The memory kernel of velocity autocorrelation function on a NiZr-liquid: theory and simulation

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Abstrak

Based on Sjögren und Sjolander's Mode-Coupling(MC)-Model, we have re-formulated and calculated the memory kernel (MK) of the velocity autocorre-lation function (VACF)on a $Ni_{0.2}Zr_{0.8}$-liquid. Reformulating means here that we have constructed the memory kernel of VACF for our binary system, in-stead of one for one atomic system of the Sjögren und Sjolander's model. The data required for the theoretical calculations have been obtained from molec-ular dynamics (MD) simulations. The theoretical results then are compared with those directly obtained from computer simulation. We found, although it exists a qualitative agreement between theoretical predictions and simula-tion results, that quantitatively there is an deviations between both results, especially for Zr-subsystem.

I. INTRODUCTION

Since last decade and until today, one important goal of modern research in condensed matter is to find a good quantitative description of the glassy dynamics in liquids. Theo-retically there is a established theory, the so-called mode-coupling theory (MCT), that can describe and predict important parameters and quantities in glassy systems qualitatively good. Work in the last decade has provided evidence [1] that MCT [2] is able to describe the slow dynamics of *fragile* liquids in the weakly supercooled state. The recent work of Kob et.al. [3] has also showed that theory able to accurately describe the non-ergodicity parameters of simple as well as of network-forming liquids. The one important statement of the MCT is that the dynamics processes at long times is driven by a memory kernel which is included in MCT's integro-differential equation.

In previously paper [4] we have studied the memory kernel of incoherent intermediate scattering function. Further, we have compared the memory kernels $M_i^s(q,t)$ evaluated from the MCT formula with the kernels $M_i^0(q,t)$ from inverting the time evolution of the intermediate scattering functions. The comparison shows encouraging agreement at 900 to 1100 K while significant deviations are found at 1200 K. It is an open question whether for this temperature an improved agreement between calculated $M_i^s(q,t)$ and estimated $M_i^0(q,t)$ can be obtained by inclusion of the coupling to transversal currents in the memory kernel formula as provided, e.g., by Gudowski et.al. [5].

The main objective of paper is to give one of the answer of above open question. But instead of the memory kernel of incoherent intermediate scattering function, we investigated the memory kernel $K(t)$ of the velocity autocorrelation function (VACF) for temperature $T = 1500$ K. By calculating the memory kernel we included all coupling as proposed by Sjögren und Sjolander's Mode-Coupling(MC)-Model [6]. The calculated memory function then is compared with the kernel from inverting the time evolution of VACF.

Our paper is organized as follows: In Section III, we present the model and give some details of the computations. Section II gives a brief discussion of some aspects of the Sjögren und Sjolander's Mode-Coupling(MC)-Model as used here. Results of our MD-simulations and their analysis are then presented and discussed in Section IV.

II. SJÖGREN-SJÖLANDER'S MODE COUPLING MODEL

As we know, the VACF can be studied through the formalism developed by Zwanzig and Mori [10], which is based on a following integral equation:

$$\frac{d\psi(t)}{dt} = -\int_0^t K(t')\psi(t-\tau)dt' \qquad (1)$$

In this paper the Sjögren und Sjolander's (SS) Mode-Coupling(MC)-Model [6] is used. In this model memory kernel $K(t)$ of VACF $\psi(t)$ was proposed for a simple liquid according to a combination of kinetic and mode coupling concepts.

The basic idea of the model is that memory-kernel can be divided into two term. The first term comes from the uncorrelated binray collisions and the other from correlated collisions. The former is related to the fast decay of kernel at short times. The latter is expresses the mode-coupling term which incorporate more sophisticated processes that appear at longer times. Moreover, this term is based on the idea that the motion of a tagged particle is influenced by constraints collectively imposed by its neighboring particles. The memory kernel $K(t)$ of VACF take also the following relation

$$K(t) = K_B(t) + K^{MC}(t) \qquad (2)$$

According to SS-Model the mode-coupling effects take into account four different coupling-term: density-density coupling, two contributions from density-longitudinal current couplings, and density-transverse current coupling (s. Sjögren (1980/81) [11,12], Gudowski et.al. (1993) [5], Canales et.al. (1997) [13]).

To compute the memory kernel of VACF, we follow method used by Sjögren (1980/81), Gudowski et.al. (1993), Canales et.al. (1997). If by these authors one atomic systems only were investigated, here we investigate a binary system. Also we have to develop and construct the formulation of coupling terms for our binary system.

Here are the results of our reformulation of $K(t)$ for our binary system. The binary term is defined by [14]

$$K_{B\alpha}(t) = \Omega_{E\alpha}^2 \exp(-t^2/\tau_\alpha^2), \qquad (3)$$

where $\Omega_{E\alpha}^2$ is the Einstein-frequency of α-component [15],

$$\Omega^2_{E\alpha} = \frac{1}{3m_\alpha} \sum_\beta \int g_{\alpha\beta}(r)\nabla^2\phi_{\alpha\beta}(r)d^3r \tag{4}$$

and τ_α can be determined by the following equation

$$\frac{\Omega^2_{E\alpha}}{\tau^2_\alpha} = -\frac{1}{2}\ddot{K}(0) \tag{5}$$

The coupling terms is expressed by

$$K^{MK}_\alpha(t) = K_{00\alpha}(t) + K_{01\alpha}(t) + K_{11\alpha}(t) + K_{22\alpha}(t). \tag{6}$$

Here $K_{00\alpha}(t)$ describes the density-density coupling, $K_{01\alpha}(t)$ and $K_{11\alpha}(t)$ the density-longitudinal currents couplings, and $K_{22\alpha}(t)$ the density-transverse current coupling.

The Laplace transforms of these terms can be written

$$\widetilde{K}_{00\alpha}(z) = \tilde{R}_{00\alpha}(z), \tag{7}$$

$$\widetilde{K}_{01\alpha}(z) = \tilde{R}_{01\alpha}(z)\left[\widetilde{K}_{B\alpha}(z) + \widetilde{K}_\alpha(z)\right], \tag{8}$$

$$\widetilde{K}_{11\alpha}(z) = \widetilde{K}_{B\alpha}(z)\tilde{R}_{11\alpha}(z)\widetilde{K}_\alpha(z), \tag{9}$$

$$\widetilde{K}_{22\alpha} = \left[\widetilde{K}_{B\alpha}(z) + \tilde{R}_{00\alpha}(z) + \widetilde{K}_{B\alpha}(z)\tilde{R}_{01\alpha}(z)\right]\tilde{R}_{22\alpha}(z)\widetilde{K}_\alpha(z), \tag{10}$$

where $\widetilde{K}_{B\alpha}(z)$ und $\widetilde{K}_\alpha(z)$ are repectively the Laplace transform of the binary term and the total memory kernel. The Laplace transform of the total Memory kernel is as follows

$$\widetilde{K}_\alpha(z) = \left[\widetilde{K}_{B\alpha}(z) + \tilde{R}_{00\alpha}(z) + \widetilde{K}_{B\alpha}(z)\tilde{R}_{01\alpha}(z)\right]/X \tag{11}$$

with

$$X = 1 - \tilde{R}_{01\alpha}(z) - \widetilde{K}_{B\alpha}(z)\tilde{R}_{11\alpha}(z) - \\ \left[\widetilde{K}_{B\alpha}(z) + \tilde{R}_{00\alpha}(z) + \widetilde{K}_{B\alpha}(z)\tilde{R}_{01\alpha}(z)\right]\tilde{R}_{22\alpha}(z) \tag{12}$$

where $\tilde{R}_{ij\alpha}$ are the Laplace transform of "recollision" terms $R_{ij\alpha}(t)$. Assuming isotropic systems $R_{ij\alpha}(t)$ can be expressed as follows

$$R_{00\alpha}(t) = \frac{k_BT}{6\pi^2m_\alpha\rho}\int_0^\infty q^4(cF)_\alpha(q,t)\triangle F_{s\alpha}(q,t)dq, \tag{13}$$

with

$$(cF)_\alpha(q,t) = [c_{\alpha\alpha}(q)]^2 F_{\alpha\alpha}(q,t) + \\ 2c_{\alpha\alpha}(q)c_{\alpha\beta}(q)F_{\alpha\beta}(q,t) + [c_{\alpha\beta}(q)]^2 F_{\alpha\alpha}(q,t);\ \alpha \neq \beta \tag{14}$$

$$R_{01\alpha}(t) = -\frac{1}{6\pi^2\Omega_{E\alpha}^2\rho}\int_0^\infty q^2(LF')_\alpha(q,t)\triangle F_{s\alpha}(q,t)dq, \tag{15}$$

with

$$(LF')_\alpha(q,t) = c_{\alpha\alpha}(q)\left[\gamma_{L\alpha\alpha}(q) + \frac{k_BTq^2}{m_\alpha x_\alpha}c_{\alpha\alpha}(q)\right]F'_{\alpha\alpha}(q,t) + \tag{16}$$

$$c_{\alpha\alpha}(q)\left[\gamma_{L\alpha\beta}(q) + \frac{k_BTq^2}{m_\alpha x_\beta}c_{\alpha\beta}(q)\right]F'_{\alpha\beta}(q,t) +$$

$$c_{\alpha\beta}(q)\left[\gamma_{L\alpha\alpha}(q) + \frac{k_BTq^2}{m_\alpha x_\alpha}c_{\alpha\alpha}(q)\right]F'_{\alpha\beta}(q,t) +$$

$$c_{\alpha\beta}(q)\left[\gamma_{L\alpha\beta}(q) + \frac{k_BTq^2}{m_\alpha x_\beta}c_{\alpha\beta}(q)\right]F'_{\beta\beta}(q,t); \ \alpha \neq \beta$$

$$R_{11\alpha}(t) = -\frac{1}{6\pi^2\Omega_{E\alpha}^4\rho}\int_0^\infty q^2(BC_L)_\alpha(q,t)\triangle F_{s\alpha}(q,t)dq, \tag{17}$$

with

$$(BC_L)_\alpha(q,t) = \left[\gamma_{L\alpha\alpha}(q) + \frac{k_BTq^2}{m_\alpha x_\alpha}c_{\alpha\alpha}(q)\right]^2 C_{L\alpha\alpha}(q,t) +$$

$$2\left[\gamma_{L\alpha\alpha}(q) + \frac{k_BTq^2}{m_\alpha x_\alpha}c_{\alpha\alpha}(q)\right]\left[\gamma_{L\alpha\beta}(q) + \frac{k_BTq^2}{m_\alpha x_\beta}c_{\alpha\beta}(q)\right]C_{L\alpha\beta}(q,t) +$$

$$\left[\gamma_{L\alpha\beta}(q) + \frac{k_BTq^2}{m_\alpha x_\beta}c_{\alpha\beta}(q)\right]^2 C_{L\beta\beta}(q,t); \ \alpha \neq \beta \tag{18}$$

$$R_{22\alpha}(t) = -\frac{1}{6\pi^2\Omega_{E\alpha}^4\rho}\int_0^\infty q^2(TC_T)_\alpha(q,t)\triangle F_{s\alpha}(q,t)dq, \tag{19}$$

with

$$(TC_T)_\alpha(q,t) = [\gamma_{T\alpha\alpha}(q)]^2 C_{T\alpha\alpha}(q,t) +$$

$$2\gamma_{T\alpha\alpha}(q)\gamma_{T\alpha\beta}(q)C_{T\alpha\beta}(q,t) + [\gamma_{T\alpha\beta}(q)]^2 C_{T\alpha\alpha}(q,t) \tag{20}$$

Here $c_{\alpha\alpha}(q)$ is the Fourier transform of $\alpha\alpha-$ direct correlation function, $\gamma_{L\alpha\alpha}(q)$ and $\gamma_{T\alpha\alpha}(q)$ are q -dependent quantities, which are defined in Balucani [14]. $C_{T\alpha\alpha}(q,t)$ und $C_{L\alpha\alpha}(q,t)$ are the transverse and longitudinal current correlation functions of the $\alpha\alpha-$ parts. $\triangle F_{s\alpha}(q,t)$ is the difference between $F_{s\alpha}(q,t)$ and $F_{0\alpha}(q,t)$, where $F_{0\alpha}(q,t) = \exp(-(k_BT/2m_\alpha)q^2t^2)$ expresses the free-particle-form of intermediate incoherent scattering function.

III. SIMULATIONS

The simulations are carried out as state-of-the-art isothermal-isobaric (N, T, p) calculations. The Newtonian equations of $N = 648$ atoms (130 Ni and 518 Zr) are numerically integrated by a fifth order predictor-corrector algorithm with time step $\Delta t = 2.5 \ 10^{-15}$s in a cubic volume with periodic boundary conditions and variable box length L. With regard to the electron theoretical description of the interatomic potentials in transition metal alloys by Hausleitner and Hafner [7], we model the interatomic couplings as in [8] by a volume dependent electron-gas term $E_{vol}(V)$ and pair potentials $\phi(r)$ adapted to the equilibrium distance, depth, width, and zero of the Hausleitner-Hafner potentials [7] for $Ni_{20}Zr_{80}$ [9]. For this model, simulations were started through heating a starting configuration up to 2000 K which leads to a homogeneous liquid state. The system then is cooled continuously to various annealing temperatures with cooling rate $-\partial_t T = 1.5 \ 10^{12}$ K/s. Afterwards the obtained configurations at various annealing temperatures (here 1500-800 K) are relaxed by carrying out additional isothermal annealing runs. Finally the time evolution of these relaxed configurations is modelled and analyzed. More details of the simulations are given in [9].

IV. RESULT AND DISCUSSION

We have calculated the total memory kernel $K_\alpha(t)$ of VACF in range $0,024 \leq q \leq 4,796$ Å^{-1}. The input data are all correlation functions that are analyzed from MD data. For simplifying we have only calculated the memory kernel at $T = 1500$ K. The reason for this is, because (i) according to some authors, except binary term and density-density coupling, the other couplings could be neglected by lower temperature, i.e., the contribution of the other couplings are very small, and more smaller than the contribution of the binary term and density-density coupling [16], (ii) after our experience there is a coupling contribution which decays slowly at lower temperature. These slowly decays make us technically a problem by the Laplace transform of couplings.
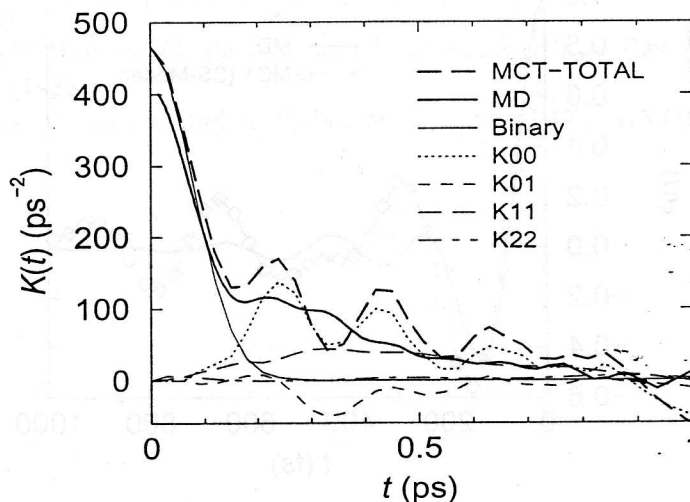
The figures (1) and (2) shows our results of the memory kernel $K_\alpha(t)$ of VACF. MD-results can be computed over the equation (1). From figures we can see that the results of SS-model do not have a good agreement with MD-results, escpecially those for Zr-atom. By Zr-atom the run of the memory kernel $K_\alpha(t)$ shows some of oscillations that by MD-results do not appear. These oscilations are primaly from the density-density coupling. According to eq.(14) the intermediate coherent scattering functions $\mathbf{F}(\mathbf{q}, \mathbf{t})$ are responsible for those oscialtions. The deviations between SS-models results and MD-results can also be shown by results in computing $\psi(t)$, e.g., on figures (3) and (4).

As shown in figures (1) and (2) the most significant contributions come from the density-density coupling, the second from the density-longitudinal current density coupling, and the least from the density-transverse current coupling.

gezeigt haben, kommt der größte Beitrag aus der Dichte-Dichte Kopplung, der 2.größte aus der Dichte-longitudinalen Strom Kopplung, und der kleinste Beitrag aus der Dichte-transversalen Strom Kopplung.
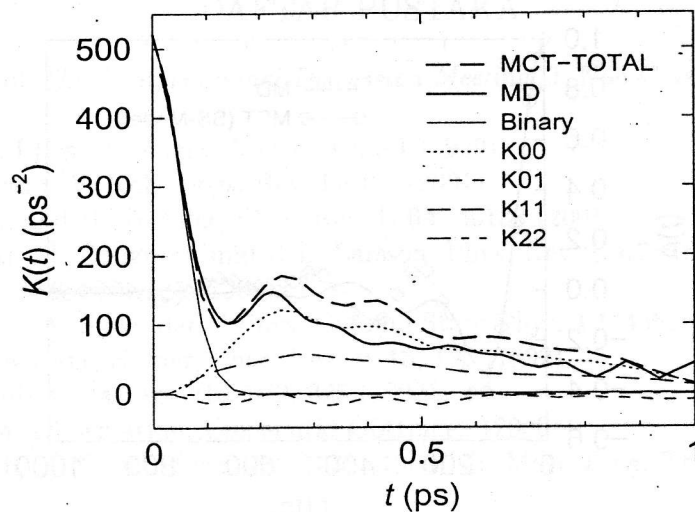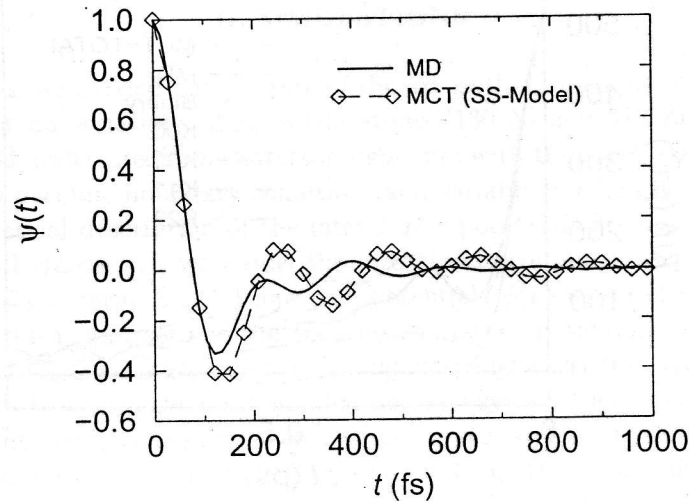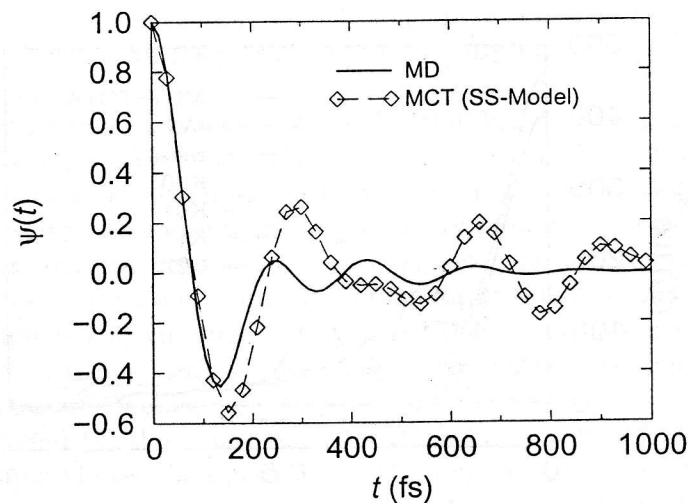
Gbr. 1. Ni - $K(t)/K(0)$.

Gbr. 2. Zr - $K(t)/K(0)$.

We have calculated the memory kernel of VACF based on SS-model. The particular used by calculating have produced from MD-simulation. We have compared the SS-model results and MD-results. Both results are shown a qualitative agreement, although quasi-titatively there is a deviations between both results, especially for Zr-subsystem. Three results are agreed with the general Mode Coupling Theory's predictions [2], namely that the most significant contribution is resulted from the density-density coupling. This coupling always is dominant when the temperature of system is lowered, and especially when the temperature of system is near the critical glass temperature T.

Gbr. 3. Ni - $\psi(t)$.

Gbr. 4. Zr - $\psi(t)$.

V. CONCLUDING REMARKS

We have calculated the memory kernel of VACF based on SS-model. The parameters used by calculating have produced from MD-simulation. We have compared the SS-model's results and MD-results. Both results are shown a qualitative agreement, although qualitatively there is a deviations between both results, especially for Zr-subsystem. These results are agreed with the generall Mode Coupling Theory's predictions [2], namely that the most significant contributions are resulted from the density-density coupling. This coupling always is dominant when the temperature of system is lowered, and especially when the temperature of system is near the critical glass temperature T_c.

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