

Origin of large Landau-Placzek ratio in a liquid metallic alloy

Taras Bryk^{1,2,a)} and J.-F. Wax³

¹*Institute for Condensed Matter Physics, National Academy of Sciences of Ukraine, 1 Svientsitskii Street, UA-79011 Lviv, Ukraine*

²*Institute of Applied Mathematics and Fundamental Sciences, National Polytechnic University of Lviv, UA-79013 Lviv, Ukraine*

³*Laboratoire de Physique des Milieux Denses, Université Paul Verlaine Metz, 1, boulevard Arago 57078 Metz Cedex 3, France*

(Received 21 July 2011; accepted 22 September 2011; published online 21 October 2011)

Dynamic structure factors for $\text{Na}_c\text{K}_{1-c}$ liquid metallic alloys and pure components are studied by molecular dynamics simulations. Large values of Landau-Placzek ratio for four compositions of the liquid alloy are analyzed by wave-number dependent contributions from relaxation and propagating processes within the generalized collective modes method. The origin of the large Landau-Placzek ratio for liquid alloys is discussed. © 2011 American Institute of Physics. [doi:10.1063/1.3651170]

I. INTRODUCTION

Theoretical and simulation studies of dynamic properties of liquids are of great interest because of permanent improvement of resolution of inelastic x-ray scattering (IXS) technique,¹ which brings important information about atomic dynamics outside the hydrodynamic regime. On macroscopic space and time scales, the hydrodynamic theory, which is in fact a continuum approach,^{2,3} predicts dynamic structure factors $S(k, \omega)$, where k and ω are wave number and frequency, respectively, that contain two Brillouin side peaks (centered at nonzero frequency) in addition to the central Rayleigh one at $\omega = 0$. In both pure and binary liquids, these side peaks stem from acoustic collective excitations over hydrodynamic ranges of wave numbers and frequencies. On the other hand, two relaxation processes connected respectively with thermal and mutual diffusivities contribute to the central peak in binary mixtures, while only the first one does, of course, in a pure liquid. In the specific case of pure liquid metals, the side peaks of the dynamic structure factor are well pronounced in agreement with a rather small Landau-Placzek ratio of integrated intensities of the central and side peaks^{4,5}

$$\frac{I_{\text{central}}}{2I_{\text{side}}} = (\gamma - 1). \quad (1)$$

As an example, the ratio of the specific heats, γ , lies between 1.06 and 1.15¹ in the case of liquid alkali metals; this means that I_{side} , the integrated intensity of Brillouin peaks, is from 3 up to 8 times as large as I_{central} , the one of the Rayleigh peak. The case of binary alloys seems to be strongly different. Indeed, for very small momentum transfer, scattering experiments on liquid Na-Cs,⁶ K-Cs,⁷ and Na-K⁸ alloys show a very strong central peak and either small side peaks or shoulders in the shape of the scattered intensities depending on resolution of the experiment. However, in spite of these striking experimental facts, the issue of the relative intensities of the central and side peaks of $S(k, \omega)$ in the case of liquid alloys has not been discussed so far in the literature.

^{a)} Author to whom correspondence should be addressed. Electronic mail: bryk@icmp.lviv.ua.

Collective dynamics of liquid alloys is also of great interest because of the contributions of many non-hydrodynamic (kinetic) effects observed beyond the hydrodynamic regime in molecular dynamics (MD) simulations, as well as in inelastic x-ray and neutron scattering experiments. These effects include propagating non-hydrodynamic modes like so-called “fast sound” in a disparate-mass binary liquid alloys,^{9,10} or optic-like modes deduced from scattering experiments on $\text{Li}_{0.3}\text{Bi}_{0.7}$ ¹¹ and $\text{Na}_{0.57}\text{K}_{0.43}$ ⁸ alloys. In this study we are mainly interested in non-hydrodynamic relaxation processes and their contributions to the central peak of $S(k, \omega)$. The most obvious non-hydrodynamic relaxation process in liquids is the structural relaxation and one of the most interesting issues is how its contribution is compared to the ones from hydrodynamic relaxation processes outside the hydrodynamic regime. It is obvious that the structural relaxation causes deviation from the standard Landau-Placzek ratio for binary liquids³ that takes into account only hydrodynamic processes.

The only theoretical method of analysis of collective dynamics of liquids that permits to separate contributions from different relaxation and propagating collective modes to various time correlation functions and corresponding dynamic structure factors is the approach of generalized collective modes (GCM).^{12,13} This method is based on an extension of hydrodynamic set of equations by additional ones that permits to describe non-hydrodynamic processes and their coupling in local approximation with hydrodynamic modes. The output of the GCM analysis is a set of wave-number-dependent dynamic eigenmodes and corresponding eigenvectors that define mode contributions to dynamic structure factors in a studied window of frequencies and wave numbers. The GCM approach in connection with MD simulations is nowadays one of the most powerful and reliable methods of analysis of collective dynamics in disordered systems. Numerous analytical GCM results on non-hydrodynamic processes such as optic-like modes,¹⁴ heat waves,¹⁵ “positive dispersion” of sound,¹⁶ or structural relaxation^{17,18} give new insight into origin of different non-hydrodynamic modes and their contributions to the time correlation functions on the boundary of hydrodynamic regime. Contributions from the optic-like modes and

“fast sound” modes in a wide range of wave numbers to the total and partial dynamic structure factors were studied intensively within the GCM approach before, however a little is known about the different contributions from relaxation processes to the central peak of dynamic structure factors for binary and many-component liquids outside the hydrodynamic region. Namely, these contributions in the long-wavelength limit are connected with the Landau-Placzek ratio.³ Therefore, our aim was to perform the GCM analysis of collective dynamics of a binary liquid alloy, estimate leading contributions to the central peak of $S(k, \omega)$, and compare them with the case of pure liquids.

The paper is organized as follows: in Sec. II, we will shortly describe the details of our MD simulations and GCM analysis. Section III will contain the analysis of the relaxing dynamic eigenmodes in liquid alloys obtained within an eight-variable thermo-viscoelastic model and their contributions to the central peak of total dynamic structure factor, and Sec. IV will summarize the conclusions of this study.

II. METHOD

A. Molecular dynamics simulations

We performed MD simulations of model systems of pure Na and K as well as of $\text{Na}_c\text{K}_{1-c}$ liquid alloys with $c = 0.2, 0.4, 0.6,$ and 0.8 at temperature 373 K. At this temperature just above Na melting point, both pure metals and the four alloys are liquid according to the phase diagram. Considering the same temperature ensures to only observe composition effects. This could be important since diffusion properties have shown to be very sensitive to temperature. Each system in simulations was containing 4000 particles under periodic boundary conditions in standard microcanonical ensemble with number density matching the experimental value. The effective pair interactions were obtained from Fiolhais’ pseudopotentials¹⁹ and Ichimaru-Utsumi local field correction.²⁰ The reliability of this model had been tested in a previous study of static properties of liquid Na-K alloys at temperature 373 K.²¹ Although more recent local-field factors exist in the literature (see Ref. 22, for instance), their impact has been shown to be negligible, at least as far as static properties are concerned.²³ The cut-off radius of effective pair potentials was 20 Å, which was 25% larger than in our previous study.²¹ Higher cut-off was needed for a better representation of energy and heat fluctuations, which were sampled directly in MD simulations with the purpose of subsequent GCM analysis of collective dynamics.

In our simulations, the time step was 10 fs and the production runs were 300 000 steps long. Each sixth configuration was used to evaluate the static averages and time correlation functions. Thus, the elements of the generalized hydrodynamic matrix are computed with an accuracy high enough to avoid any unphysical behavior of the dynamic eigenvalues, as required by the GCM approach. Twenty k -points were considered when estimating k -dependent quantities. The smallest k -values reached in the current study were in a range from 0.09 \AA^{-1} (for pure K) to 0.11 \AA^{-1} (for pure

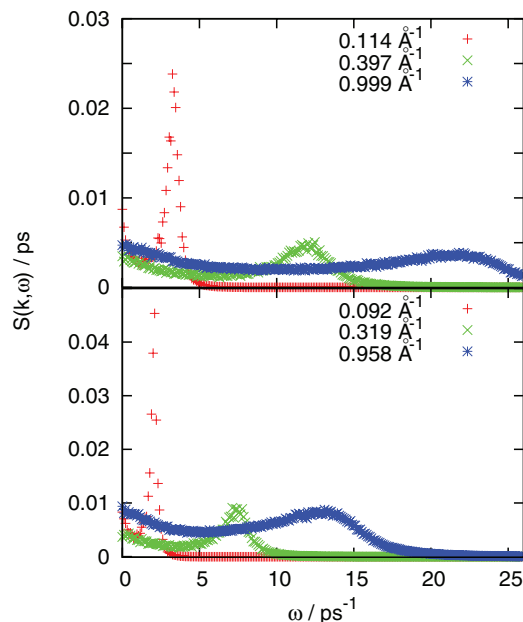


FIG. 1. Dynamic structure factors for pure Na (top frame) and K (bottom frame) at $T = 373$ K for three wavenumbers on the boundary and outside the hydrodynamic regime.

Na). Averages were performed over all the wavenumbers with identical absolute values but different directions.

Dynamic structure factors were calculated as numerical Fourier transforms of total density time autocorrelation functions, $F(q, t)$, for each pure component (Fig. 1) and of

$$F_{tt}(q, t) = cF_{\text{NaNa}}(q, t) + (1 - c)F_{\text{KK}}(q, t) + 2\sqrt{c(1 - c)}F_{\text{NaK}}(q, t) \quad (2)$$

for each liquid alloy (Fig. 2). This latter function corresponds to Bhatia-Thornton’s definition of number-number dynamic structure factor and differs from the experimentally measured quantities in the weighting by the diffusion lengths. The relative intensities of central and side peaks show completely different behaviors. For pure liquid K and Na in the region of small wave numbers, one observes pronounced Brillouin side peaks and a relatively small value of $S(k, \omega = 0)$, which is defined by thermal diffusivity according to hydrodynamic theory. The relative intensities of central and side peaks are pictured by Landau-Placzek ratio (Eq. (1)) with values of γ being close to unity for liquid metals. In this study we are interested mainly in the wavenumber region $k < 1 \text{ \AA}^{-1}$, because the Landau-Placzek ratio corresponds to hydrodynamic picture, while for large wavenumbers the non-hydrodynamic structural relaxation is responsible for leading contribution to the central peak in pure liquids. As it is seen from Fig. 2 in liquid alloys the central peaks of dynamic structure factor $S_{tt}(k, \omega = 0)$ have large amplitudes for all the studied compositions, so that the side peaks can only be distinguished on a logarithmic scale.

B. GCM approach

The essential difference between pure metals and alloys in the contributions to the central and side peaks is studied

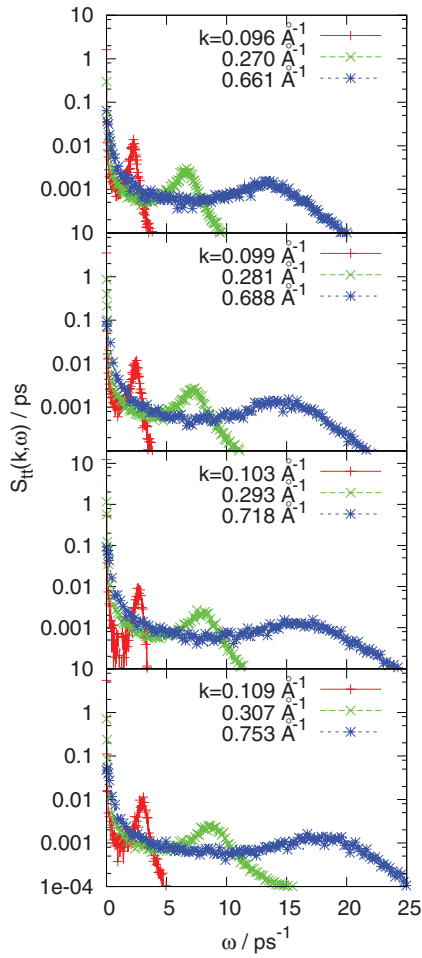


FIG. 2. Total dynamic structure factors, $S_H(k, \omega)$, at three wave numbers for four compositions of $\text{Na}_x\text{K}_{1-c}$ liquid alloys. Compositions $c = 0.2, 0.4, 0.6$, and 0.8 are displayed from top to bottom. Logarithmic scale was used in order to show large amplitudes of the central peaks in the metallic alloy.

here by the theoretical GCM approach. For pure liquid metals, the GCM analysis of time correlation functions was performed within a five-variable (thermo-viscoelastic) dynamic model

$$\mathbf{A}^{(5)}(k, t) = \{n(k, t), J^L(k, t), \varepsilon(k, t), \dot{J}^L(k, t), \dot{\varepsilon}(k, t)\} \quad (3)$$

for the case of longitudinal dynamics. Particle density $n(k, t)$, density of longitudinal mass-current $J^L(k, t)$, and energy density $\varepsilon(k, t)$ are the hydrodynamic variables defined as follows:

$$\begin{aligned} n(k, t) &= \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{-i\mathbf{k}\mathbf{r}_j}, \\ J^L(k, t) &= \frac{m}{\sqrt{N}} \sum_{j=1}^N \frac{k v_j}{k} e^{-i\mathbf{k}\mathbf{r}_j}, \\ \varepsilon(k, t) &= \frac{1}{\sqrt{N}} \sum_{j=1}^N \varepsilon_j e^{-i\mathbf{k}\mathbf{r}_j}. \end{aligned} \quad (4)$$

Here, N and m are the number and mass of particles, and ε_j is the single-particle energy of the j -th particle, which can easily be calculated in the case of effective pair potentials such as those used in our MD simulations. The dotted dynamic variables are the extended ones and represent the first time derivatives of the corresponding hydrodynamic variables (Eq. (4)).

In order to study the alloys within the same level of approximation for the treatment of fast processes, we restricted the basis set of dynamic variables to the first derivatives of energy and partial currents. Hence, binary alloys were studied within the following eight-variable dynamic model:

$$\mathbf{A}^{(8)}(k, t) = \{n_A(k, t), J_A^L(k, t), n_B(k, t), J_B^L(k, t), \varepsilon(k, t), \dot{J}_A^L(k, t), \dot{J}_B^L(k, t), \dot{\varepsilon}(k, t)\} \quad (5)$$

for the case of longitudinal dynamics.

All the dynamic variables were easily sampled straight during the MD simulations. Their time evolution has been used to estimate the (in general case 8×8) matrix of their time correlation functions $\mathbf{F}(k, t)$ with elements

$$F_{ij}(k, t) = \langle A_i^*(k, t=0) A_j(k, t) \rangle. \quad (6)$$

Note that energy density and extended variables connected with energy flux were sampled in our simulations - hence our dynamic models represented consistent extension of hydrodynamic description avoiding any fit. This is one of the advantages of actual study because almost all theoretical and simulation studies of collective dynamics in liquids except GCM either ignore heat fluctuations in the analysis or take them into account using some fitting parameters.¹

Having the matrix of time correlation functions with all the elements calculated in MD simulations one can generate the generalized hydrodynamic matrix

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

where $\tilde{\mathbf{F}}(k, z=0)$ is the matrix of Laplace-transformed correlation functions in Markovian approximation. The generalized hydrodynamic matrix was calculated for each k -point sampled in MD and corresponding eigenvalues were estimated. We recall that as many eigenvalues as considered dynamic variables are to be determined. As we will see, they can be either pure real eigenvalues (relaxation modes), $d_\beta(k)$, or pairs of complex conjugated ones (propagating modes)

$$z_\alpha(k) = \sigma_\alpha(k) \pm i\omega_\alpha(k).$$

Thus, the real part, $\sigma_\alpha(k)$, of a complex eigenvalue describes the damping of the corresponding collective excitation, while its imaginary part, $\omega_\alpha(k)$, accounts for its dispersion. Moreover, it may happen that two real eigenvalues merge into a pair of complex ones at a given k -value, or vice versa.

III. GCM ANALYSIS OF CONTRIBUTIONS TO THE DYNAMIC STRUCTURE FACTORS IN NA-K LIQUID ALLOYS

A. Generalized thermodynamic quantities

We will present the calculated generalized (i.e., wavenumber-dependent) thermodynamic quantities needed in the subsequent analysis of the collective dynamics in liquid alloys. The generalized thermodynamic quantities involving heat fluctuations are shown in Fig. 3. The generalized linear thermal expansion coefficient, $\alpha_T(k)$, behaves almost identically in the long-wavelength region, whatever the composition, while the sequence of maxima versus composition is similar to that of total static structure factor in the region of

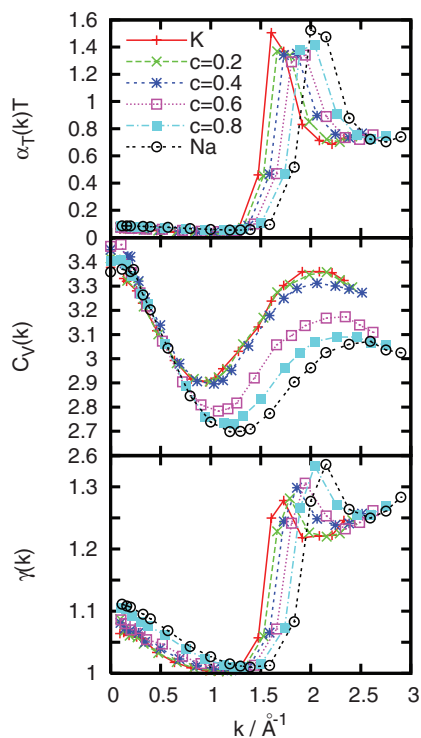


FIG. 3. Wavenumber-dependent thermodynamic quantities: generalized linear expansion coefficient, $\alpha_T(k)$, generalized specific heat at constant volume, $C_V(k)$, and generalized ratio of specific heats, $\gamma(k)$, for pure components and four compositions of the liquid alloy.

their first sharp diffraction peak. An interesting feature is observed in the wavenumber-dependence of the generalized specific heat at constant volume $C_V(k)$. In the atomic-scale region (at large wave numbers), $C_V(k)$ clearly decreases with increasing Na concentration. On the other hand, on macroscopic distances ($C_V(k=0)$ values are given in Table I), it is no more monotonously changing with concentration, but rather reflects the behavior of $S_{cc}(k=0)/c(1-c)$ as accurately determined in Ref. 21, which reveals an influence of the chemical order on this quantity. We should also mention that the limiting values agree with those obtained directly from thermal fluctuations during the MD runs. The generalized ratio of specific heats, $\gamma(k)$, is also very important for the analysis of collective dynamics in liquid alloys. It reflects coupling between thermal and viscous processes on different space scales. It is important to note that the obtained macroscopic values $\gamma(k \rightarrow 0)$ (see Table I) change gradually from 1.06 in the case of pure K to 1.12 for liquid Na, in nice agreement with experimental data for pure components.¹

B. Generalized relaxation modes

For binary liquid alloys we obtained in the long-wavelength region four real eigenvalues and two pairs of complex-conjugated eigenvalues while approximately for $k \sim 0.5 \text{ \AA}^{-1}$ another complex-conjugated pair of eigenvalues emerged and was stable for all higher wave numbers. This additional low-frequency pair of complex-conjugated eigenvalues replaced in the spectrum two real eigenmodes that were mainly connected with heat fluctuations, hence in-

TABLE I. Calculated ratio of the heat capacities, γ , heat capacity at constant volume, C_V , and Landau-Placzek ratio estimated from the long-wavelength asymptotes of Eq. (11) in liquid binary alloys $\text{Na}_c\text{K}_{1-c}$ at 373 K.

c_{Na}	γ	C_V/k_B	LP ratio
0.0	1.06	3.378	0.10
0.2	1.07	3.415	3.33
0.4	1.08	3.451	4.43
0.6	1.09	3.465	7.19
0.8	1.11	3.406	5.53
1.0	1.12	3.359	0.12

dicating the origin of the low-frequency branch of propagating modes as heat waves.^{15,24} The heat waves are non-hydrodynamic excitations and therefore they cannot exist in the long-wavelength region while can be important for heat transport on nanoscales.

In Fig. 4 three most important lowest real eigenvalues (relaxing modes) obtained for compositions $c = 0.2$ (top frame) and $c = 0.6$ (bottom frame) are shown. The mode d_2 is mainly of thermal origin and for $k > 0.5 \text{ \AA}^{-1}$ it disappears from the spectrum of eigenmodes being replaced by heat waves. The relaxation process $d_3(k)$ has complete analogy in pure liquids and is connected with structural relaxation. This is a non-hydrodynamic relaxation process that tends to a non-zero value in the long-wavelength limit:¹⁸

$$d_3(k \rightarrow 0) = \frac{c_\infty^2 - c_s^2}{D_L},$$

where D_L is kinematic viscosity, c_∞ and c_s are the high-frequency and adiabatic speeds of sound. Comparing the relaxing eigenmodes of binary alloys with the standard case of pure liquids one has to mention that there appears an additional slow relaxation process $d_1(k)$ with hydrodynamic asymptote $\sim k^2$ in the long-wavelength limit.

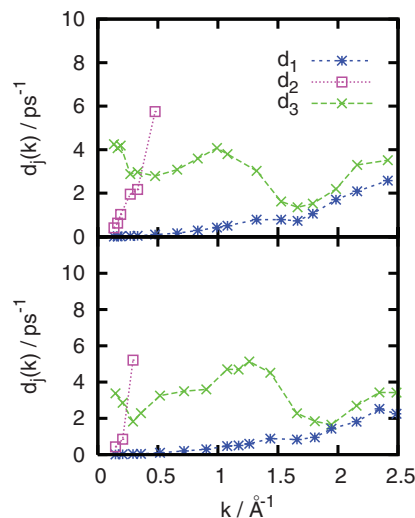


FIG. 4. Three lowest real eigenvalues in liquid binary alloys $\text{Na}_c\text{K}_{1-c}$ for $c = 0.2$ (top) and $c = 0.6$ (bottom). The hydrodynamic modes $d_1(k)$ and $d_2(k)$ correspond in the long-wavelength region to coupled relaxations connected with mutual and thermal diffusivity. The mode $d_3(k)$ is the wave-number-dependent structural relaxation mode.

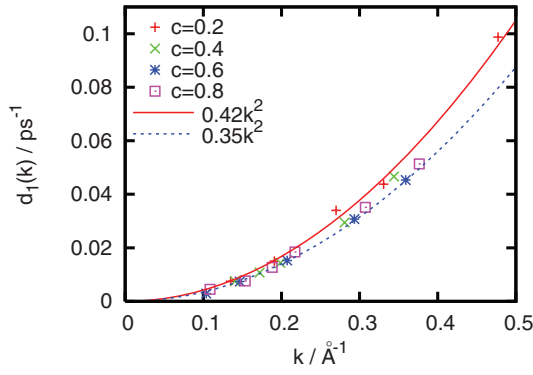


FIG. 5. Lowest relaxation modes in liquid binary alloys $\text{Na}_c\text{K}_{1-c}$ for four different compositions, connected with mutual diffusion of species, and corresponding fit with k^2 -dependence.

The lowest relaxing mode is shown in the long-wavelength range for each composition in Fig. 5. According to its parabolic behavior, this collective mode represents a hydrodynamic process that is absent in pure components. In binary liquids, only two relaxing modes have asymptotes $\sim k^2$ in the hydrodynamic limit: $d_j(k) = D_j k^2$, $j = 1, 2$,³ where coefficients D_j are obtained as:

$$D_j \equiv D_{\pm} = \frac{1}{2} [D_{12}\zeta + D_T \pm \sqrt{(D_{12}\zeta + D_T)^2 - 4D_{12}D_T}], \quad (7)$$

where D_{12} and D_T are mutual and thermal diffusivity, respectively, and the factor ζ describes the coupling between heat and concentration fluctuations and depends on thermal diffusion ratio, specific heat at constant pressure C_p , and factor $Z(k=0)$, which is connected with the long-wavelength limit of static concentration-concentration structure factor.³ In case of very weak coupling between concentration and heat fluctuations, these two relaxing modes can solely be ascribed to relaxing concentration mode

$$d_1(k) \approx D_{12}k^2 \quad (8)$$

and heat mode

$$d_2(k) \approx D_T k^2. \quad (9)$$

The latter is analogous to the hydrodynamic heat mode connected with thermal diffusivity in pure liquids. From the k^2 asymptotes shown in Fig. 5, the relaxing eigenvalues can be fitted to the corresponding hydrodynamic asymptotes with values D_1 , which are in reasonable agreement with the mutual diffusivities calculated directly from MD data in Ref. 21. This is another evidence that coupling between concentration and heat fluctuations is quite small in $\text{Na}_c\text{K}_{1-c}$ liquid binary alloys especially for low concentrations. This perhaps gives evidence that there is stronger effect of thermal fluctuations on behavior of the lowest relaxing collective modes and that approximate expressions (8) and (9) cannot be used for higher concentrations of K for precise calculation of mutual and thermal diffusivities. The increasing effect of thermal fluctuations with concentration of K is supported by the increasing values of the ratio of specific heats shown in Table I.

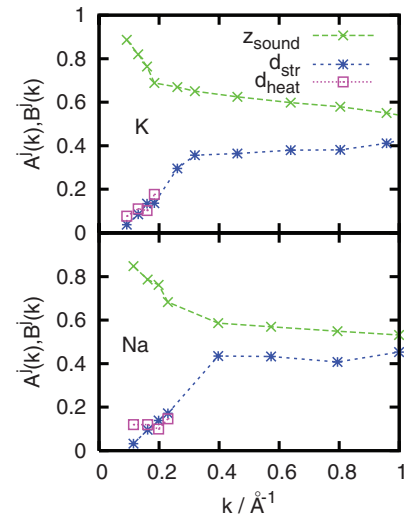


FIG. 6. Mode strengths of propagating and relaxing modes in collective dynamics of pure components K and Na.

C. Mode contributions to dynamic structure factors

One of the important advantages of the GCM approach over the other theoretical analysis schemes is the possibility to represent the density-density time correlation functions of liquids (and corresponding dynamic structure factors) as a separable sum of contributions from hydrodynamic and non-hydrodynamic collective modes. The expression for GCM replicas with real weight coefficients estimated from eigenvectors associated with each eigenvalue writes:

$$\frac{F_{ij}^{(N_v)}(k, t)}{F_{ij}(k)} = \sum_{\alpha=1}^{N_{\text{relax}}} A_{ij}^{\alpha}(k) e^{-d_{\alpha}(k)t} + \sum_{\alpha=1}^{N_{\text{prop}}} [B_{ij}^{\alpha}(k) \cos(\omega_{\alpha}(k)t) + D_{ij}^{\alpha}(k) \sin(\omega_{\alpha}(k)t)] e^{-\sigma_{\alpha}(k)t}. \quad (10)$$

The number of terms in this expression is defined by the number of relaxing, N_{relax} , and propagating, N_{prop} , eigenmodes via $N_v = N_{\text{relax}} + 2N_{\text{prop}}$, where N_v is the number of dynamic variables in the basis set. In Eq. (10), $A_{ij}^{\alpha}(k)$ are the amplitudes of the non-propagating relaxing modes contributions, while $B_{ij}^{\alpha}(k)$ and $D_{ij}^{\alpha}(k)$ are those of symmetric and asymmetric contributions of the α -th propagating mode, respectively.

In the case of pure components, the leading contributions to the density time autocorrelation functions are shown in Fig. 6. In complete agreement with hydrodynamics, the symmetric contribution of sound excitations and that of thermal relaxation process tend to $1/\gamma$ and $(\gamma - 1)/\gamma$ in the long-wavelength limit, respectively. For pure K and Na, the difference in the ratio of specific heats γ (see Table I) is reflected in the little difference between corresponding contributions in Fig. 6. Hence, the strong manifestation of the Brillouin peaks in dynamic structure factors of pure liquid K and Na shown in Fig. 1 is connected with close-to-unity values of γ for both liquid metals. The non-hydrodynamic process of structural relaxation does not contribute to $S(k, \omega)$ in long-wavelength limit, however its contribution to the central peak becomes predominant for $k > 0.5 \text{ \AA}^{-1}$. In the same region, thermal processes do not contribute significantly to $S(k, \omega)$.

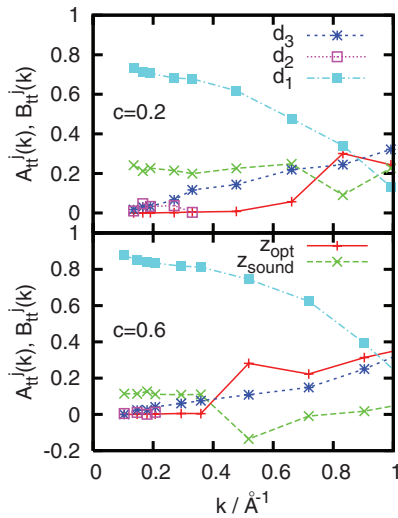


FIG. 7. Mode strengths of propagating and relaxing modes in collective dynamics of liquid binary alloys $\text{Na}_c\text{K}_{1-c}$ for concentration 0.2, 0.6.

Leading mode contributions for two compositions of the $\text{Na}_c\text{K}_{1-c}$ liquid alloy are shown in Fig. 7, where a striking difference with the mode contribution in the case of pure liquid metals can be seen. For binary liquid alloys, the main contribution to the central peak of $S_{tt}(k, \omega)$ comes from the relaxation process connected mainly with mutual diffusivity $d_1(k)$. This large contribution completely changes the mutual strengths of relaxation and propagating processes, known as Landau-Placzek ratio, when compared to the case of pure liquid metals. The expression of Landau-Placzek's ratio of binary liquids derived from the GCM mode contributions in the long-wavelength limit

$$\frac{I_{\text{central}}}{2I_{\text{side}}} = \lim_{k \rightarrow 0} \frac{A_{tt}^1(k) + A_{tt}^2(k)}{B_{tt}^{\text{sound}}(k)} \quad (11)$$

explains the shape of MD-derived total dynamic structure factors shown in Fig. 2. Extrapolating the mode contributions to $k \rightarrow 0$, we can estimate the Landau-Placzek ratio according to (Eq. (11)); for $c = 0.2$, it is about 3 ($B_{tt}(k) \approx 0.23$ for $k \rightarrow 0$) and it reaches ~ 7 for $c = 0.6$ ($B_{tt}(k) \approx 0.12$ for $k \rightarrow 0$). This is in agreement with Fig. 2, where the central peak is highest at the concentration $c = 0.6$.

Note that in Ref. 8 the mode contributions to the liquid alloy $\text{Na}_{0.56}\text{K}_{0.44}$ were studied in another form. The weight of the α -th propagating mode was represented via absolute values of the normalized complex GCM coefficients $G_{ij}^\alpha(k)$.⁸ However, the representation of GCM-replicas via real weight coefficients (10), as it was suggested in Ref. 25, is more informative because it allows to separate the parts responsible for the height (coefficients $B_{ij}^\alpha(k)$) and asymmetry (coefficients $D_{ij}^\alpha(k)$) of the side peaks in the shape of dynamic structure factors $S_{ij}(k, \omega)$. Moreover, the fitting scheme proposed in Ref. 8 for analyzing the IXS experiment made use of only the first three sum rules. On the other hand, expression (10) within the $\mathbf{A}^{(8)}(k, t)$ basis set yields GCM replicas fulfilling at least six sum rules for partial density-density time correlation functions: five for short-time behavior and another one for the corresponding correlation time.

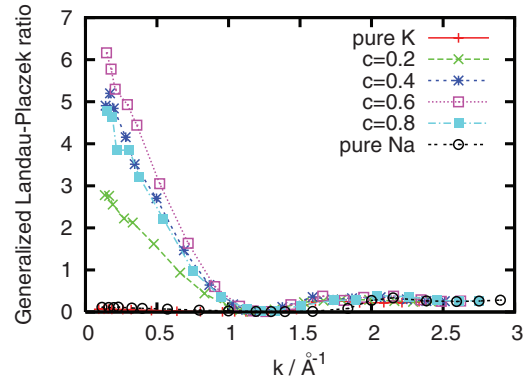


FIG. 8. Generalized Landau-Placzek ratio (12) as a function of wavenumber for different compositions of the liquid $\text{Na}_c\text{K}_{1-c}$ alloy.

Another interesting issue is on the contributions from the non-hydrodynamic structural relaxation, i.e., generalized mode $d_3(k)$, to the central peak of dynamic structure factors. It is seen from Fig. 7 that this non-hydrodynamic process becomes important already for $k \sim 0.2 \text{ \AA}^{-1}$, and its contribution increases with wave number reaching the same value as from the extended hydrodynamic mode $d_1(k)$ close to $k \sim 1 \text{ \AA}^{-1}$. This means that outside the hydrodynamic regime mainly two modes contribute to the central peak of total dynamic structure factor: extended hydrodynamic mode $d_1(k)$ connected mainly with mutual diffusivity and non-hydrodynamic mode of structural relaxation $d_3(k)$. The contributions from thermal processes outside the hydrodynamic region are negligible. This means that the heat waves cannot be detected in the spectrum of density fluctuations for metallic liquid binary alloys.

In Ref. 3, another expression of the Landau-Placzek ratio as a function of thermodynamic quantities has been reported. Its generalization to wave-number-dependent thermodynamic quantities allows us to use the MD-calculated values of linear thermal expansion coefficient, generalized specific heats, and their ratio, shown in Fig. 3. The $N - C$ dilatation $\delta(k)$ and $Z(k)$ -factor are directly connected to the Bhatia-Thornton static structure factors.²¹ Hence we were able to calculate also the generalized Landau-Placzek ratio from generalized thermodynamic quantities as follows:

$$\frac{I_{\text{central}}(k)}{2I_{\text{side}}(k)} = (\gamma(k) - 1) \left[1 + \frac{\delta^2(k)C_P(k)}{Z(k)T\alpha_T^2(k)} \right]. \quad (12)$$

In Fig. 8, we show the generalized Landau-Placzek ratio of pure components and four compositions of the liquid $\text{Na}_c\text{K}_{1-c}$ alloy. It is remarkable that these generalized Landau-Placzek ratios reach much larger values in the case of binary alloys, in agreement with the GCM analysis performed before, which impute this situation to slow relaxation mode, connected mainly with mutual diffusivity. The $k \rightarrow 0$ limits are in very good agreement with the corresponding values calculated via the mode-contributions amplitudes (Eq. (11)) and shown in Table I, giving evidences of the applicability of both approaches to estimate the Landau-Placzek ratio in binary liquids.

IV. CONCLUSION

We have studied the composition dependence of relaxation modes and their contributions to dynamic structure factors for four concentration of binary liquid alloy $\text{Na}_c\text{K}_{1-c}$ and pure liquid metals K and Na. Time correlation functions derived in molecular dynamics simulations were analyzed by extended dynamic models of generalized hydrodynamics within the approach of generalized collective modes. The main conclusions of this study can be formulated as follows.

- (i) In comparison with one-component liquid metals, the binary liquid alloys $\text{Na}_c\text{K}_{1-c}$ contain a slow relaxation mode, which is mainly defined by mutual diffusivity. This relaxation mode is making the main contribution to the central peak of total dynamic structure factor.
- (ii) It has been shown that the Landau-Placzek ratio for binary alloys $\text{Na}_c\text{K}_{1-c}$ can be calculated by two ways: using generalized thermodynamic quantities or GCM amplitudes of mode contributions from relaxation processes and sound excitations to the total dynamic structure factors.
- (iii) The composition dependence of the Landau-Placzek ratio permits to explain correctly the shape of dynamic structure factors obtained in MD at different concentrations.

Considering that Na-K is a rather random mixture with no marked chemical order, it would be interesting to extend this study to either homo- or hetero-coordinated alloys. Another interesting issue is to study evolution of contributions from relaxation processes to $S_{it}(k, \omega)$ in binary liquids versus density, especially in supercritical region where it is possible to change the density in very broad range. For the case of dense binary gases a kinetic approach based on revised Enskog theory can be applied in the study of relaxation processes. In Ref. 26 analytical expressions for partial time correlation functions of binary systems were obtained within the revised Enskog theory, but satisfying correct short-time behavior only to some level. It seems possible to separate in those expressions contributions from thermal and diffusion processes, estimate their strengths and compare with the results obtained by the GCM approach in this study. Another possibility is to understand how the relaxation processes connected with Enskog's diffusion coefficient^{27,28} can be related to some of generalized collective modes obtained from extended hydrodynamic GCM approach. This will be studied elsewhere.

ACKNOWLEDGMENTS

T.B. was supported by the Joint SFFRU-RFFR Program under Project No. $\Phi 28.2/037$. The allocation time at the SCIT-3 cluster of the Institute of Cybernetics of NASU is acknowledged.

- ¹T. Scopigno, G. Ruocco, and F. Sette, *Rev. Mod. Phys.* **77**, 881 (2005).
- ²C. Cohen, J. W. H. Sutherland, and J. M. Deutch, *Phys. Chem. Liq.* **2**, 213 (1971).
- ³A. B. Bhatia, D. E. Thornton, and N. H. March, *Phys. Chem. Liq.* **4**, 97 (1974).
- ⁴J.-P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).
- ⁵J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).
- ⁶P. R. Gartrell-Mills, R. L. McGreevy, W. van der Lugt, and C. van der Marel, *J. Phys. F: Met. Phys.* **17**, 2353 (1987).
- ⁷L. E. Bove, F. Sacchetti, C. Petrillo, and B. Dorner, *Phys. Rev. Lett.* **85**, 5352 (2000).
- ⁸S. Cazzato, T. Scopigno, T. Bryk, I. Mryglod, and G. Ruocco, *Phys. Rev. B* **77**, 094204 (2008).
- ⁹J. Bosse, G. Jacucci, M. Ronchetti, and W. Schirmacher, *Phys. Rev. Lett.* **57**, 3277 (1986).
- ¹⁰P. H.K. de Jong, P. Verkerk, C. F. de Vroege, L. A. de Graaf, W. S. Howells, and S. M. Bennington, *J. Phys.: Condens. Matter* **6**, L681 (1994).
- ¹¹L. E. Bove, F. Formisano, E. Guarini, A. Ivanov, C. Petrillo, and F. Sacchetti, *Europhys. Lett.* **79**, 16002 (2007).
- ¹²I. M. deSchepper, E. G.D. Cohen, C. Bruin, J. C. van Rijs, W. Montfrooij, and L. A. de Graaf, *Phys. Rev. A* **38**, 271 (1988).
- ¹³I. M. Mryglod, *Condens. Matter Phys.* **1**, 753 (1998).
- ¹⁴T. Bryk and I. Mryglod, *J. Phys.: Condens. Matter* **14**, L445 (2002).
- ¹⁵T. Bryk and I. Mryglod, *Phys. Rev. E* **63**, 051202 (2001).
- ¹⁶T. Bryk, I. Mryglod, T. Scopigno, G. Ruocco, F. Gorelli, and M. Santoro, *J. Chem. Phys.* **133**, 024502 (2010).
- ¹⁷T. Bryk and I. Mryglod, *Condens. Matter Phys.* **7**, 471 (2004).
- ¹⁸T. Bryk and I. Mryglod, *Condens. Matter Phys.* **11**, 139 (2008).
- ¹⁹C. Fiolhais, J. P. Perdew, S. Q. Armster, J. M. MacLaren, and M. Brajczewska, *Phys. Rev. B* **51**, 14001 (1995).
- ²⁰S. Ichimaru, K. Utsumi, *Phys. Rev. B* **24**, 7385 (1981).
- ²¹J.-F. Wax, *Physica B* **403**, 4241 (2008).
- ²²S. Moroni, D. M. Ceperley, and G. Senatore, *Phys. Rev. Lett.* **75**, 689 (1995).
- ²³J.-F. Wax and J.-L. Bretonnet, *J. Non-Cryst. Solids* **250–252**, 30 (1999).
- ²⁴D. D. Joseph and L. Preziosi, *Rev. Mod. Phys.* **61**, 41 (1989).
- ²⁵T. Bryk and I. Mryglod, *J. Phys.: Condens. Matter* **13**, 1343 (2001).
- ²⁶I. de Schepper and W. Montfrooij, *Phys. Rev. A* **39**, 5807 (1989).
- ²⁷T. Scopigno, R. Di Leonardo, L. Gomez, A. Q. R. Baron, D. Fioretto, and G. Ruocco, *Phys. Rev. Lett.* **94**, 155301 (2005).
- ²⁸T. Scopigno, R. Di Leonardo, L. Gomez, A. Q. R. Baron, D. Fioretto, G. Ruocco, and W. Montfrooij, *Phys. Rev. Lett.* **95**, 269602 (2005).