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Single-particle motion in liquid and supercooled $Mg_{70}Zn_{30}$ alloy

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Abstract

We have calculated the velocity autocorrelation functions (VAF) in a self-consistent mode-coupling (MC) approach for liquid and supercooled $Mg_{70}Zn_{30}$ and have compared these results with data obtained in molecular-dynamics (MD) simulations. We have used a simple Gaussian *ansatz* for the 'binary' part of the memory functions while the MC contributions contain the coupling of the density fluctuations. The intermediate scattering functions, required in these MC integrals, are calculated in the viscoelastic approximation whereas the incoherent scattering functions are determined in a self-consistent manner from the VAF. In the direct comparison with MD-data agreement between the theoretical and the simulation data is observed for the liquid alloy while the discrepancies encountered in the supercooled state are found to be due to the viscoelastic approximation for the intermediate scattering functions. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The dynamical properties of the metallic glass $Mg_{70}Zn_{30}$ have been the subject of several experimental and theoretical investigations; from the experimental point of view this system is very appropriate for neutron scattering measurements because it scatters neutrons coherently; on the other hand, from the theoretical point of view, both Mg and Zn are simple s–p bonded metals and their effective pair potentials can easily be derived from pseudopotential theory [1]. While, for instance, the dispersion relations of the collective modes and the dynamical structure factor in the amorphous state have been determined by inelastic neutron scattering experiments [2] as well as in computer simulations [3] much less attention has been devoted to the microscopic dynamics in the liquid and in the supercooled states. We have therefore devoted this contribution to an analysis of the velocity autocorrelation functions (VAF) of these states. Among the different theoretical approaches that have been proposed to explain the phenomena governing the liquid–glass transition, mode-coupling (MC) theory [4] was found to be a very appropriate tool: it is not only able to give a *qualitative*, but it can also – at least in some cases – give a *quantitative* description of long-time dynamics in binary systems for supercooled states.

2. Basic theory

Our system is characterized by a set of effective pair potentials $V_{ij}(r)$ at a temperature T, the partial

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number densities n_i, and the masses of the two species m_i. The normalized VAF of species i is defined as

$$\Phi_i(t) = \left\langle \vec{v}_i(t)\vec{v}_i(0)\right\rangle / \left\langle v_i^2\right\rangle , \qquad (i = 1, 2), \tag{1}$$

where $\langle v_i^2\rangle = 3k_BT/m_i$ and the angular brackets indicate an equilibrium average. The corresponding memory function (MF) of $\Phi_i(t)$, i.e., $K_i(t)$, is defined in t as well as in Laplace-space via

$$\frac{\mathrm{d}}{\mathrm{d}t}\Phi_i(t) = -\int_0^t \mathrm{d}\tau K_i(\tau)\Phi_i(t-\tau)$$
$$\tilde{\Phi}_i(z) = \left[z + \tilde{K}_i(z)\right]^{-1}. \tag{2}$$

The formalism of MC theory is able to develop closed expressions for the MF, which can be split into two contributions [5]: a short-time part, describing the effect of uncorrelated binary collisions, and a long-time 'mode-coupling' part that represents non-linear couplings of slowly varying collective variables, $K_i(t) = K_i^{\mathrm{B}}(t) + K_i^{\mathrm{MC}}(t)$.

The binary part $K_i^{\mathrm{B}}(t)$ contains all the contributions to $K_i(t)$ up to order t^2. Since $K_i(t) \approx K_i^{\mathrm{B}}(t)$ for small ts, the values for the binary decay time τ_i^{B} can be determined from the short-time expansion of $K_i(t)$, $\tau_i^{\mathrm{B}} = \sqrt{(2K_i(0)/|\ddot{K}_i(0)|)}$, where the $K_i(0) = \Omega_i^2$ are the Einstein frequencies; explicit expressions for the $\ddot{K}_i(0)$ are given in [6]. Since the detailed features of the short-time ('binary') dynamics of systems with continuous potentials are in general rather poorly known [7], we make the ansatz $K_i^{\mathrm{B}}(t) = \Omega_i^2 \exp(-t/\tau_i^{\mathrm{B}})^2$ which is able to reproduce qualitatively the correct short-time behaviour [8]. We have also calculated the decay time τ_i^{B} by fitting a Gaussian function to $K_i^{\mathrm{B}}(t)$ and have used these values in the following calculations: this was done for the reason that the fitted values differ – as we already know from the one-component case [9] – from the calculated ones by up to 10–20%.

The mode-coupling part of the MF $K_i^{\mathrm{MC}}(t)$ can be written as [10,7] (and neglecting the density–current contributions)

$$K_i^{\mathrm{MC}}(t) = \frac{n_i k_B T}{6\pi^2 m_i}\int_0^\infty \mathrm{d}q\, q^4 \sum_{j,l=1}^{2} c_{ij}(q)c_{il}(q) \times [F_i^{\mathrm{s}}(q,t)F_{jl}(q,t) - F_i^{\mathrm{sB}}(q,t)F_{jl}^{\mathrm{B}}(q,t)], \tag{3}$$

where the $c_{ij}(q)$ are the direct correlation functions, the $F_{ij}(q,t)$ are the intermediate scattering functions, and the $F_i^{\mathrm{s}}(q,t)$ are the self-intermediate scattering functions, with their binary parts, $F_{ij}^{\mathrm{B}}(q,t)$ and $F_i^{\mathrm{sB}}(q,t)$ respectively.

The $F_{ij}(q,t)$ were calculated in the viscoelastic approximation [11]. For the calculation of the binary part, $F_{ij}^{\mathrm{B}}(q,t)$, we have applied a simple approximation proposed by Sjögern for the one-component liquid [5]

$$F_{ij}^{\mathrm{B}}(q,t) = \frac{F_i^0(q,t)}{F_i^{\mathrm{s}}(q,t)}F_{ij}(q,t). \tag{4}$$

and $F_i^{\mathrm{sB}}(q,t) = F_i^0(q,t) = \exp[-(k_BT/2m_i)q^2t^2]$ is the free-particle form of $F_i^{\mathrm{s}}(q,t)$. Assuming in a first step a three-pole approximation for the $F_i^{\mathrm{s}}(q,t)$ [7], we are now ready to start the iterative procedure: we evaluate $K_i^{\mathrm{B}}(t)$ and $K_i^{\mathrm{MC}}(t)$ and, by solving Eq. (2), the corresponding VAF. The knowledge of $\Phi_i(t)$) allows one to compute the mean square displacement from which we calculate a new and improved value for the $F_i^{\mathrm{s}}(q,t)$ via the Gaussian approximation

$$F_i^{\mathrm{s}}(q,t) = \exp\left[-\tfrac{1}{6}q^2\delta r_i^2(t)\right]. \tag{5}$$

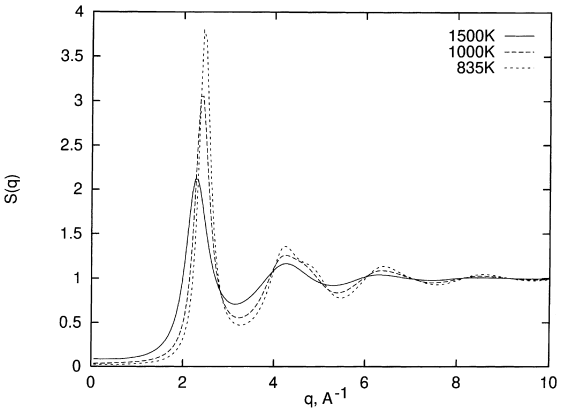

Fig. 1. Static structure factor for the $Mg_{70}Zn_{30}$ states considered in this study.

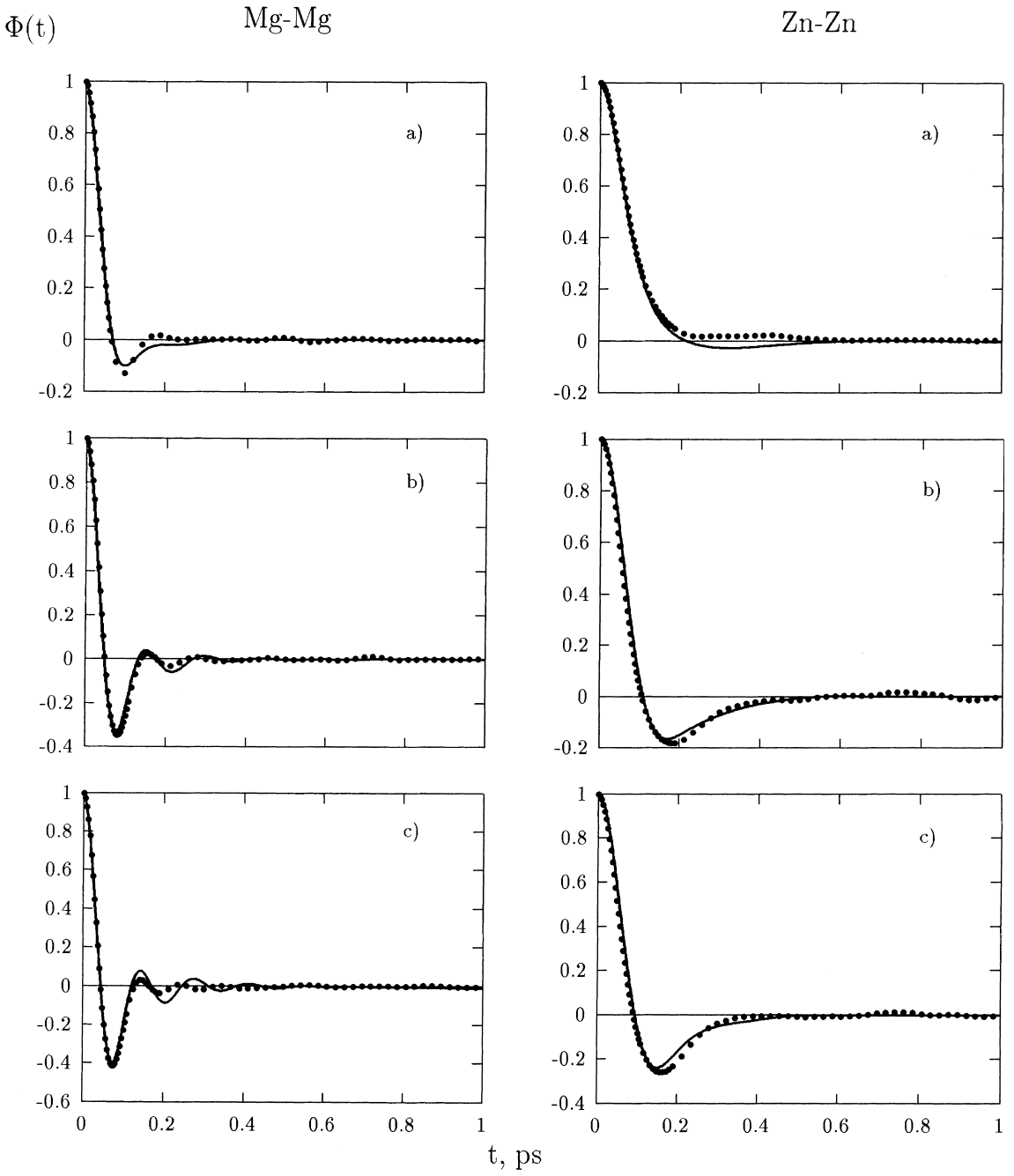

Fig. 2. Velocity autocorrelation functions of both species in $Mg_{70}Zn_{30}$ for three different states: (a) $T = 1500$ K – high-temberature liquid; (b) $T = 1000$ K – 'normal' liquid and (c) $T = 835$ K – supercooled. Lines – MC data and • – MD results.

Thus we obtain a new MC-contribution to the MF via Eq. (3) and we iterate this procedure until self-consistency is achieved in a numerical sense. We should also mention that similar approaches have been realized for the one-component case [9,12].

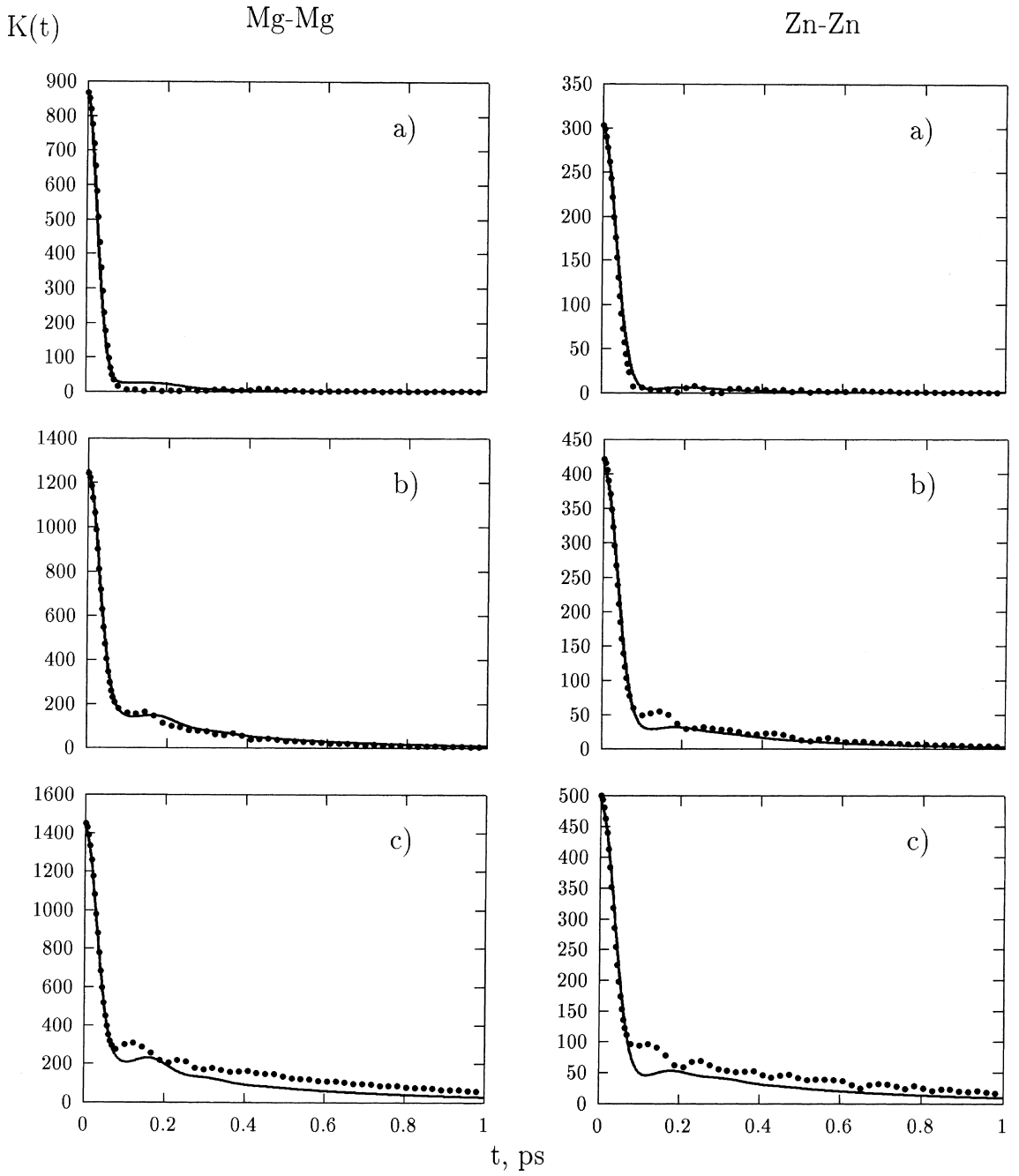

Fig. 3. Memory functions $K_i(t)$ of the VAF for $Mg_{70}Zn_{30}$ for three different states. Notations and symbols are the same as in Fig. 2.

3. Results

We investigated the VAF for $Mg_{70}Zn_{30}$ for three different states: the high-temperature liquid ($T=1500$ K, $n=0.03080$ Å^{-3}), a 'normal' liquid ($T=1000$ K, $n=0.03773$ Å^{-3}) and a supercooled state ($T=835$ K, $n=0.04102$ Å^{-3}); we have performed both a MC-analysis as well as microca-

nonical MD simulations with a 1372-particle ensemble. The $V_{ij}(r)$ are derived from pseudopotential theory using optimized OPW-pseudopotentials [13]. The supercooled state was created by cooling down from a liquid state (at 1000 K) with a quenching rate of approximately 2×10^{13} K/s. The static structure factors for the systems under investigation are presented in Fig. 1. In particular we observe that for $T = 835$ K the second peak starts to split, a feature that is often observed for supercooled liquids.

The results for the VAF $\Phi_i(t)$ calculated within the MC formalism and the corresponding MF $K_i(t)$ are compared with MD simulation data and are presented in Fig. 2 and Fig. 3. We found that in general four iterations are sufficient for a satisfactory convergence. In the high-temperature state the VAF of the minority component Zn decays monotonically with time, indicating that a tagged Zn particle moves freely, without many-body correlations. Discrepancies for Zn may on one hand be attributed to the smaller number of particles. Furthermore it is well-known that in particular for high temperatures the (neglected) density–current contributions to $K_i^{\mathrm{MC}}(t)$ become important. As the temperature is decreased a deep minimum in the VAF for the Zn-particles emerges, while the VAF for the Mg-component has an oscillatory behaviour that is typical for the 'cage effect': the tagged particle has frequent collisions within the cage formed by the surrounding particles.

In the supercooled state the contribution of the mode-coupling part to the memory functions becomes more significant. The binary contribution $K_i^{\mathrm{B}}(t)$ turns out to be less sensitive to the temperature and density variations and is governed by $\ddot{K}_i(0)$. However, noticeable discrepancies between the MD and MC results for $K_i(t)$ have been observed in the supercooled state. They may be attributed to the insufficient description of the intermediate scattering functions $F_{ij}(q,t)$ by the viscoelastic approximation in the supercooled liquids. Improvements of the present formalism to be realized in the near future are the following: inclusion of the density–current coupling in the $K_i^{\mathrm{MC}}(t)$ and a self-consistent determination of the $F_{ij}(q,t)$ within the MC formalism.

4. Conclusions

We have presented an analysis of the VAF and their memory functions for $Mg_{70}Zn_{30}$ in three different liquid and supercooled states, comparing MD simulations with the corresponding MC results. The main conclusion of this study is that the present version of MC-theory describes correctly the self-motion in binary liquids near the melting point and for higher temperatures. Discrepancies between the theoretical and simulated functions in the high-temperature liquid are mainly due to the neglect of density–current couplings which form an additional decay channel that is in particular important at low densities. In the supercooled state our viscoelastic approximation is unable to describe in an adequate way the behaviour of the $F_{ij}(q,t)$.

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