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LETTER TO THE EDITOR

Longitudinal optical-like excitations in binary liquid mixtures

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Abstract

Diffusive-like and propagating solutions of the generalized Langevin equation for mass–concentration fluctuations for liquid non-ionic binary mixtures are studied. A condition of existence for longitudinal optical-like excitations is derived. The results obtained from the approach developed are compared against simulation results for the dense mixtures KrAr and $He_{0.65}Ne_{0.35}$. Amplitudes of contributions from optical-like excitations to the spectral functions are discussed.

Collective dynamics in binary liquids has been for a long time a matter of debate, especially as regards the existence of high-frequency propagating excitations and the possibility of observing their manifestation in experimental intensity spectral functions. While for coulombic liquids [1] the existence of propagating charge waves (by analogy with optical phonons in solids they have been called optical-like excitations) is well established, it is not known how one should interpret high-frequency excitations in non-ionic mixtures. In recent papers [2, 3] we studied the transverse dynamics of Lennard-Jones and metallic mixtures within the generalized collective modes (GCM) approach [4] and found that transverse optical-like excitations can exist even in non-ionic binary liquids. It was shown that the damping of mass–concentration propagating modes is very important for estimation of their dispersion relations. In the long-wavelength limit the damping of transverse optical-like excitations is determined by the value of the mutual diffusion and the static structure factor $S_{xx}(k)$, which at $k = 0$ is a measure of how close the binary mixture is to demixing. In this letter we report a GCM study of longitudinal high-frequency dynamics in binary mixtures. The main aim is to show that there exist optical-like solutions for the generalized Langevin equation. Using an analytical three-variable model to treat mass–concentration fluctuations, we will show that optical-like (mass–concentration) propagating excitations must exist in non-ionic liquid mixtures, but may be suppressed in some cases by special conditions. Numerical examples from MD simulations of two binary

mixtures, the Lennard-Jones liquid KrAr and a 'fast-sound' gas mixture $He_{0.65}Ne_{0.35}$, will be used to show the applicability of the approach developed.

Let us introduce a dynamical variable for the mass–concentration density:

$$n_x(k,t) = \frac{1}{\bar{m}}\{m_1x_2n_1(k,t) - m_2x_1n_2(k,t)\}, \tag{1}$$

where

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

are the ordinary variables for partial densities, m_α and $x_\alpha = m_\alpha c_\alpha/\bar{m}$, are the atomic masses and mass–concentration factors, respectively, and $\bar{m} = m_1c_1 + m_2c_2$. The reason for introducing a dynamical variable $n_x(k,t)$ in the form (1) is that it is proportional to the ordinary concentration density $n_c(k,t)$ and at the same time it is connected to the longitudinal component of the mass–concentration current $J_x^L(k,t)$ (introduced in [2]) by a simple relation:

$$\frac{\partial n_x}{\partial t} = \frac{\mathrm{i}k}{\bar{m}}J_x^L(k,t). \tag{2}$$

The mass–concentration density $n_x(k,t)$ is a hydrodynamic variable and, along with dynamical variables for the total density $n_t(k,t)$, the total mass–current density $\boldsymbol{J}_t(k,t)$ and the energy density $\varepsilon(k,t)$, is commonly used for the hydrodynamic description of binary systems in the liquid state. It was shown in [2] that $\boldsymbol{J}_x(k,t)$ is a dynamical variable orthogonal to $\boldsymbol{J}_t(k,t)$, and its real-space representation reflects the out-of-phase motion for neighbours of different kinds.

In the case of longitudinal dynamics the basis set for our *analytical* GCM treatment of mass–concentration fluctuations consists of three dynamical variables:

$$\boldsymbol{A}^{(3x)} = \{n_x(k,t),\, J_x^L(k,t),\, \dot{J}_x^L(k,t)\}. \tag{3}$$

Here, $\dot{J}_x^L(k,t)$ is the first time derivative of the longitudinal mass–concentration current. The only hydrodynamic variable in this basis set is $n_x(k,t)$; the other two dynamical variables describe shorter-time fluctuations. The basis set (3) corresponds to the same level of short-time fluctuation treatment as was applied in the analytical study of transverse dynamics in binary liquids [2, 3]. Solving the generalized Langevin equation in terms of the dynamical eigenmodes with finite lifetimes is reduced within the GCM method to the eigenvalue problem for a generalized hydrodynamic matrix $\mathbf{T}(k)$ generated using a chosen set of dynamical variables. When the hydrodynamic basis set is used, one obtains within the GCM method the well-known expressions for hydrodynamic modes and hydrodynamic time correlation functions.

The generalized hydrodynamic matrix for description of solely mass–concentration fluctuations (for simplicity we neglect the coupling to total density and energy fluctuations) can be constructed using the basis set of dynamical variables $\boldsymbol{A}^{(3x)}$:

$$\mathbf{T}(k) = \begin{pmatrix} 0 & -\mathrm{i}k\bar{m}^{-1} & 0 \\ 0 & 0 & -1 \\ -\mathrm{i}\bar{m}k^{-1}[\langle\bar{\omega}_k^4\rangle - \langle\bar{\omega}_k^2\rangle]\tau_{xx}^{-1} & \langle\bar{\omega}_k^4\rangle & [\langle\bar{\omega}_k^4\rangle\langle\bar{\omega}_k^2\rangle^{-1} - 1]\tau_{xx}^{-1} \end{pmatrix}. \tag{4}$$

Here, the correlation time

$$\tau_{xx}(k) = S_{xx}^{-1}(k)\int_0^\infty F_{xx}(k,t)\,\mathrm{d}t, \qquad F_{xx}(k,t) = \langle n_x(k,0)n_x^*(k,t)\rangle$$

is associated with mass–concentration fluctuations in non-ionic liquid mixtures and behaves like k^{-2} in the limit $k \to 0$. The normalized frequency moments are expressed, via statistic averages of microscopic quantities as follows:

$$\langle\bar{\omega}_k^2\rangle = \frac{k^2\langle J_x^L J_x^L\rangle}{\bar{m}^2\langle n_x n_x\rangle} \equiv \frac{k^2x_1x_2k_BT}{\bar{m}S_{xx}(k)}, \qquad \langle\bar{\omega}_k^4\rangle = \frac{\langle\dot{J}_x^L\dot{J}_x^L\rangle}{\langle J_x^L J_x^L\rangle}, \tag{5}$$

where the static average $\langle \dot{J}_x^L \dot{J}_x^L \rangle$ tends to a constant in the $k \to 0$ limit [5]. Eigenvalues of the matrix $\mathbf{T}(k)$ represent mass–concentration collective modes with finite lifetimes, which either correspond to purely relaxing behaviour (real eigenvalues $d_i(k)$) or describe propagating processes (pairs of complex conjugate eigenvalues $z_i^{\pm}(k)$).

Solving the three-by-three eigenvalue problem for the matrix $\mathbf{T}(k)$ in the limit $k \to 0$, one gets within the precision $\mathrm{O}(k^2)$ that the lowest eigenvalue is simply

$$d(k) = \tau_{xx}^{-1}(k) \equiv D_{12}k^2, \tag{6}$$

where D_{12} is the mutual diffusion coefficient [6] taking into account that no other processes contribute to the shape of $F_{xx}(k, t)$ within our model. The other two eigenvalues tend in the long-wavelength limit to the constant values

$$z^{\pm}(k \to 0) = \Gamma(k) \pm \sqrt{\Gamma^2(k) - \langle \bar{\omega}_k^4 \rangle}, \qquad \Gamma(k) = \frac{\langle \bar{\omega}_k^4 \rangle}{2\tau_{xx}(k)\langle \bar{\omega}_k^2 \rangle}. \tag{7}$$

If the quantity under the square root in equation (7) is negative, the eigenvalues $z^{\pm}$ correspond to the propagating modes with the damping coefficient $\Gamma(k)$ and frequency $\omega(k) = \sqrt{\langle \bar{\omega}_k^4 \rangle - \Gamma^2(k)}$. Thus, we have arrived at the condition for existence for mass–concentration wave (optical-like) excitations:

$$\delta_x(k) = \frac{\langle \bar{\omega}_k^4 \rangle}{(2\tau_{xx}(k)\langle \bar{\omega}_k^2 \rangle)^2} < 1, \tag{8}$$

which, in the limit $k \to 0$, reads as follows:

$$\delta_x = \frac{\langle \bar{\omega}_{k=0}^4 \rangle D_{12}^2 S_{xx}^2(k=0)\bar{m}^2}{4(x_1 x_2 k_B T)^2} < 1. \tag{9}$$

This condition is, remarkably, of the same form as that obtained for the case of transverse optical-like excitations [2, 3] using the two-variable basis set $\boldsymbol{A}^{(2T)} = \{J_x^T(k, t), \dot{J}_x^T(k, t)\}$:

$$\delta_x^T = \frac{\langle \bar{\omega}_{k=0}^{2,T} \rangle D_{12}^2 S_{xx}^2(k=0)\bar{m}^2}{4(x_1 x_2 k_B T)^2} < 1. \tag{10}$$

The only difference is that the normalized second frequency moment $\langle \bar{\omega}_{k=0}^{2,T} \rangle$ of the transverse current–current spectral function $C_{xx}^T(k, \omega)$ appears instead of the normalized fourth frequency moment $\langle \bar{\omega}_{k=0}^4 \rangle$ of the dynamic structure factor $S_{xx}(k, \omega)$ for the longitudinal case (9). These quantities differ at $k = 0$ only in the case of long-range Coulomb interaction between particles (ionic liquids), while for mixtures of non-ionic particles, for symmetry reasons, they take the same values in the long-wavelength limit.

In order to illustrate how good the analytical GCM approach applied above to the analysis of mass–concentration fluctuations is, we show in figure 1 the imaginary parts of the propagating eigenvalues for the equimolar mixture KrAr at 116 K and the dense gas mixture with disparate masses $\mathrm{He}_{0.65}\mathrm{Ne}_{0.35}$ at 39.5 K. The spectra of longitudinal collective excitations have been obtained within the numerical parameter-free 14-variable GCM approach using the extended basis set

$$\begin{aligned}\boldsymbol{A}^{(14)}(k, t) = \{&n_t(k, t), n_x(k, t), J_t^L(k, t), J_x^L(k, t), \varepsilon(k, t), \dot{J}_t^L(k, t), \dot{J}_x^L(k, t), \dot{\varepsilon}(k, t),\\ &\ddot{J}_t^L(k, t), \ddot{J}_x^L(k, t), \ddot{\varepsilon}(k, t), \dddot{J}_t^L(k, t), \dddot{J}_x^L(k, t), \dddot{\varepsilon}(k, t)\},\end{aligned} \tag{11}$$

which allows one to take into account the cross-correlations between long- and short-time processes of different origin (total density, mass–concentration and heat fluctuations). All the matrix elements of the 14×14 generalized hydrodynamic matrix $\mathbf{T}(k)$ were evaluated directly in MD simulations, so no free parameters have been used in our approach. MD simulations

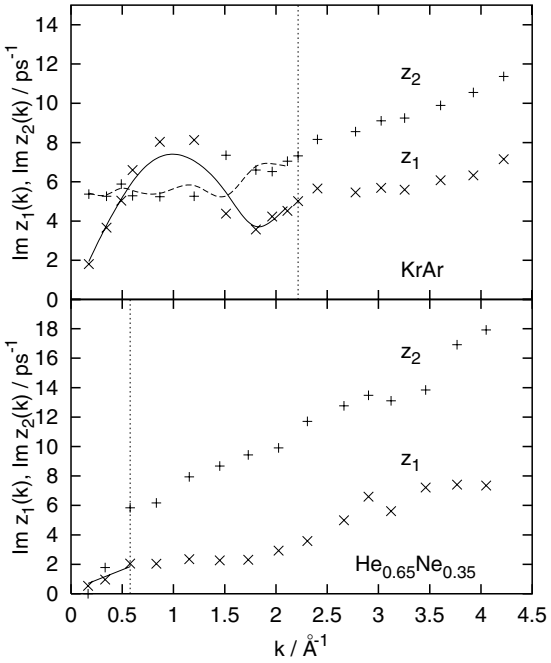

Figure 1. Dispersions of sound ($z_1(k)$) and high-frequency ($z_2(k)$) excitations in the equimolar Lennard-Jones mixture KrAr at 116 K and the dense gas mixture $He_{0.65}Ne_{0.35}$ at 39.3 K, calculated numerically in the GCM approach for the basis set $\boldsymbol{A}^{(14)}(k,t)$. Dashed and solid curves correspond to dynamical eigenmodes obtained by separate treatment of the dynamics using the sets $\boldsymbol{A}^{(5x)}(k,t) = \{n_x, J_x^L, \dot{J}_x^L, \ddot{J}_x^L, \dddot{J}_x^L\}$ and $\boldsymbol{A}^{(5t)}(k,t) = \{n_t, J_t^L, \dot{J}_t^L, \ddot{J}_t^L, \dddot{J}_t^L\}$, respectively. Dotted vertical lines approximately separate the short-wavelength regions of 'partial' behaviour of branches. The branch $z_2(k)$ corresponds in the long-wavelength region to optical-like excitations in KrAr, while for $He_{0.65}Ne_{0.35}$ the optical-like excitations are suppressed.

were performed in a standard microcanonical ensemble with systems of 864 and 1000 particles for KrAr and $He_{0.65}Ne_{0.35}$, respectively. The smallest wavenumbers $k_{\min}$ reached in the MD simulations were 0.1735 $Å^{-1}$ for KrAr and 0.1664 $Å^{-1}$ for $He_{0.65}Ne_{0.35}$. The time evolution of dynamical variables from the basis set $\boldsymbol{A}^{(14)}(k,t)$ was recorded from the production run over 3×10^5 time steps. The number of dynamical variables was chosen to be in agreement with the nine-variable basis set used for the case of simple liquids [9, 10] with time derivatives of hydrodynamic variables up to the third order included, which allowed us to obtain a good description of the sound and heat wave branches for simple liquids. Let us analyse the results for the KrAr mixture first. The branch $z_1(k)$ corresponds to the hydrodynamic sound excitations with linear dispersion in the small-wavenumber region. Branch $z_2(k)$ in the long-wavelength limit is caused by mass–concentration fluctuations and can be reproduced by treatment of solely dynamical variables describing mass–concentration fluctuations (the dashed curve in figure 1).

Dotted vertical lines in figure 1 separate two regions of wavenumbers in which the collective (small-k) or partial (large-k) forms of dynamics prevail. The main ideas of such specialized studies can be found in [2, 3]. We note that only for larger wavenumbers can the dispersion of propagating modes, shown in figure 1, be described well in terms of 'partial' properties of light (high-frequency branch $z_2(k)$) and heavy (low-frequency one, $z_1(k)$) particles based on separate sets of 'partial' dynamic variables. One can see in figure 1 that for

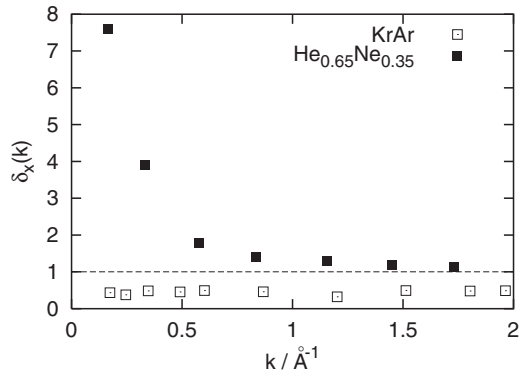

Figure 2. The condition for existence of optical-like excitations $\delta_x(k)$ (8) as a function of wavenumber for KrAr and $He_{0.65}Ne_{0.35}$. Optical-like excitations exist in the long-wavelength region only when $\delta_x(k) < 1$.

the case of the dense gas mixture $He_{0.65}Ne_{0.35}$ the short-wavelength region of 'partial' dynamics begins at much smaller wavenumbers than that for KrAr. Moreover, in the long-wavelength limit, in contrast to the branch patterns in KrAr, there exists only one branch of propagating sound excitations $z_1(k)$ with linear dispersion (the estimated speed of sound is 324 m s^{-1}), while the branch $z_2(k)$ is suppressed in the $He_{0.65}Ne_{0.35}$ mixture when $k \to 0$. Note that the treatment of solely mass–concentration dynamical variables in the small-k region does not produce an optical-like branch (the dashed line is absent for $He_{0.65}Ne_{0.35}$). The analytical approach, developed above, allows us to explain the structure of the eigenmodes in the $k \to 0$ limit via the condition (9), which is valid in the case of KrAr and is not fulfilled for $He_{0.65}Ne_{0.35}$. For comparison, for $He_{0.65}Ne_{0.35}$ the mutual diffusion coefficient $D_{12} = 12.55 \times 10^{-5}$ cm^2 s^{-1} is more than five times larger than for KrAr ($D_{12} = 2.5 \times 10^{-5}$ cm^2 s^{-1}), and in addition the mixture $He_{0.65}Ne_{0.35}$ shows a stronger tendency of demixing that is reflected in the larger value of the structure factor $S_{xx}(k)$ at $k = 0$ (see [7]). In particular, this explains why the 'partial' branch $z_2(k)$ for $He_{0.65}Ne_{0.35}$ does not display the crossover to optical-like character with decreasing wavenumbers and vanishes at the non-zero value $k \simeq 0.16$ $Å^{-1}$. In figure 2 one can see that the condition for existence of optical-like excitations (8) is fulfilled in the case of KrAr and not for $He_{0.65}Ne_{0.35}$, which is a consequence of the high damping coefficient $\Gamma(k)$ (7) due to the high mutual diffusion and tendency of demixing in $He_{0.65}Ne_{0.35}$.

Along with frequencies and damping coefficients of the collective excitations, it is important to find the relative strength of each mode contribution to the time correlation function (or relevant dynamic structure factor) which we are interested in. The GCM approach enables us to represent any dynamical structure factor (or relevant spectral function), describing the correlations between two dynamical variables $\alpha(k, t)$ and $\beta(k, t)$ from the set $\boldsymbol{A}^{(M)}(k, t)$, as a sum of mode contributions:

$$\frac{S_{\alpha\beta}(k,\omega)}{S_{\alpha\beta}(k)} = \sum_{i}^{M_{rl}} \frac{A_i^{\alpha\beta}(k) d_i(k)}{\omega^2 + d_i^2(k)} + \sum_{i}^{M_{pr}} \frac{B_i^{\alpha\beta}(k)\Gamma_i(k) + C_i^{\alpha\beta}(k)(\omega \pm \omega_i(k))}{(\omega \pm \omega_i(k))^2 + \Gamma_i^2(k)} \quad (12)$$

with amplitudes $A_i^{\alpha\beta}(k)$, $B_i^{\alpha\beta}(k)$ and $C_i^{\alpha\beta}(k)$, which can be expressed via the eigenvectors associated with the relevant eigenvalues. The GCM expression (12) generalizes the hydrodynamic form, known for dynamical structure factors [6], to the case of M_{rl} relaxing modes and M_{pr} pairs of propagating excitations, supported by a liquid. Within the analytical three-variable treatment (3), when one hydrodynamic relaxing mode (6) and the pair of

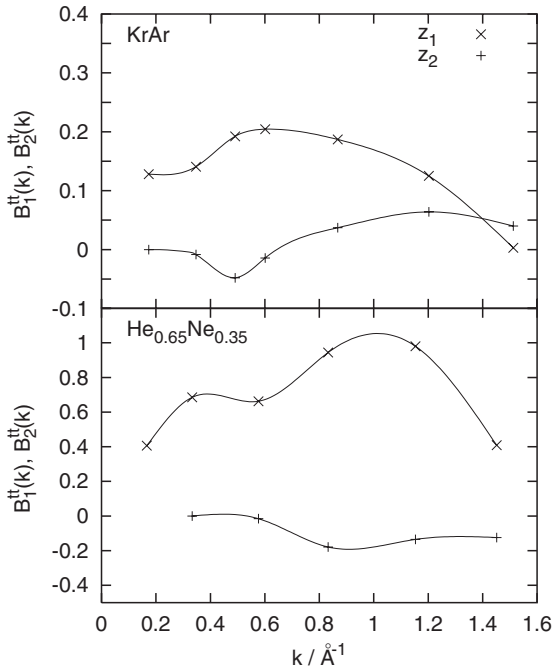

Figure 3. Symmetric amplitudes $B^{tt}(k)$ of contributions from the hydrodynamic sound ($z_1(k)$) and high-frequency ($z_2(k)$) branches to the dynamical structure factor $S_{tt}(k,\omega)$. The spline interpolation is shown by solid curves.

propagating optical-like excitations (7) have been found, the amplitudes $A^{xx}(k)$ and $B^{xx}(k)$ corresponding to the dynamical structure factor $S_{xx}(k,\omega)$ can be written in the long-wavelength limit as follows:

$$A^{xx}(k) = 1 + k^2\Delta + \mathrm{O}(k^4), \qquad B^{xx}(k) = -k^2\Delta + \mathrm{O}(k^4) \tag{13}$$

with

$$\Delta = \frac{1}{\Gamma^2(0) + \omega^2(0)}\{2\Gamma(0)D_{12} - x_1x_2k_BT\bar{m}^{-1}\}. \tag{14}$$

It is seen in (14) that, depending on the values of the mutual diffusion coefficient, the temperature and the damping of the optical-like branch $\Gamma(0)$ at $k = 0$, the factor Δ can be either positive or negative. Note that the expression (13) is quite general for description of contributions from non-hydrodynamic propagating modes to hydrodynamic spectral functions, and this is the main reason that such modes are practically *invisible in real experiments* for small k.

In figure 3 the k-dependences of the amplitudes $B_1^{tt}(k)$ and $B_2^{tt}(k)$ from the two propagating branches $z_1(k)$ and $z_2(k)$ to the total dynamical structure factor $S_{tt}(k,\omega)$, calculated for KrAr and $He_{0.65}Ne_{0.35}$, are shown. These modes describe the density fluctuations and were obtained numerically within the GCM approach using the basis set $\boldsymbol{A}^{(14)}(k,t)$. For both systems the amplitude of the hydrodynamic sound mode $z_1(k)$ tends in the $k \to 0$ limit to the constant value γ^{-1}, predicted by the hydrodynamic theory, while the contribution from the high-frequency optical-like mode $z_2(k)$ shows a fast decay when k decreases. The observed behaviour of $B_2^{tt}(k)$ strongly supports the recent experimental results obtained by Bafile *et al* [8] for $He_{0.77}Ne_{0.23}$, in which clear side peaks in $S_{tt}^{\exp}(k,\omega)$ were observed at frequencies that follow the linear

hydrodynamic sound dispersion up to $k \simeq 1.8$ Å^{-1}. A similar picture of small contributions to $S_{tt}(k, \omega)$ from optical-like excitations $z_2(k)$ in comparison with the hydrodynamic sound ones is observed for the KrAr mixture. However, it is possible to observe the contributions from optical-like modes to one of the ten independent hydrodynamic spectral functions that can be estimated for conserved dynamical variables. And, as follows from our previous papers [2, 3], to obtain the correct dispersion of the high-frequency branch one must study in the small-wavenumber region the positions of the maxima of the spectral function $C_{xx}(k, \omega)$, and not those of the partial current–current spectral functions $C_{ii}(k, \omega)$, $i = 1, 2$, because the 'partial' picture of the two branches is not valid in the small-wavenumber region (see, e.g., [11, 12]).

We conclude by making the following remarks:

(i) It is shown in general that there exist propagating solutions of the generalized Langevin equation for mass–concentration fluctuations, which correspond to optical-like excitations in a binary mixture.
(ii) We derived the condition for their existence in the small-k region.
(iii) It is shown that the high mutual diffusion and tendency of demixing (when mainly like atoms surround a tagged particle) suppress the optical-like branch, and in this case the damping of optical-like excitations is very strong and the frequency tends to zero at non-zero wavenumber.
(iv) The analysis of mode contributions shows that for the systems considered it is impossible to observe the optical-like branch $z_2(k)$ for the experimental total structure factor $S_{tt}(k, \omega)$, because its contribution to $S_{tt}(k, \omega)$ decays as k^2 when k decreases.

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