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Glassy behavior of molecular crystals: A comparison between results from MD-simulation and mode coupling theory

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Abstract

We have investigated the glassy behavior of a molecular crystal built up with chloroadamantane molecules. For a simple model of this molecule and a rigid fcc lattice a MD-simulation was performed from which we obtained the dynamical orientational correlators $S_{\lambda\lambda'}(\mathbf{q},t)$ and the 'self' correlators $S^{(s)}_{\lambda\lambda'}(t)$, with $\lambda=(\ell,m)$, $\lambda'=(\ell',m')$. Our investigations are for the diagonal correlators $\lambda=\lambda'$. Since the lattice constant decreases with decreasing temperature which leads to an increase of the steric hindrance of the molecules, we find a strong slowing down of the relaxation. It has a high sensitivity on λ, λ'. For most (ℓ,m), there is a two-step relaxation process, but practically not for $(\ell,m)=(2,1)$, $(3,2)$, $(4,1)$ and $(4,3)$. Our results are consistent with the α-relaxation scaling laws predicted by mode coupling theory from which we deduce the glass transition temperature $T_c^{MD}\cong 217$ K. From a first-principle solution of the mode coupling equations we find $T_c^{MCT}\cong 267$ K. Furthermore mode coupling theory reproduces the absence of a two-step relaxation process for $(\ell,m)=(2,1)$, $(3,2)$, $(4,1)$ and $(4,3)$, but underestimates the critical nonergodicity parameters by about 50 per cent for all other (ℓ,m). It is suggested that this underestimation originates from the anisotropic crystal field which is not accounted for by mode coupling theory. Our results also imply that phonons have no essential influence on the long time relaxation.

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1. Introduction

The mode coupling theory (MCT) [1] is the most successful *microscopic* approach to describe glassy dynamics of supercooled liquids on a qualitative, and partly even on a quantitative level [2–4]. Particularly, *first-principle* comparisons between the solutions of MCT equations and results from experiments and simulations for various systems like the binary Lennard–Jones liquid [5], liquids of diatomic molecules [6,7], water [8,9], silica melt [10] and a model for orthoterphenyl [11] have confirmed the quality of MCT. These comparisons were restricted to the glass order parameters, the nonergodicity parameters. Going beyond that, even time-dependent quantities, like the intermediate scattering function, have been compared with each other for the binary Lennard–Jones liquid [12], binary mixtures of hard spheres [13,14] and the polydisperse quasi-hard-sphere system [15], again demonstrating consistency with MCT.

Glassy dynamics of systems with self-generated disorder is not restricted to liquids. Molecular crystals in their plastic phase exhibit glassy behavior as well. This has been found experimentally three decades ago [16]. Recently two of the present authors have extended MCT to molecular crystals [17]. Using the static structure factors from Percus–Yevick theory [18] the orientational glass transition of uniaxial hard ellipsoids on a simple cubic lattice has been

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investigated [17]. There it has been found that this transition is not driven by an orientational cage effect, analogous to supercooled liquids, but by the growth of orientational order. This growth manifests itself in an increase of the *static* orientational correlators at the Brillouin center or edge, which in turn leads to an increase of the memory kernel. However, before the corresponding orientational correlation length diverges at the corresponding equilibrium phase transition line, the nonlinear feedback mechanism of MCT results in an orientational glass transition. The same mechanism has been identified for a liquid of uniaxial hard ellipsoids [19]. Accordingly, the MCT glass transition line is located within the orientationally disordered ergodic phase [17,19] and not in the supercooled regime.

One may ask whether there also exists a cage-effect-driven glass transition for molecular crystals. Good candidates are plastic crystals which undergo a first order equilibrium phase transition to an orientationally ordered phase. Several such systems exist such as cyanoadamantane, ethanol, cyclooctanol, difluorotetrachloroethane or C_{60} [20]. Another one is chloroadamantane, which exhibits an equilibrium phase transition at $T_{\rm eq}^{\rm exp} \cong 244$ K [21]. A simple model for chloroadamantane (see next section) has been studied by MD-simulations [22,23]. A MCT analysis for the critical amplitudes and the α-relaxation time have demonstrated consistency with MCT predictions [23]. These predictions can really be extended from liquids to plastic crystals because the MCT equations for the latter have the same mathematical structure than for multi-component simple liquids [17].

It is the main goal of the present paper to perform a first-principle comparison between the results for chloroadamantane from a MD-simulation and MCT. The outline of our contribution is as follows. In Section 2 we will describe the model, introduce the orientational correlation functions, give some details of the simulational procedure and shortly describe the relevant MCT equations. Results are presented and discussed in Section 3 and Section 4 contains a summary and some conclusions.

2. Model and technical details

Chloroadamantane $C_{10}H_{15}Cl$ is a rather huge molecule which belongs to the substituted adamantane family. It shows a plastic phase structure isomorphous to cyanoadamantane, but the chloroadamantane molecule possesses a smaller substitute and a faster dynamics well adapted for MD-simulation investigations. Chloroadamantane undergoes at $T_{\rm eq}^{\rm exp} \cong 244$ K a first order transition from an ordered monoclinic structure to a rotator phase with face-centered-cubic (fcc) symmetry [21]. The plastic–liquid transition occurs at $T_{\rm m} \simeq 442$ K [21].

The simulated system is composed of rigid linear molecules with two sites: one chlorine atom (noted Cl) and one super atom (noted Adm) that models the adamantane part $C_{10}H_{15}$. The distance of both pointlike atoms is 3.3 Å and the molecule's moment of inertia is 302.733 amu Å^2. Molecular dynamics calculations were performed on a system of $N = 256$ molecules ($4 \times 4 \times 4$ fcc crystalline cells) interacting through a Lennard–Jones short range site–site potential of the form

$$v(r) = 4\epsilon((\sigma/r)^p - (\sigma/r)^q),$$

where r is the distance between two different sites. The parameters ϵ, σ, p and q are specified in Table 1.

The chloroadamantane molecule possesses a relatively large dipolar moment $\vec{\mu}$ (2.39 D) which is parallel to the molecular axis. The electrostatic interactions were handled by the Ewald method with two partial charges ($q = \pm 0.151e$) localized on both sites. Newton's equations of motion were solved with a time step of $\Delta t = 5$ fs. We worked in the NPT (constant number of molecules, temperature and pressure) and NVT (constant number of molecules, temperature and volume) statistical ensembles with periodic boundaries conditions. The sample was first equilibrated in the NPT ensemble. Then, MD runs at constant volume using the average volume determined from the NPT simulations were performed.

Since our molecule-model has one rotational symmetry axis we can use the angles $\Omega_n(t) = (\Theta_n(t), \phi_n(t))$ to characterize the orientation of the nth molecule at site n and time t. The microscopic local orientational density is given by

$$\rho_n(\Omega, t) = \delta(\Omega|\Omega_n(t)) \tag{1}$$

with $\delta(\Omega|\Omega') = (\sin\Theta)^{-1}\delta(\Theta - \Theta')\delta(\phi - \phi')$. Expansion with respect to spherical harmonics $Y_\lambda(\theta, \phi)$, $\lambda = (\ell, m)$ and performing a lattice Fourier transform leads to the tensorial orientational density modes:

$$\rho_\lambda(\mathbf{q}, t) = i^l \sum_{n=1}^{N} Y_\lambda(\Omega_n(t)) e^{i\mathbf{q}\mathbf{R}_n}, \tag{2}$$

where N is the number of lattice sites and $\mathbf{R}_n$ the lattice vector of the nth lattice site. The reader should note that we assume a *rigid* lattice and that $\mathbf{q}$ is restricted to the 1. Brillouin zone. Introducing the fluctuations $\delta\rho_\lambda(\mathbf{q}, t) = \rho_\lambda(\mathbf{q}, t) - \langle\rho_\lambda(\mathbf{q}, t)\rangle$ we can define the time dependent, tensorial orientational correlators:

$$S_{\lambda\lambda'}(\mathbf{q}, t) = \frac{4\pi}{N}\langle\delta\rho_\lambda^*(\mathbf{q}, t)\delta\rho_{\lambda'}(\mathbf{q}, 0)\rangle, \tag{3}$$

where $\langle\cdots\rangle$ denotes the canonical average over the initial conditions. Note that the absence of a head–tail symmetry leads to nontrivial correlators for all $\ell \geqslant 1$, while the absence of phonons leads to $S_{\lambda\lambda'}(\mathbf{q}, t) = 0$ for $\lambda = (0, 0)$ and/or $\lambda' = (0, 0)$ within the 1. Brillouin zone.

Table 1
Parameters for the two-site chloroadamantane model

Site–Site	p	q	ϵ (kJ/mol)	σ (Å)
Cl–Cl	12	6	1.441	3.350
Cl–Adm	14	8	3.087	4.786
Adm–Adm	16	11	12.47	6.200