Collective dynamics in liquid lead. II. Mode contributions to time correlation functions

Taras Bryk[1,2] and Ihor Mryglod[2]

[1]*Department of Chemistry, University of Houston, Houston, Texas 77204*
[2]*Institute for Condensed Matter Physics, National Academy of Sciences of Ukraine, 1 Svientsitskii Street, UA-79011 Lviv, Ukraine*

Mode contributions of different collective excitations to the density-density time correlation function in liquid lead are studied within the nine-variable approach of generalized collective modes. It is shown, that a kinetic relaxing mode, caused by slow density fluctuations, defines almost completely the shape of density-density time correlation function for wave numbers close to the main peak position of the static structure factor. The physical meaning of this mode is discussed.

Collective dynamics in pure and complex liquids is usually studied by means of an analysis of time correlation functions. As an example, the density-density time correlation function $F_{nn}(k,t)$, obtained in an analytical theory or in computer experiment, can be used for interpretation of experimental dynamical structure factor $S(k,\omega)$, which is, in fact, the spectral function of $F_{nn}(k,t)$ with k and ω being wave number and frequency, respectively. It is obvious that any time correlation function, obtained in molecular dynamics (MD) simulations, contains already in its shape the contributions of all the collective excitations typical for the liquid considered. The simplest picture of different mode contributions to the time correlation functions can be obtained within the hydrodynamic treatment [1,2] when values of k and ω are small enough (the hydrodynamic region). In this case for a simple liquid one has three main contributions to the density-density time correlation function $F_{nn}(k,t)$, namely,

$$\frac{F_{nn}^{h}(k,t)}{F_{nn}^{h}(k,0)} = \frac{\gamma-1}{\gamma}e^{-D_{T}k^{2}t} + \frac{1}{\gamma}\left[\cos\{c_{s}kt\}\right.$$
$$\left. + \frac{(3\Gamma-b)k}{c_{s}}\sin\{c_{s}kt\}\right]e^{-\Gamma k^{2}t}, \quad (1)$$

where c_{s}, Γ, D_{T}, γ, and b are the adiabatic sound velocity, sound attenuation coefficient, thermal diffusivity, ratio of specific heats, and a constant dependent on thermodynamic parameters, respectively. One can easily distinguish the contribution to $F_{nn}(k,t)$ from the purely relaxing thermodiffusive mode $d_{T}(k)=D_{T}k^{2}$, and two oscillating contributions (symmetric and asymmetric ones) from the propagating sound excitations $z_{s}^{\pm}(k)=\Gamma k^{2}\pm ic_{s}k$. The asymmetric term in Eq. (1) has the leading order $\sim k$ and, because of asymmetry with respect to t, does not contribute to the static value $F_{nn}(k,0)$. Thus, in the hydrodynamic region the collective dynamics of a pure liquid is well described by the set of three hydrodynamic [see Eq. (1)] collective excitations, which correspond to the most slow time-dependent processes in small-(k,ω) region. Note that from the point of view of several microscopic time scales the expression (1) means also, that any nonhydrodynamic collective modes existing in a liquid do not contribute sufficiently to the density-density time correlation function in the hydrodynamic region (such contributions should be at least higher order in magnitude than k).

Beyond the hydrodynamic region the short-time processes become more important in liquid dynamics. Kinetic collective modes (relaxing and propagating ones) begin to contribute sufficiently to all time correlation functions. Therefore, the simple expression (1) cannot be applied for the study of dynamical properties of liquids as well as for correct estimation of collective mode spectrum. As examples of kinetic excitations are known in the literature, we can mention optic-like excitations in ionic liquids, so-called "fast sound" and "slow sound" modes in binary mixtures, and shear waves in transverse dynamics of liquids. All these kinetic propagating collective modes cannot be described within the standard hydrodynamic treatment.

One of the most efficient methods for the study of collective dynamics of liquids in a wide range of k and ω is the approach of generalized collective modes (GCM) [3,4]. This method is based on the concept of generalized collective excitations and allows one, in particular, to derive more general expression for the function $F_{nn}(k,t)$, which contains already the contributions from the kinetic collective excitations [5]. In our recent study of microscopic dynamics in liquid Pb [6] we reported the results obtained for spectra of generalized collective excitations in liquid lead within the nine-variable approximation of GCM approach at two temperatures. Beyond the hydrodynamic region three pairs of kinetic propagating modes were found in addition to the generalized sound modes. It was shown that two of them describe the propagation of heat waves. We found also one purely relaxing kinetic mode with the damping coefficient being the smallest one in the region of intermediate wave numbers. This implied a strong effect of this relaxing mode onto the density-density time correlation function for wave numbers k being in the range of the main maximum of the static structure factor $S(k)$. In order to verify the last statement a more detailed numerical and analytical studies of the origin of the kinetic relaxing mode and the mode contributions to density-density time correlation function have to be performed. Recently, similar studies have been done for longitudinal dynamics in liquid bismuth [7,5] as well as for the transverse dynamics in several binary liquids [8]. To our knowledge the results for the separated mode contributions, which include the data for kinetic collective modes, were reported in these papers for the first time.

The goal of this study is to investigate the mode contributions from the generalized hydrodynamic and kinetic col-

lective excitations to the density-density time correlation function of liquid lead. We focus special attention on the role of relaxing kinetic collective modes and discuss this problem in more detail. In our study we use the results for generalized collective excitations, obtained in [6] for both thermodynamic points considered.

Within the N_v-variable approximation of the GCM approach the solutions for time correlation functions could be written (see, e.g., [5]) in an analytical form via the eigenvalues and eigenvectors of the generalized hydrodynamic operator:

$$F_{ij}(k,t) = \sum_{\alpha=1}^{N_r} A_{ij}^{\alpha}(k) e^{-d_{\alpha}(k)t} + \sum_{\alpha=1}^{N_p} \{ B_{ij}^{\alpha}(k) \cos[\omega_{\alpha}(k)t]$$

$$+ C_{ij}^{\alpha}(k) \sin[\omega_{\alpha}(k)t] \} e^{-\sigma_{\alpha}(k)t}, \qquad (2)$$

where the amplitudes $A_{ij}^{\alpha}(k)$, $B_{ij}^{\alpha}(k)$ and $C_{ij}^{\alpha}(k)$ are the real functions of wave number and are easily expressed via eigenvectors associated with relaxing $d_{\alpha}(k)$ or propagating $z_{\alpha}(k) = \sigma_{\alpha}(k) \pm i\omega_{\alpha}(k)$ eigenvalues. Expression (2) is a generalization of hydrodynamic solution (1) onto the case of N_r relaxing and N_p pairs of propagating collective modes. By taking Fourier transform of Eq. (2) one obtains the expression for a spectral function $\widetilde{F}_{ij}(k,\omega)$ with the separated mode contributions. It is seen from Eq. (2) that $\widetilde{F}_{ij}(k,\omega)$ will contain the contributions from N_r central Lorentzians, $2N_p$ noncentral Lorentzians (symmetric contributions) at frequencies $\pm \omega_{\alpha}$, and $2N_p$ nonLorentzian corrections (asymmetric contributions), respectively.

In Figs. 1(a)–1(c) the leading mode contributions to the function $F_{nn}(k,t)$, calculated for liquid lead at the temperature of $T_h = 1170$ K (see [6]), are shown for three values of k. These results are obtained on the basis of our expression (2). By solid lines the molecular dynamics (MD)-derived functions $F_{nn}(k,t)$ are shown. Dashed lines correspond to the GCM functions (2) and almost coincide with MD functions, that means very good quality of the nine-variable approximation, used in our calculations. Note that the GCM approach does not require any adjustable or fitting parameters. Dotted lines show the total contribution from the generalized sound excitations $z_2(k)$, i.e., the sum of symmetric and asymmetric terms associated with the sound modes. Dash-dotted lines correspond to the heat excitations: inside the propagation gap for the heat waves, i.e., for $k < k_H$ (see [6]), this line represents the contribution, caused by the thermodiffusive relaxing mode $d_1(k)$, while for $k > k_H$ it gives the total contribution from the heat waves $z_1(k)$ (the sum of symmetric and asymmetric terms). Purely relaxing mode $d_2(k)$ causes the contributions shown by two-dash lines. It is well seen in Fig. 1(a), that in complete agreement with predictions of the hydrodynamic theory [1,2], the shape of density-density time correlation function for the smallest k value, considered in our study, is almost completely determined by the contributions from the hydrodynamic excitations [the pair of propagating sound excitations $z_2(k)$ and the thermodiffusive mode $d_1(k)$]. For k values slightly beyond the propagation gap $(k > k_H)$ the heat waves cause rather
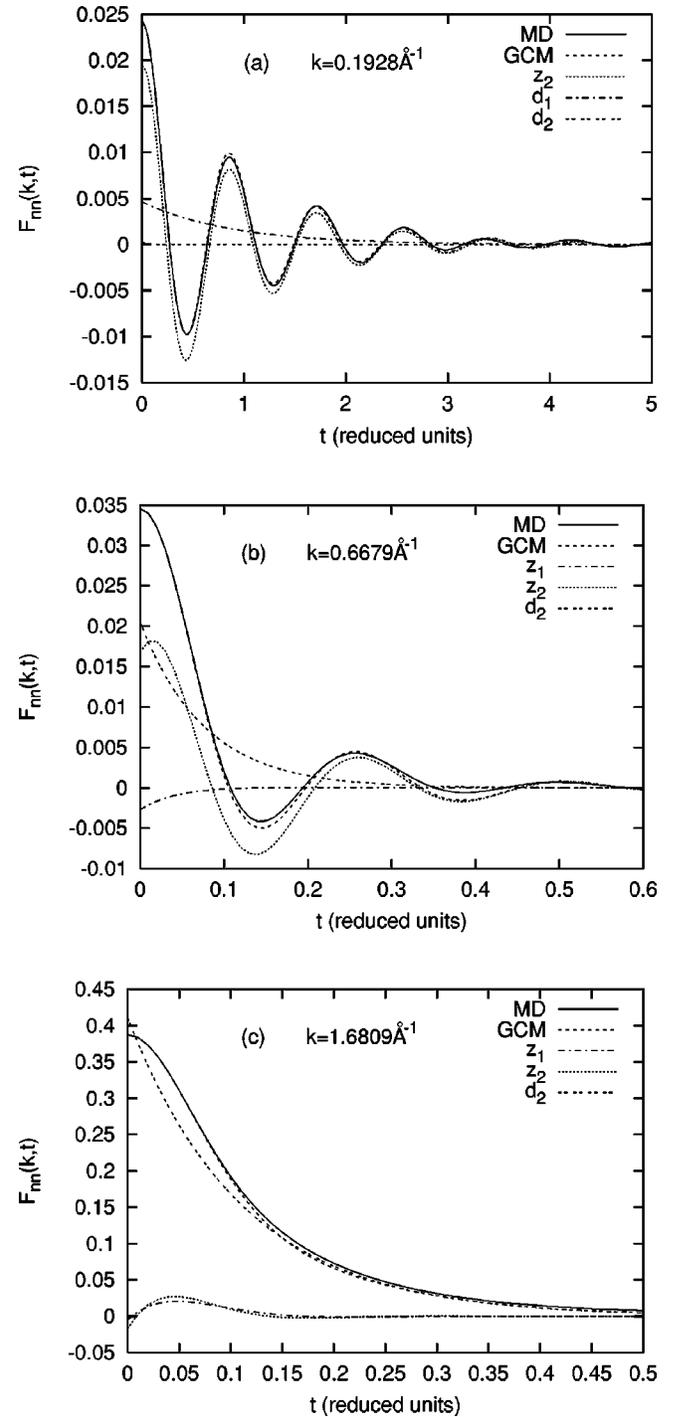

FIG. 1. Separated mode contributions to the density-density time correlation function $F_{nn}(k,t)$ for three-k values at $T_h = 1170$ K. The MD-derived function and the result of nine-variable GCM study are shown by solid and dashed lines. Mode contributions from the low-frequency kinetic heat waves $z_1(k)$, the sound excitations $z_2(k)$, and the kinetic relaxing mode $d_2(k)$ are plotted by dash-dotted, dotted, and two-dash lines, respectively. For the smallest k value the contribution from the thermodiffusive mode $d_1(k)$ is shown by dash-dotted line. Time scale is $\tau_h = 2.3935$ ps.

small negative contribution, while the shape of function $F_{nn}(k,t)$ is formed mainly by the sound excitations $z_2(k)$ and the relaxing kinetic mode $d_2(k)$ in comparable amounts. When k increases further and gets closer to the main peak of static structure factor $k \sim k_p$, the contributions of the low-frequency heat waves and the sound excitations become comparable and much smaller than the term associated with the kinetic relaxing mode $d_2(k)$, so that the long-time tail of $F_{nn}(k,t)$ in the region $k \sim k_p$ is completely defined by the kinetic relaxing mode $d_2(k)$. Similar behavior was observed as well for the lower temperature $T_l = 623$ K.

The relaxing kinetic mode $d_2(k)$ is well reproduced within the viscoelastic subset of dynamical variables $\mathbf{A}^{(5)}(k,t)$ [see Eq. (23) in [6]]. Hence, its origin is mainly defined by viscoelastic processes. This is in contrast with hydrodynamic behavior (1), where the relaxing contribution to density-density time correlation function is only due to thermodiffusive processes. To study the origin of relaxing mode $d_2(k)$ in more detail let us consider the simplest case of dynamics when only one dynamic variable $\mathbf{A}^{(1)} = \{n(k,t)\}$, namely, the particles' density $n(k,t)$ is taken into account. This gives immediately the solution for the unique collective mode $d_0(k)$, which has very simple form:

$$d_0(k) = \tau_{nn}^{-1}(k).$$

The quantity $\tau_{nn}(k)$ was defined in [6] and is the generalized correlation time, associated with the density-density time correlation function (see Eq. (14) in [6]). In Fig. 2 we show the results for two eigenvalues $d_0(k)$ and $d_2(k)$, obtained within the one- (line with triangles) and nine-variable (closed boxes) approximations of GCM approach at $T_l = 623$ K and $T_h = 1170$ K. In the low-temperature state a quantitative agreement between two eigenvalues for $k \sim k_p$ is a striking feature. This implies that at low temperatures the slow density fluctuations for k values being in the region of the main peak's position (what corresponds in fact to the short-range fluctuations with the average interparticle distance $\langle a \rangle$, $k_p \approx 2\pi/\langle a \rangle$) *are well separated in time* (see Fig. 6 in [6]) from the thermal processes as well as from the fast density fluctuations, which are responsible for sound propagation in this region, and *determine almost completely* the shape of the density-density time correlation function. Hence, one concludes that the well-known de Gennes slowing the density fluctuations [9] can be directly associated with the relaxing kinetic mode $d_2(k)$.

For the higher temperature the quantitative agreement between the results, found for $d_2(k)$ and $d_0(k)$, is not so perfect due to stronger coupling with the thermal fluctuations, found in [6]. However, the contribution from the mode $d_2(k)$ to $F_{nn}(k,0)$ is still dominant when k is close to k_p [see, e.g., Fig. 1(c) for the wave number $k = 1.6809$ Å^{-1}]. In particular, such a specific behavior can explain why the mode-coupling theory of freezing was so successful by treating just the density fluctuations nearby the region of the main peak of static structure factor and completely ignoring the thermal properties.

Within the simplified one-variable theory one gets the expression for the density-density time correlation function
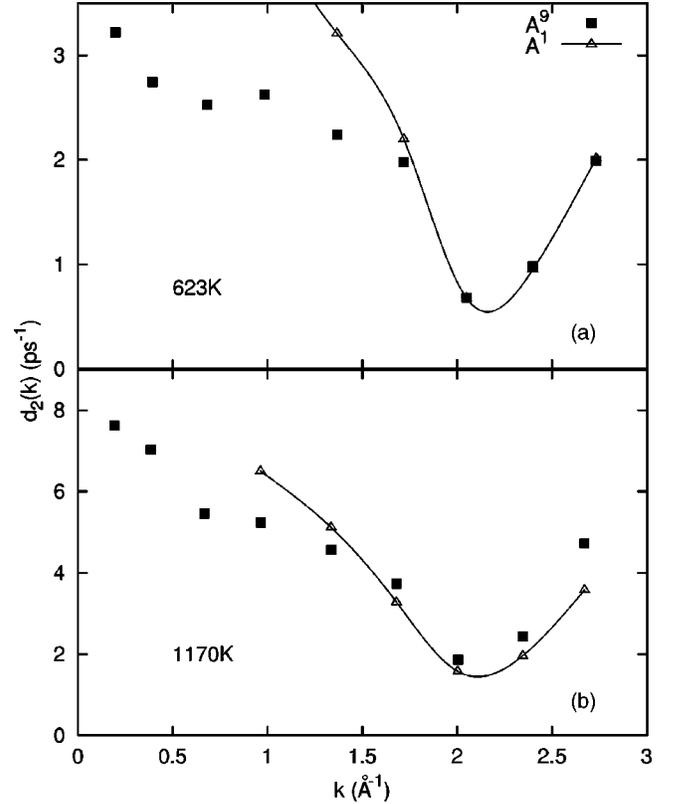

FIG. 2. Relaxing kinetic mode $d_2(k)$ (symbols) obtained in the nine-variable approximation for the basis set $\mathbf{A}^{(9)}$ at the temperatures: (a) $T_l = 623$ K, and (b) $T_h = 1170$ K. The one-variable relaxing mode $d_0(k)$ is shown by spline-interpolated dashed line with triangles.

$F_{nn}(k,t)$ in the following single-exponential form:

$$F_{nn}^1(k,t) = G_{nn}^1(k) \exp\{-d_0(k)t\} \equiv S(k) \exp\{-t/\tau_{nn}(k)\}. \tag{3}$$

Thus, within such a treatment the function $\tau_{nn}(k)$ gives in fact the estimation for some specific time of relaxation, which, in particular, for $k = k_p$ has a meaning of the particle's lifetime in the cage of nearest neighbors. Note also that for $k \sim k_p$ the kinetic relaxing mode $d_2(k)$ can be directly connected with so-called cage diffusion [10]. Thus, one can call this mode as the *structural relaxation mode*.

In the hydrodynamic range the damping coefficient of the mode $d_2(k)$ tends to nonzero value, and its contribution to the density-density time correlation function $F_{nn}(k,t)$ becomes negligible. However, we point out that the role of relaxing kinetic mode $d_2(k)$ increases rapidly when k becomes larger. Our recent results [7], obtained for liquid metallic Cs and a semimetallic liquid Bi, show obviously, that beyond the small-k region the relaxing mode $d_2(k)$ is the lowest one and this mode makes the leading contribution to the shape of density-density time correlation function for intermediate and large wave numbers in complete agreement with the results found in this study for liquid Pb. Note that the normalized mode amplitude, describing the contribution from $d_2(k)$ to $F_{nn}(k,t)$, can even be larger than unity, while the sound excitations at $k \sim k_p$ contribute to the shape of density-density time correlation function with the negative

sign, $B_{nn}^2(k \approx k_p) < 0$ [compare the contributions from $d_2(k)$ and $z_2(k)$ at $t = 0$ in Fig. 1(c)]. For both temperatures, $T_l = 623$ K and $T_h = 1170$ K, we obtained the negative symmetric amplitudes for sound excitations with $k \approx k_p$, although for the low-temperature state they were extremely small.

Negative sign of amplitudes from sound excitations in the region of wave numbers close to main peak position of $S(k)$ was found previously for a liquid Ar in Ref. [11], where the fitting procedure for dynamical structure factor to the three-Lorentzian expression was used by the authors. Later, using the "damped harmonic oscillator" model (DHO) de Schepper and co-workers [12] explained the negative sign of sound amplitudes for the case of liquid He. The DHO model is based on the treatment of just two dynamical variables $\{n(k,t), J(k,t)\}$. However, as it is shown above, the relaxing kinetic mode $d_2(k)$ reflects the most slow density fluctuations, described well in the region $k \approx k_p$ even by the dynamics of single variable $n(k,t)$.

Using the three-variable basis set $\{n(k,t), J(k,t), \dot{J}(k,t)\}$ and assuming that this set would be more appropriate for the description both the relaxing eigenvalue $d(k) \approx d_2(k)$ and the propagating sound mode $z(k) \approx z_2(k)$, we derived an analytical expression for density-density time correlation function and found

$$\frac{F_{nn}^3(k,t)}{F_{nn}^3(k,0)} = \bar{A}_{nn}(k)e^{-d(k)t} + [\bar{B}_{nn}(k)\cos\{\omega(k)t\}$$
$$+ \bar{C}_{nn}(k)\sin\{\omega(k)t\}]e^{-\sigma(k)t}, \quad (4)$$

with the normalized amplitudes

$$\bar{A}_{nn}(k) = \frac{\sigma^2(k) + \omega^2(k) - \langle \bar{\omega}_k^2 \rangle}{[d(k) - \sigma(k)]^2 + \omega^2(k)},$$

$$\bar{B}_{nn}(k) = \frac{d(k)[d(k) - 2\sigma(k)] + \langle \bar{\omega}_k^2 \rangle}{[d(k) - \sigma(k)]^2 + \omega^2(k)},$$

$$\bar{C}_{nn}(k) = \frac{d^2(k)\sigma(k) + d(k)[\omega^2(k) - \sigma^2(k)] - \langle \bar{\omega}_k^2 \rangle[d(k) - \sigma(k)]}{([d(k) - \sigma(k)]^2 + \omega^2(k))\omega(k)}, \quad (5)$$

where the quantity $\langle \bar{\omega}_k^2 \rangle$ denotes the normalized second order frequency moment of $S(k,\omega)$. It is seen that depending on the ratio between $d(k)$ and the damping coefficient $\sigma(k) = \text{Re}\, z(k)$ one can obtain either positive or negative amplitudes of the symmetric contribution $\bar{B}_{nn}(k)$. In particular, this explains why the normalized amplitude $\bar{A}_{nn}(k)$ can be bigger than unity at $k \approx k_p$. It is also seen from the expression for $\bar{B}_{nn}(k)$, that for strongly overdamped sound excitations, when $\sigma(k) \gg d(k)$, and small values of second frequency moment $\langle \bar{\omega}_k^2 \rangle$ (heavy atoms and low temperatures), the amplitude $\bar{B}_{nn}(k)$ will be negative. Thus, in this case one obtains within three-variable model the negative amplitudes of sound contribution to the density-density time correlation function or dynamic structure factor $S(k,\omega)$.

We conclude with the main results of this study:

(i) The kinetic relaxing mode $d_2(k)$ makes the leading contribution to the shape of density-density time correlation function in the region of wave numbers close to the position of main peak $k = k_p$ of the static structure factor $S(k)$. This kinetic relaxing mode is caused by slow density fluctuations and is well separated from all the other collective excitations when $k \sim k_p$;

(ii) In the wide range of wave numbers k the low-frequency heat waves do not contribute sufficiently to the density-density time correlation function;

(iii) The negative amplitudes, describing the contribution of sound excitations to the function $F_{nn}(k,t)$ in the region $k \approx k_p$, can be understood within the standard three-variable viscoelastic model.

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