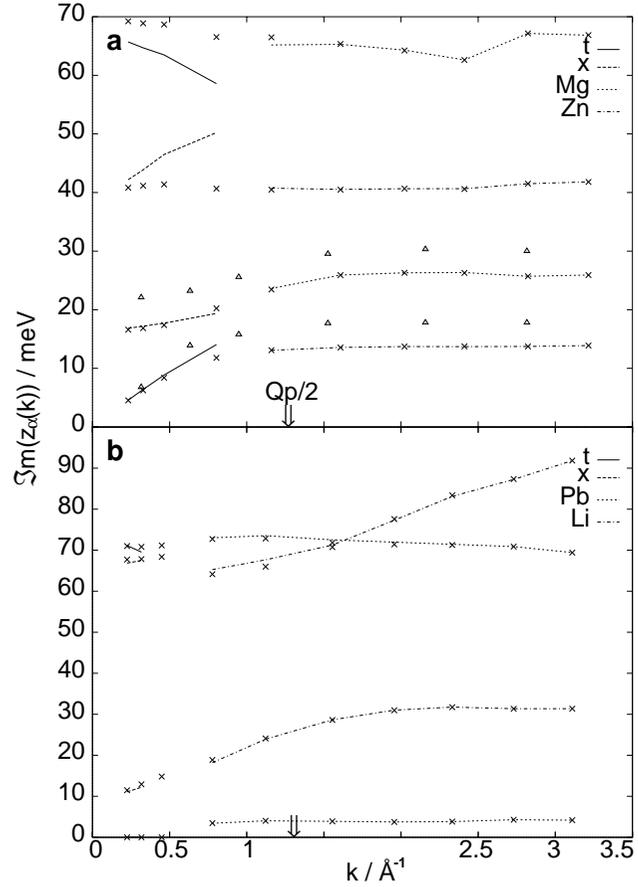


Figure 2. The imaginary parts of eigenvalues for liquid metallic alloys: (a) $\text{Mg}_{70}\text{Zn}_{30}$; (b) Li_4Pb . Triangles show the spectrum of transverse collective excitations found for amorphous $\text{Mg}_{70}\text{Zn}_{30}$ at room temperature (from Ref. [13]). All other settings are as in Figure 1.

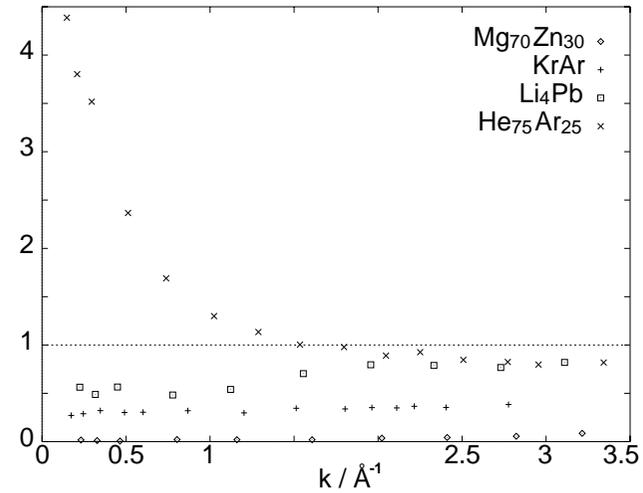


Figure 3. Left side of condition (7) as a function of k for: $\text{Mg}_{70}\text{Zn}_{30}$, Kr-Ar, Li_4Pb , and $\text{He}_{75}\text{Ar}_{25}$. Reduced units $k_B T = 1$, $\bar{m} = 1$, and $k_{\min} = 1$ are used, where k_{\min} is the smallest k -value available in molecular dynamics.

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Збудження оптичного типу в бінарних рідинах: поперечна динаміка

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