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Spectra of transverse excitations in liquid glass-forming metallic alloy $Mg_{70}Zn_{30}$: temperature dependence

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The temperature dependence of the dispersion and damping coefficients of transverse excitations in metallic alloy $Mg_{70}Zn_{30}$ at the number density $n = 0.0435$ Å^{-3} is studied using the method of generalized collective modes. The spectra of generalized transverse modes have been obtained within the four-variable approximation for three temperatures 1210 K, 833 K and 713 K. It is shown that the propagating gap which characterizes the crossover between hydrodynamic fluid-like and viscoelastic solid-like behaviour reduces when the temperature decreases. The generalized k-dependent shear viscosity $\eta(k)$ calculated within the same approximation increases rapidly at $k = 0$ and its shape becomes more narrow by transition from a well-defined liquid state to an undercooled one.

Key words: *transverse excitations, shear waves, glass-forming fluids, metallic alloy, collective modes*

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1. Introduction

Dynamical properties of the glass-forming metallic alloy $Mg_{70}Zn_{30}$ were the subject of numerous experimental [1–4] and theoretical [5–7] studies due to well-defined collective phonon-like excitations in amorphous state. The spectra of collective excitations of another glass-forming system $Zr_{67}Ni_{33}$ have been investigated in [8] at four different thermodynamic points both above and below the melting temperature. However, the region of very small wavenumbers, where the transverse propagating gap could be located, has not been reached. In the cited theoretical investigations a very simple analysis of power spectrum of 'current-current' correlation functions was applied to derive the dispersion of collective excitations.

In this paper we report investigations of the generalized transverse excitations spectra in glass-forming metallic alloy $Mg_{70}Zn_{30}$ based on the modern method of generalized collective modes (GCM) [11,12], which enables us to analyze MD-derived time correlation function in terms of partial contributions corresponding to eigenmodes of the system considered.

As far as we can judge, this work is the first application of the *parameter-free* GCM approach to the study of transverse excitations in a binary mixture. Most attention in our research is paid to the study of two main objectives: (i) the calculation of collective transverse mode spectrum in $Mg_{70}Zn_{30}$ and the study of temperature dependence of the propagating gap width; (ii) the investigation of the generalized static shear viscosity behaviour in liquid glass-forming binary alloy by decreasing temperature into undercooled region.

2. Theoretical framework

The general expressions of the GCM method (see [12,14,15]) can be applied to the system investigated through the appropriate choice of basis set of dynamical variables. Since there is only one conserved transverse variable the basis set $\mathbf{A}(k,t)$ of dynamic variables for the transverse fluctuations in a binary liquid consists of the *total* transverse current operator $J(k,t)$

$$J(k,t) \equiv J_t(k,t) = J_t^1(k,t) + J_t^2(k,t) = \frac{1}{\sqrt{N}} \sum_{\alpha=1}^{2} \sum_{i=1}^{N_\alpha} m_\alpha v_{\alpha i}^t \exp(\mathrm{i}\mathbf{k}\mathbf{r}_{\alpha i}t), \qquad (2.1)$$

($\mathbf{r}_{\alpha i}$, $v_{\alpha i}^t$ denote a position and a transverse component of velocity of the ith particle for the αth species) and its first time derivatives up to the s-th order, namely,

$$\mathbf{A}(k,t) = \{A_i(k,t)\} = \{J(k,t), \dot{J}(k,t), \ddot{J}(k,t), \ldots, (\mathrm{i}L_N)^s J(k,t)\}, \qquad (2.2)$$

where $\mathrm{i}L_N$ is the Liouville operator and $\dot{J}(k,t) = \mathrm{i}L_N J(k,t)$, $\ddot{J}(k,t) = (\mathrm{i}L_N)^2 J(k,t)$. Thus, we have $A_i(k,t) \equiv (\mathrm{i}L_N)^{i-1} J(k,t)$, $i = 1, 2, \ldots, s+1$.

To obtain the expression for transverse 'current-current' time correlation function $F_{JJ}^{(t)}(k,t)$ in the hydrodynamic limit it is enough to consider the only variable $J(k,t)$ [14], and this corresponds to the case $s = 0$. Thus, the well-known single-exponential form for $F_{JJ}^{(t)}(k,t)$ [9,10],

$$F_{JJ}^{(t)}(k,t) \simeq \frac{M}{N} k_{\mathrm{B}} T \exp\{-\eta k^2 t/\rho\} = \rho k_{\mathrm{B}} T \exp\{-t/\tau_{JJ}^h\}, \qquad (2.3)$$

is easily reproduced, where $\rho = M/V$ and η are a mass density and shear viscosity, respectively. Note that $M = m_1 N_1 + m_2 N_2$ and $N = N_1 + N_2$. For the intermediate values of wavenumbers k and frequencies ω, where the short-time kinetic properties become more important, one has to consider an extended set of dynamic variables. In our study we use the basis set of dynamic variables (2.2) with $s = 3$ containing the total current operator and its first three time derivatives as well. This means that the first frequency moments of the function $F_{JJ}^{(t)}(k,t)$ are explicitly reproduced

up to and including the sixth order moment [14]. This result can be improved in a systematic way by taking into account the higher-order time derivatives in (2.2).

To calculate the generalized collective mode spectrum one has to solve the eigenvalues problem for the matrix $\mathbf{T}(k)$ which is simply expressed via the matrices of static correlation functions $\mathbf{F}(k) = \mathbf{F}(k, t = 0)$ and the Laplace transforms $\tilde{\mathbf{F}}(k) = \tilde{\mathbf{F}}(k, z = 0)$ [12–16]. The explicit expressions for these matrices for $s = 3$ can be found in [14]. It is worth mentioning that all the matrix elements of $\mathbf{F}(k)$ and $\tilde{\mathbf{F}}(k)$ are the static correlation functions which can be directly determined by molecular dynamics. Only one exception is a quantity $\tau_{JJ}(k)$,

$$\tau_{JJ}(k) = \frac{1}{F_{JJ}(k, 0)} \int_0^\infty F_{JJ}(k, t) \mathrm{d}t, \qquad (2.4)$$

which is of dynamical origin and is called the transverse correlation time [12,13]. However, as it is seen from (2.4), $\tau_{JJ}(k)$ can be calculated in computer experiments as well.

To carry out calculations in the region of extremely small k-values, having not been accessed in MD, we used the extrapolation procedure developed for describing the k-dependence of matrix elements $F_{ij}(k)$ and $\tilde{F}_{ij}(k)$ in [16]. This procedure has been successfully applied to the study of transverse excitations in liquid Cs near the melting point [16].

3. Results and concluding remarks

To study the liquid metallic alloy $Mg_{70}Zn_{30}$ we have performed MD simulations of a system composed of 864 particles with the number density $n = 0.0435$ Å^{-3} at constant volume $V = L^3$. The effective two-body oscillating potentials $\Phi_{ij}(r)$ obtained from the optimized OPW-pseudopotentials have been taken from [5]. Three different temperatures $T = 1210$ K, 833 K and 713 K have been considered. Due to a strong pressure of 4.8 kbar in MD simulations the second and the third states corresponded to an undercooled liquid. The states at different temperatures were prepared from the same liquid state (~ 2000 K) by a very slow scaling of the velocities avoiding a high-speed quench. The results for the generalized transverse collective modes obtained within the four-variables approximation at different temperatures are shown in figure 1. At $T = 1210$ K (see figures 1a and 1b) for $k > 0.116$ Å^{-1} the spectrum of transverse excitations consists of two pairs of complex-conjugated propagating modes with

$$z_j^\pm(k) = \pm \mathrm{i}\omega_j(k) + \sigma_j(k), \qquad \sigma_j = \mathrm{Re} \; z_j^\pm(k) > 0, \qquad j = 1, 2. \qquad (3.1)$$

The k-dependence of the damping coefficients $\sigma_j(k)$ is quite typical of the fluids (see [14,16]). When k is small, the damping coefficient of the high-frequency mode is nearly six times bigger than the damping coefficient of the lower lying mode. This means that for small wavenumbers the contribution of the higher lying propagating kinetic mode into all dynamical processes will be negligibly small. For larger
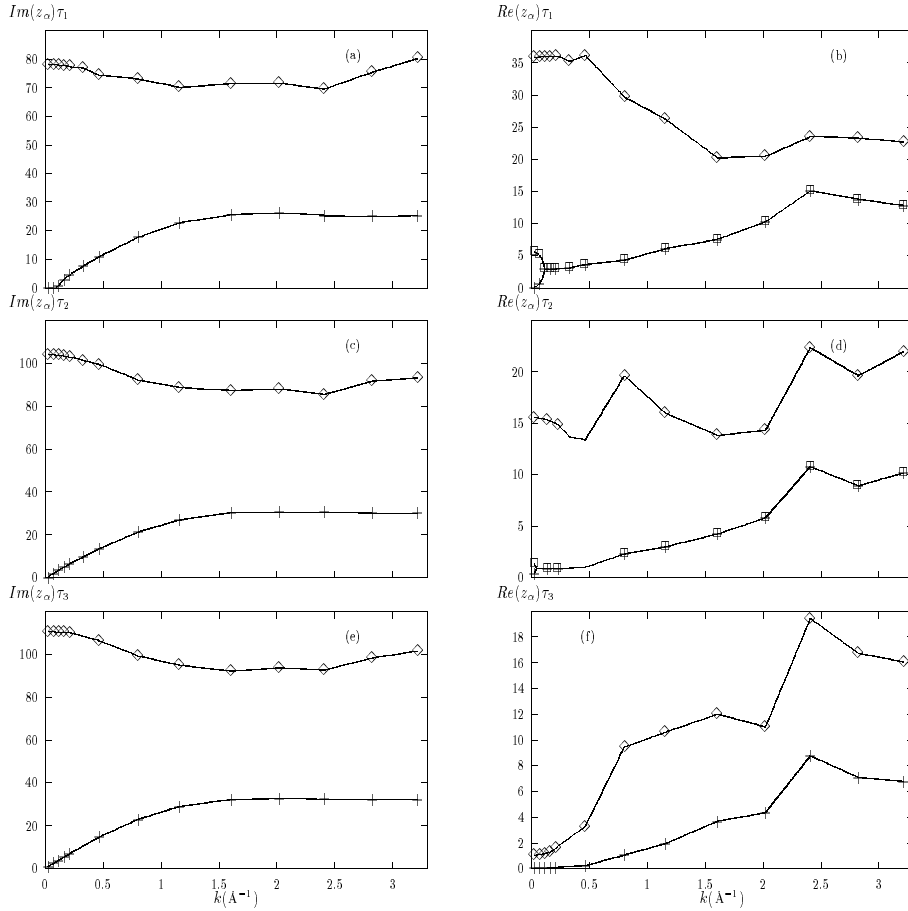
Figure 1. Dispersions and damping coefficients of transverse excitations for $Mg_{70}Zn_{30}$ at T =1210 K (a,b), T =833 K (c,d), and T =713 K (e,f). Time scales τ_1=0.826 ps, τ_2=0.991 ps, τ_3=1.071 ps.

wavenumbers the ratio of damping coefficients decreases, so that the role of kinetic processes is becoming more important.

The most interesting for the analysis is the range of small wavenumbers where the crossover from hydrodynamic regime to an intermediate behaviour takes place. We see in figures 1a and 1b that at $k_H = 0.116$ Å^{-1} the pair of lower-lying propagating modes disappears and transforms into two modes with purely real eigenvalues. This means that in a liquid state, shear waves cannot propagate when $k < k_H$ and k_H is the width of the propagating gap. For $k > k_H$, when the system supports shear propagating excitations the liquid behaves like a viscoelastic solid-like medium. Note also that for $k < k_H$ one of the purely real eigenvalues behaves like $z^h(k) \simeq \eta k^2/\rho$ when k tends to zero in full agreement with the hydrodynamics. Another one tends, within this limit, to a finite damping coefficient, so this mode is called a kinetic one.

When the temperature decreases the propagating gap becomes narrower. We found $k_H = 0.0464$ Å^{-1} for $T = 833$ K (see figures 1c and 1d) and in deep under-cooled state at $T = 713$ K (see figure 1e and 1f) the width of propagating gap is extremely small, at least smaller than the minimal value $k_0 = 0.0232$ Å^{-1} consid-

ered in our study[1]. Comparing the results obtained, one can conclude that: (i) the imaginary part of the low-lying propagating modes for small wavenumbers becomes closer to the linear function of k when T decreases; (ii) the damping coefficient of the high-frequency pair of propagating kinetic modes decreases, when the temperature decreases. This means that in order to reproduce more precisely the time dependence of $F_{JJ}^{(t)}(k,t)$ for an undercooled liquid the higher order approximations can be needed; (iii) another important thing is that for $k > 1.5$ Å^{-1} the dispersion of low-lying propagating modes is very flat and its temperature dependence is rather weak. Practically the same relates to the dispersion of the higher lying modes in a whole range of k considered. In figure 2 we plot the dispersions of the generalized trans-
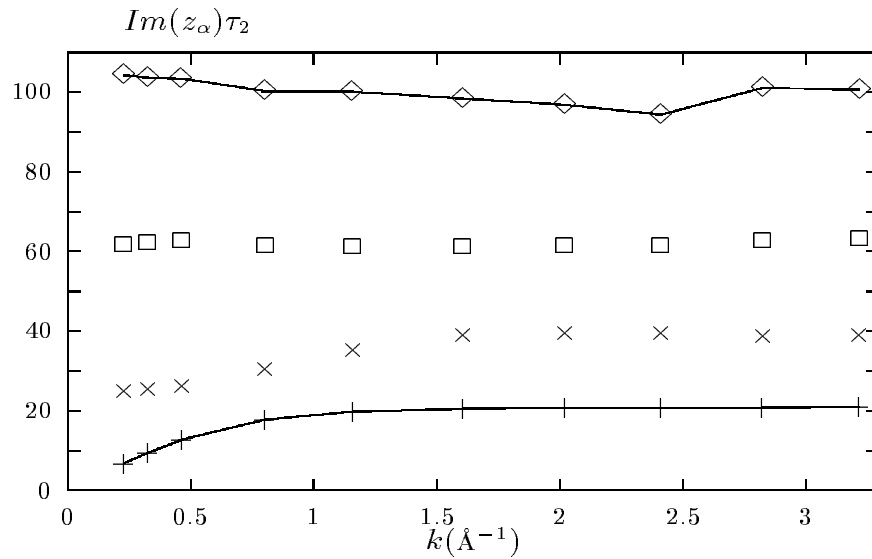

Figure 2. Imaginary parts of eigenvalues for $Mg_{70}Zn_{30}$ at $T =833$ K obtained in the eight-variable approximation. Time scale $\tau_2=0.991$ ps.

verse excitations obtained within the eight-variable description at $T = 833$ K. The basis set of dynamic variables (with $s = 3$) contained the partial currents $J_t^1(k,t)$ and $J_t^2(k,t)$ and their time derivatives. Hence, the total number of variables was twice as big as before. It is seen, that the lower and the upper curves in figure 2 are nearly the same as those obtained for the four-variable description (compare with figure 1c). Two more new pairs of propagating kinetic modes have appeared. They resemble the dispersions of optic phonons in solid-like medium and describe the processes related to the difference in motion of Mg and Zn atoms. One may suppose that one of these modes (labelled by crosses in figure 2) having transferred into the amorphous state will transform into 'the optic mode' found by Hafner [5] in amorphous $Mg_{70}Zn_{30}$.

The generalized k-dependent shear viscosity $\eta(k)$ is simply expressed via the transverse correlation time $\tau_{JJ}(k)$, which has been used as one of the input parameters of the GCM approach (see (2.4)), namely, $\eta(k) = \rho/k^2\tau_{JJ}(k)$. Using this

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[1]The minimal wavenumber $k_{\min}$ in our molecular dynamics simulations was $k_{\min} = 0.232$ Å^{-1}.

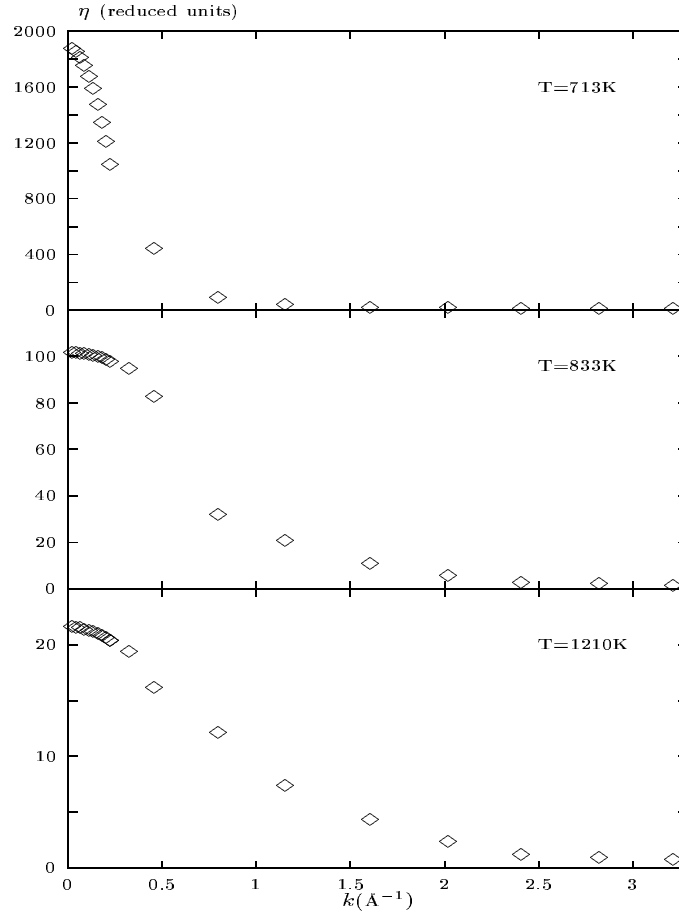**Figure 3.** Generalized static shear viscosity $\eta(k)$ for $Mg_{70}Zn_{30}$ at $T = 713$ K, $T = 833$ K and $T = 1210$ K.

expression the function $\eta(k)$ has been calculated, and the obtained results in dimensionless form are shown in figure 3. It is seen that for small wavenumbers the generalized shear viscosity has a Lorentian-like shape, and in the free-particle limit $\eta(k)$ behaves as $1/k$. The values of shear viscosity, obtained in the limit k tends to zero, could be compared with experimental data, namely, we found: $3.642 \cdot 10^{-3}$ Pa·s at $T = 1210$ K; $1.428 \cdot 10^{-2}$ Pa·s at $T = 833$ K, and $2.444 \cdot 10^{-1}$ Pa·s at $T = 713$ K. Note that the shear viscosity increases rapidly when the temperature decreases and the system reaches an undercooled state.

We conclude with the following remarks:

(i) Applying the free-parameter GCM approach to the study of the dense metallic binary alloy $Mg_{70}Zn_{30}$ we have obtained the spectra of generalized transverse collective modes and estimated the width of propagating gap that displayed the crossover from the hydrodynamic fluid-like behaviour to the viscoelastic solid-like behaviour;

(ii) It is shown that the propagating gap becomes narrower when the temperature decreases. For the state of undercooled liquid at $T = 713$ K its width is extremely small (less than 0.023 Å^{-1} reached in our study) and the transverse sound-like

excitations are well defined;

(iii) Within the four-variable approximation of GCM approach, used in our study, the transverse 'current-current' time correlation function can be found in the form which reproduces explicitly the sum rules up to and including the sixth order frequency moment. For comparison, the memory function formalism, being in a common practice, takes usually into account the frequency moments up to the second order only;

(iv) The temperature dependence of the generalized shear viscosity $\eta(k)$ for a liquid metallic binary alloy has been investigated. We found that the value of this function at $k = 0$ increases and the shape becomes narrower when the temperature decreases from a well-defined liquid state to an undercooled state.

References

1. Suck J.-B., Rudin H., Guntherodt H.-J., Beck H. Short-wavelength transverse collective modes in a metallic glass. // J. Phys. C, 1980, vol. 13, No. 36, p. L1045–L1051.
2. Suck J.-B., Rudin H., Guntherodt H.-J., Beck H. Dynamical structure factor and vibrational density of states of the metallic glass $Mg_{70}Zn_{30}$ measured at room temperature. // J. Phys. C, 1981, vol. 14, No. 17, p. 2305–2317.
3. Suck J.-B., Egelstaff P.A., Robinson R.A., Sivia D.S., Taylor A.D. Neutron Brillouin scattering in a metallic glass. // J. Non-Cryst. Sol., 1992, vol. 150, p. 245–250.
4. Benmore C.J., Oliver B.J., Suck J.-B., Robinson R.A., Egelstaff P.A. A neutron Brillouin scattering study of $Mg_{70}Zn_{30}$. // J. Phys.: Cond. Matt., 1995, vol. 7, p. 4775–4785.
5. Hafner J. Dispersion of collective excitations in a metallic glass. // J. Phys. C, 1983, vol. 16, p. 5773–5792.
6. Hafner J. Phonons in amorphous metals. In: *Ab Initio* Calculations of Phonon Spectra. Eds.: Devreese J.T., Van Doren V.E., Van Camp P.E., New York - London, Plenum Press, 1983.
7. Saxena N., Bhandari D., Pratap A., Saxena M. Structure and dynamics of a two-component metallic glass. // J. Phys.: Cond. Matt., 1990, vol. 2, p. 9475–9480.
8. Aihara T., Masumoto T. Dispersion of collective excitations of amorphous and liquid $Zr_{67}Ni_{33}$ alloys. // J. Phys.: Cond. Matt., 1995, vol. 7, p. 1525–1541.
9. Hansen J.P., McDonald I.R. Theory of Simple Liquids. 2nd ed., London, Academic Press, 1986.
10. Boon J.P., Yip S. Molecular Hydrodynamics. New-York, McGraw-Hill Inc., 1980.
11. de Schepper I.M., Cohen E.G.D., Bruin C., van Rijs J.C., Montrooij W., Graaf L.A. Hydrodynamic time correlation functions for Lennard-Jones fluids. // Phys. Rev. A, 1988, vol. 38, No. 1, p. 271–287.
12. Mryglod I.M., Omelyan I.P., Tokarchuk M.V. Generalized collective modes for the Lennard-Jones fluid. // Mol. Phys., 1995, vol. 84, No. 2, p. 235–259.

13. Omelyan I.P., Mryglod I.M. Generalized collective modes of a Lennard-Jones fluid. High-mode approximation. // Cond. Matt. Phys. (Ukraine), 1994, vol. 4, p. 128–160.

14. Mryglod I.M., Omelyan I.P. Generalized mode approach: 1. Transverse time correlation functions and generalized shear viscosity of a Lennard-Jones fluid. // Mol. Phys., 1997, vol. 90, No. 1, p. 91–99.

15. Bryk T.M., Mryglod I.M., Kahl G. Generalized collective modes in a binary $He_{0.65}$-$Ne_{0.35}$ mixture. // Phys. Rev. E, 1997, vol. 56, No. 3, p. 2903–2915.

16. Bryk T., Mryglod I. Transverse excitations and generalized shear viscosity in liquid Cs near the melting point. // J. Phys. Studies (Ukraine), 1998, vol. 2, No. 3, p. 322–330.

Спектри поперечних збуджень у рідкому склоформуючому металічному сплаві $Mg_{70}Zn_{30}$: вплив температури

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Методом узагальнених колективних мод досліджується температурна залежність дисперсії та коефіцієнтів згасання поперечних збуджень у металічному сплаві $Mg_{70}Zn_{30}$ з густиною частинок $n = 0.0435$ $Å^{-3}$. Спектри поперечних збуджень розраховані у чотиримодовому наближенні для трьох значень температури: 1210 K, 833 K і 713 K. Показано, що розмір пропагаторної щілини, яка визначає перехід від гідродинамічної рідинної поведінки до поведінки властивої пружному твердотільному середовищу, зменшується при пониженні температури. Проведено розрахунок узагальненої (залежної від модуля хвильового вектора k) зсувної в'язкості $\eta(k)$ і показано, що її величина при $k = 0$ швидко зростає, а функція $\eta(k)$ стає більш вузькою при переході від добре визначеного рідкого стану до стану переохолодженої рідини.

Ключові слова: *поперечні збудження, зсувні хвилі, склоформуючі рідини, металічний сплав, колективні моди*

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