Is There Something of Mode Coupling Theory in Orientationally Disordered Crystals?

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Molecular dynamics simulations have been performed on the orientationally disordered crystal chloroadamantane. We stress that universal behavior, relatively well described by the mode coupling theory, is shared by systems whose dynamics are almost completely controlled by translations or rotations. This investigation also shows the existence of a second remarkable dynamical crossover at the temperature $T_x > T_c$, consistent with a previous NMR and molecular dynamics study [F. Affouard *et al.,* Europhys. Lett. **53**, 611 (2001)]. This allows us to support clearly the existence of a "landscape-influenced" regime as recently proposed [S. Sastry *et al.,* Nature **393**, 554 (1998)].

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In recent years, a great deal of work has been done to obtain a fundamental understanding of the glassy state and the glass formation but no well-accepted theory has emerged so far [1]. At present, the only theory which gives precise predictions of the supercooled liquids' dynamics is the mode coupling theory (MCT) [2]. It particularly predicts an ergodic-to-nonergodic transition at the critical temperature T_c usually found above the calorimetric glass formation temperature T_g. T_c is now commonly considered as the crossover temperature to an activated dynamical regime recently called "landscape dominated" by Sastry *et al.* [3] since it is suspected that dynamics can be described by hopping processes between the different inherent structures of the potential energy landscape [4]. It must be noted that MCT does not intrinsically take into account these ergodicity-restoring processes, and deviations from the prediction of this theory are clearly observed below T_c. The existence of a second remarkable crossing temperature, denoted by T_x in this Letter, was recently shown from computer simulations [3–5]. The precise nature of this temperature found above T_c remains unclear but should correspond to the onset of nonexponential relaxation and non-Arrhenius temperature dependence of the relaxation times.

During the past ten years, a variety of experiments and molecular dynamics (MD) computer simulations have provided considerable insight into the nature of supercooled liquids [6]. Significant advances were particularly obtained concerning the role of the translational degrees of freedom, for which MCT gives detailed predictions, in the underlying mechanism of slow dynamics. Most glass formers also possess orientational degrees of freedom (ODOF) which are certainly involved in the glass formation. However, their relative importance during the dynamical slowing down remains unclear and have been the subject of very few thorough investigations. It should be noted that MCT was extended recently to liquids of nonspherical molecules [6,7]. One class of compounds offers attractive possibilities to focus mainly on the role of the partially overlooked ODOF and provides a valuable alternative to the molecular liquid glass formers. Indeed, some molecular crystals show a high temperature *plastic* phase in which the average positions of the centers of mass are ordered on a lattice while the orientations are dynamically disordered [8]. Some of them, called *glassy crystals* [9], such as cyanoadamantane [10], ethanol [11,12], carboranes [13], or cyclooctanol [14], can be deeply supercooled and present many properties characteristic of the conventional glass formers.

In this Letter, we discuss precisely, by means of a case study of chloroadamantane, if dynamical universal behavior is shared by orientationally disordered crystals and molecular liquids. Indeed, since both systems possess the same striking features of glass and glass formation, one can expect that some common microscopic mechanism is involved. One particularly has to mention numerical works made on very simple models of plastic crystal which exhibit typical dynamical features of supercooled liquids: Brownian planar rotors based on a uniformly frustrated *XY* model on a square lattice [15] and colliding hard needles distributed on a lattice [16]. Stimulated by these previous studies and by the various predictions of MCT, we have chosen to study the chloroadamantane $C_{10}H_5Cl$ (noted Cla in the following) plastic crystal. This compound belongs to the substituted adamantane family which presents excellent experimental candidates [10]. Very recently, by means of a NMR experiment and MD computer simulation, we have shown that this system exhibits a dynamical crossover transition at $T_x \simeq 350$ K in the pico-nanosecond regime [17]. It was interpreted as the first indication of a change in the energy landscape topography, as was recently proposed [3]. A two-step $(\alpha\text{-}\beta)$ relaxation was also observed to emerge but there were some indications that the T_x probably did not correspond to the T_c of the MCT, as developed for structural glass formers.

MD simulation of orientationally disordered molecular crystal Cla was performed at different temperatures from $T = 220$ to 500 K. Despite the very long MD runs, equilibrium of the system could not be obtained below $T \simeq 220$ K. A simple model was used which is described in detail in [17], so only the essential details are given in [18].

Figure 1 shows the orientational self-intermediate scattering function $F_u^s(q,t)$, for the arbitrary wave vector $q = 3.06$ Å^{-1}, as defined by Lewis and Wahnström in [19], where only the ODOF are taken into account. Clearly, by lowering the temperature, as already observed for the orientational correlation functions $C_l(t) = \langle P_l[\vec{\mu}(t) \cdot \vec{\mu}(0)\rangle$ in [17], the rotator phase of Cla exhibits a two-step relaxation. At intermediate times, $F_u^s(q,t)$ shows a plateaulike region which reveals the existence of an *orientational cage effect,* i.e., the rotational analog of the translational cage effect observed in liquids. This transient regime is followed by a slow decay to a nonzero value called the elastic incoherent structure factor (EISF) and denoted by $A_0(q) = \lim_{t\to\infty} F_u^s(q,t)$ [8] which gives information on the time-averaged orientational geometry of the molecular motions. $A_0(q)$ is displayed in Fig. 2 for different wave vectors and exhibits an unusual temperature dependence which confirms, as already seen in [17], the existence of a change of the rotational dynamics. Indeed, at high temperature, an isotropic diffusion rotation model gives a good description of the dynamics. By lowering the temperature, discrepancies of this model are clearly seen in Fig. 2 and a jumplike motion between preferred orientations may be assumed.

In the following, we try to describe our data in the MCT framework. The idealized version [2] of this theory predicts a two-step relaxation scenario (fast β, slow α) of all the time dependent correlators $\phi(q,t)$. MCT particularly states the following points: At short time, $\phi(q,t)$ decays to a plateau value, the so-called nonergodicity parameter classically noted f_q^c. The dynamical regime associated with this plateau is called β. It is centered around the rescaling time t_σ which is given by $t_\sigma = t_0|\sigma|^{-1/2a}$, where t_0 is a characteristic microscopic time and σ is proportional to $|T - T_c|$. Above T_c, the late β regime or the early α relaxation is described by the following power law (going beyond first order):

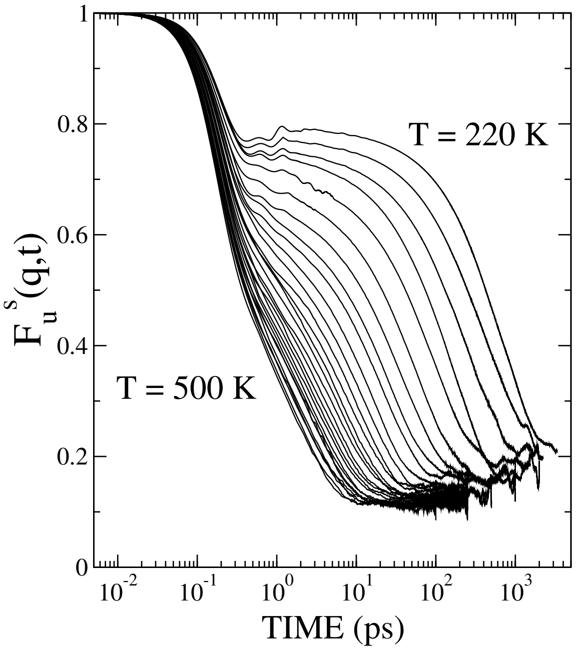

FIG. 1. Orientational self-intermediate scattering function $F_u^s(\vec{q},t)$ as a function of time t for wave vector $q = 3.06$ Å^{-1}. $F_u^s(\vec{q},t)$ is defined as $\sum_{i=1}^{N}\sum_{a=1}^{N_a}\langle \exp[i\vec{q} \cdot (\vec{u}_{i,a}(t) - \vec{u}_{i,a}(0))]\rangle$, where $\vec{u}_{i,a} = \vec{R}_{i,a} - \vec{R}_i^{\text{c.m.}}$. $\vec{R}_i^{\text{c.m.}}$ is the center of mass of molecule i and $\vec{R}_{i,a}$ denotes the position of site a in each molecule ($N_a = 2$ in this paper).

$$\phi(q,t) = f_q^c - h_q^{(1)} \cdot (t/\tau)^b + h_q^{(2)} \cdot (t/\tau)^{2b}, \qquad (1)$$

where the first two terms correspond to the classical von Schweidler law, the last term is a second-order correction, and $\tau = t_0|\sigma|^{-\gamma}$ with $\gamma = 1/2a + 1/2b$. At long time, MCT also predicts that the previous fast regime is followed by a slow relaxation, called α, with the characteristic time τ. Furthermore, parameters a and b are temperature and q independent and related via $\Gamma^2(1 - a)/\Gamma(1 - 2a) = \Gamma^2(1 + b)/\Gamma(1 + 2b)$, where $\Gamma(x)$ is the gamma function.

In order to verify the validity of those scaling laws, we first tried to fix the exponent b by using the factorization theorem in the β regime, where hopping processes are not supposed to be dominant. The ratio $R_\phi(t) = [\phi(t) - \phi(t_1)]/[\phi(t_2) - \phi(t_1)]$, where (t_1, t_2) are two different arbitrary times in the β regime, has been calculated at different temperatures and for different correlators ϕ [$F_u^s(q,t)$ for several wave vectors and $C_l(t)$ for $l = 1, 2$ as defined in [17]]. The results are displayed in Fig. 3. Clearly, there exists a time domain where the different correlation functions collapse onto a master curve in the β regime, as predicted by MCT. Assuming

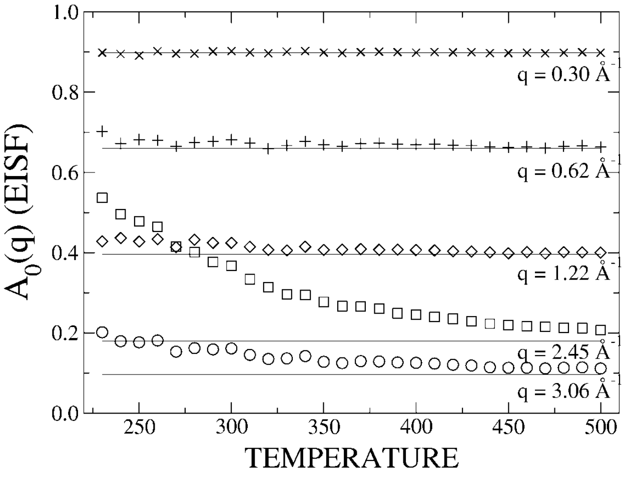

FIG. 2. Elastic incoherent structure factor as a function of temperature for the arbitrary wave vectors $q = 3.06$, 2.45, 1.22, 0.62, and 0.30 Å^{-1}. For a rotational diffusion model (solid lines), the EISF for one scattering atom moving on a sphere of radius a can be written as $A_0(q) \sim j_0(q \cdot a)$, where j_0 is the zero-order spherical Bessel function [8].

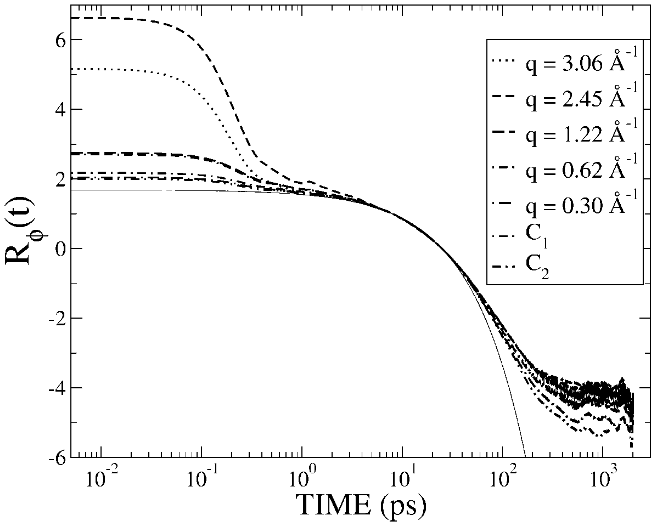

FIG. 3. Ratio $R_\phi(t) = [\phi(t) - \phi(t_1)]/[\phi(t_2) - \phi(t_1)]$, where (t_1, t_2) are two different arbitrary times in the β regime at $T = 260$ K. The following correlation functions have been used: $\phi(t) = F_u^s(q, t)$, for wave vectors $q = 3.06$, 2.45, 1.22, 0.62, and 0.30 Å^{-1}, and $\phi(t) = C_l(t)$, for $l = 1, 2$ angular correlation functions (see [17]). The master curve (solid line), obtained by the von Schweidler law with the exponent $b = 0.79$, is also displayed.

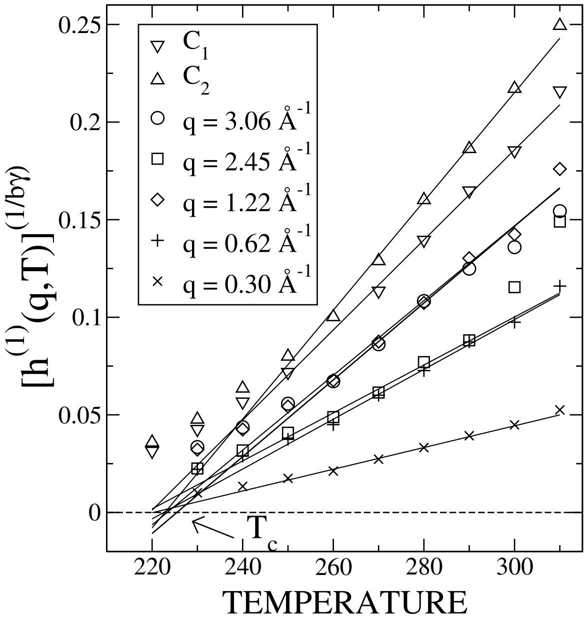

FIG. 4. Total prefactor $[\tilde{h}^{(1)}]^{1/b\cdot\gamma}$ as a function of temperature for all investigated correlators (see Fig. 3). The fitting procedure reveals a linear dependence (solid lines) of the total prefactor which extrapolates to zero at the critical temperature $T_c \simeq 225 \pm 8$ K for all correlators.

the correlator function ϕ departs from the plateau with a von Schweidler law, it is possible to show that the master curve depends only on the exponent b. Using a fitting procedure performed at several different temperatures for all correlators mentioned previously, we obtained the best results for $b = 0.79$ which corresponds to $a = 0.36$ and $\gamma = 2.02$. Then, fixing these values, we performed individual fits of the different correlators in the late β regime using Eq. (1) with free parameters f_q^c, $\tilde{h}^{(1)} = h^{(1)}(q) \cdot \tau^{-b}$, and $\tilde{h}^{(2)} = h^{(2)}(q) \cdot \tau^{-2b}$. Only the temperatures below 330 K, where the plateau region is clearly defined, were considered. The total prefactor $\tilde{h}^{(1)}$ is displayed in Fig. 4. $\tilde{h}^{(2)}$ is not shown in this Letter but it exhibits the same temperature dependence. A temperature dependence is clearly found which extrapolates to zero at the critical temperature $T_c \simeq 225 \pm 8$ K for the different correlators. A deviation to the linear evolution is observed close to T_c which could be attributed to the occurrence of hopping processes. The nonergodicity parameter f_q^c shows a relatively smooth temperature evolution but we have no clear evidence of a cusp at T_c due to the lack of data at low temperature.

In the α regime, we defined the relaxation time τ_q as the time it takes for the different correlators to decay from 1 to $1/e$. It is assumed that any characteristic times belonging to the α regime show asymptotically the same temperature dependence $\tau_q \sim \tau$. The τ_1 and τ_2 relaxation times are defined similarly for the orientational correlation functions $C_{l=1,2}$. For a direct comparison, orientational self-intermediate scattering functions were rescaled with the EISF as $[F_u^s(t) - A_0(q)]/[1 - A_0(q)]$ in order to decay with time from 1 to 0. According to MCT, the α relaxation times, $\tau_q^{-1/\gamma}(T)$, should yield straight lines intersecting the abscissa at $T = T_c$. Figure 5 shows that for all investigated correlators this prediction holds well over a relatively large temperature range. Extrapolation of the temperature dependence gives a critical temperature of $T_c \simeq 225 \pm 8$ K, consistent with the β-regime analysis. About 40 K above T_c, discrepancies with the MCT power law prediction are seen, as already shown in the fast regime, and are certainly due to the hopping processes. Furthermore, the time-temperature superposition principle was also checked and we found that all correlators fall onto a master curve in the α time domain when plotted as a function of the rescaled time t/τ_q (not display in this Letter). However, at high temperatures, close to the dynamical crossover previously observed at T_x in [17], a clear deviation of the α relaxation from the MCT prediction is found. At $T > T_x \simeq 350$ K, we have calculated that our data can be very well reproduced by a simple Arrhenius law. The T_x crossing temperature alters slightly for the different correlators. At present, we have no clear interpretation of this feature.

Very recently, we obtained promising results concerning the energy landscape description of this model. Since further investigations are necessary, they are not included in this Letter. It was particularly observed that the average energy of the inherent structures does not change significantly above T_x while it decreases progressively below this temperature. As has been clearly demonstrated for a binary Lennard-Jones MD simulation in [3–5], we obtained in this paper a strong indication of the existence of a

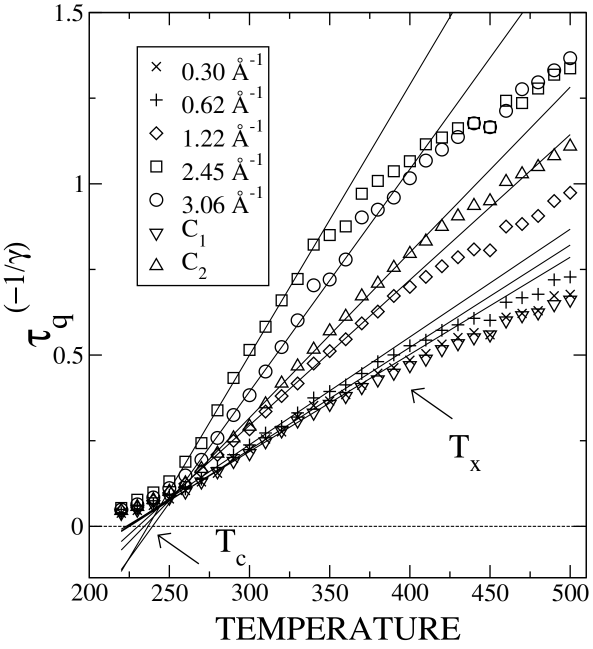

FIG. 5. α relaxation time $\tau_q^{-1/\gamma}$ as a function of temperature for all investigated correlators (see Fig. 3). The exponent $\gamma = 2.02$ has been extracted from the MCT analysis in the β regime. The solid lines indicate MCT fit using the linear law $\tau_q^{-1/\gamma} \sim (T - T_c)$. Deviation from the MCT prediction is found at $T > T_x \simeq 350$ K, where τ_q can be fitted with a simple Arrhenius law.

landscape-influenced regime occurring in the temperature range $[T_c - T_x]$.

In conclusion, this study reveals that systems whose dynamics are almost completely controlled by ODOF share some common dynamical features with liquid glass formers, relatively well described by the idealized version of the MCT. It was recently shown that the asymptotic predictions of this theory which initially described simple van der Waals atomic liquids still hold for molecular systems [6,7]. Nevertheless, an extension of the MCT to systems, which possess ODOF only, has not been developed so far. Our work suggests such a possibility. Furthermore, this investigation confirms the existence of a second remarkable dynamical crossover at the temperature $T_x > T_c$, consistent with previous calorimetric [20], NMR, and MD studies [17]. This allows us to determine precisely the temperature range $[T_x - T_c]$ of the landscape-influenced regime in this system as defined recently by Sastry *et al.* [3] for a model glass forming liquid. Our results obtained for Cla call for new investigations: (i) It would be of great interest to study the q dependence of the different parameters f_q^c, $h_q^{(1)}$, or τ_q which was not performed in this Letter for Cla due to the limited number of investigated wave vectors. (ii) Experimental and numerical extensions of this Letter to other well-documented orientationally disordered crystals such as cyclooctanol, carboranes, or ethanol are needed to fully validate the MCT picture. (iii) Theoretical studies are highly desirable in order to clarify the precise nature of the dynamical crossover occurring at T_x which remains unclear at present.

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