Is there something of the MCT in orientationally disordered crystals?

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Molecular Dynamics simulations have been performed on the orientationally disordered crystal chloroadamantane: a model system where dynamics are almost completely controlled by rotations. A critical temperature \( T_c \approx 225 \text{ K} \) as predicted by the Mode Coupling Theory (MCT) \(^6\). The idealized version of this theory particularly predicts an ergodic to nonergodic transition at the critical temperature \( T_c \), which is usually depicted as an ideal-glass transition. However, experimentally, no sharp transition is observed at \( T_c \) and the real glass formation only occurs at the calorimetric temperature \( T_g < T_c \). It is suspected that some not so well understood processes \( \text{i.e.} \) thermally activated hopping restore ergodicity below \( T_c \) (‘landscape-dominated’ regime). During the past ten years, a variety of experiments \(^1\) (time-of-flight neutron, Raman, depolarized light scattering, dielectric spectroscopy, optical Kerr effect) and Molecular Dynamics (MD) computer simulations have been made to validate MCT. It has been particularly shown that MCT gives an outstanding good description of simple liquids (binary Lennard-Jones, hard sphere) while for molecular liquids where both translational and orientational degrees of freedom (TDOF, ODOF) coexist, the predictions of the MCT seem only in fair agreement with the experimental or the simulation data. This raises particularly the question, which remains a matter of debate at present, of the relative importance of rotations and translations in molecular liquids during the dynamical slowing down.

One class of compounds offers attractive possibilities to focus mainly on the role of the ODOF and provides a valuable alternative to the structural molecular liquid glass-formers. Indeed, some molecular crystals show a high temperature plastic phase in which the average position of the centers of mass are ordered on a lattice while the orientations are dynamically disordered. Some of them, called glassy crystals \(^8\), such as cyanoadamantane \(^8\), ethanol \(^4\) \(^5\) \(^9\) or cyclooctanol \(^1\), can be deeply supercooled and present many properties characteristic of the conventional molecular liquid glasses such as a step in the specific heat at the glass transition or a non-Arrhenius behaviour of the relaxation times.

In the present Letter, we discuss precisely, by means of a case study of chloroadamantane, the validity of MCT in orientationally disordered crystals. Indeed, although many experimental facts have been collected for this class of compounds in the deep supercooled domain, we have to emphasize that it really exist very few informations of dynamics far above \( T_g \). This particularly raises the question if MCT could be valid for such systems where dynamics are mainly controlled by rotations. One have to mention a numerical investigation made by Renner \textit{et al.} in \(^1\) where a system of colliding hard needles distributed on a lattice, \( \text{i.e.} \) a simple model of plastic crystal, has shown a rotational dynamical decoupling. Stimulated by this study and by the various predictions of MCT, we have chosen to study the chloroadamantane \( \text{C}_{19}\text{H}_{15}\text{Cl} \) (noted Cla in the following) molecular crystal. This compound belongs to the substituted adamantane family which presents excellent experimental candidates \(^8\). Very recently, by means of NMR experiment and MD computer simulation, we have shown that this system exhibits a dynamical crossover transition at \( T_x \approx 350 \text{ K} \) in the pico-nanosecond regime \(^1\). It was interpreted as an indication of a a change of the energy landscape topography as it has been recently proposed \(^4\). In addition, this crossover was suspected to be the analogue of the Goldstein crossing temperature between quasi-free diffusion and activated regime predicted in liquids. Two-step (\( \alpha - \beta \)) relaxations was also observed to emerge but there were some indications that \( T_x \) 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 have been performed at different temperatures from \( T = 220 \) to \( 500 \text{ K} \). Owing to the very long MD runs, equilibrium of the system could not be obtained below \( T \approx 220 \text{ K} \). A simple model was used which is completely described in \(^3\) \(^4\), so only the essential details are given in \(^3\).

Fig. \(^1\) shows the orientational self intermediate scat-
FIG. 1: Orientational self intermediate scattering function \( F'_u(q,t) \) as function of time \( t \) for wave vector \( q = 3.06 \text{ Å}^{-1} \). \( F'_u(q,t) \) is defined as \( \sum_{i=1}^{N} \sum_{a=1}^{N_a} \langle \exp[iq.(\vec{u}_{i,a}(t) - \vec{u}_{i,a}(0))] \rangle \) where \( \vec{u}_{i,a} = \vec{R}_{i,a} - \vec{R}_{i,m} \). \( \vec{R}_{i,m} \) is the center of mass of molecule \( i \) and \( \vec{R}_{i,a} \) denotes the position of site \( a \) in each molecules (\( N_a = 2 \) in the present study).

FIG. 2: Elastic incoherent structure factor (EISF) as function of temperature for arbitrary wave vector \( q = 3.06, 2.45, 1.22, 0.62 \) and 0.30 \( \text{Å}^{-1} \). For a rotational diffusion model (solid lines), the EISF for one scattering atom moving on a sphere of radius \( a \) can be written: \( A_0(q) \sim j_0(q,a) \) where \( j_0 \) is the 0-order spherical Bessel function [14].

tering function \( F'_u(q,t) \), for arbitrary wave vector \( q = 3.06 \text{ Å}^{-1} \) \( (q = (q,0,0)) \), as defined by Lewis et al. in [17] where only the ODOF are taken into account. Clearly, lowering the temperature, as already observed for the orientational correlation functions \( C_l(t) = \frac{1}{N} \sum_{i=1}^{N} \langle \hat{R}_l \cdot (\hat{R}(t) - \hat{R}(0)) \rangle \) in [1], the rotator phase of Cl shows a plateau-like region which reveals the existence of an orientational cage effect i.e. the rotational analogue of the translational cage effect observed in liquids. This transient regime is followed by a slow decay to a non zero value called elastic incoherent struc-

ture factor (EISF) and noted \( A_0(q) = \lim_{t \to \infty} F'_u(q,t) \) [10] which gives information on the time-average orientational geometry of the molecular motions. \( A_0(q) \) is displayed in the figure 2 for different wave vectors and exhibits an unusual temperature dependence which confirms, as already seen in [1], the existence of a change of the rotational dynamics. Indeed, at high temperature, an isotropic diffusion rotation model gives a good description of dynamics. Lowering the temperature, discrepancies of this model are clearly seen in the figure 2 and a jump-like between preferred orientations type of motion are to be assumed.

In the following, we try to describe our data in the MCT framework. The idealized version [3] of this theory predicts a two-step relaxation scenario (fast \( \beta \), slow \( \alpha \)) 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 \( f_\beta \). The dynamical regime associated to this plateau is called \( \beta \). It is centered around the rescaling time \( t_\sigma \) which is given by \( t_\sigma = t_0 |\sigma|^{-1/2a} \) where \( t_0 \) is a characteristic microscopic time and \( \sigma \) is proportional to \( |T - T_c| \). Above \( T_c \), the late \( \beta \) regime or the early \( \alpha \) relaxation is described by the following power law (going beyond first order):

\[
\phi(q,t) = f_\beta^{(1)}(t/\tau)^{b} + h_q^{(2)}(t/\tau)^{2b}
\]

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 \( \alpha \), with the characteristic time \( \tau \). Furthermore, parameters \( a \) and \( b \) are temperature and \( q \) independent and related via \( \Gamma(1-a)/\Gamma(1-2a) = \Gamma^2(1+b)/\Gamma(1+2b) \) where \( \Gamma(x) \) is the gamma function. In order to verify the validity of those scaling laws, we first tried to fit the exponent \( b \) using the factorization theorem in the \( \beta \) 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 \( \beta \) regime, has been calculated at different temperatures and for different correlators \( \phi(F'_u(q,t)) \) for several wave vectors and \( C_l(t) \) for \( l = 1,2 \) as defined in [1]. Results are displayed in the figure 3. Clearly, it exists a time domain where the different correlation functions collapse onto a master curve in the \( \beta \) regime as it is predicted by MCT. Assuming the correlator function \( \phi \) 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 fit of the different correlators in the late \( \beta \) regime using the equation [3] with free pa-
same temperature dependence. A temperature dependence is clearly found which extrapolates to zero at the critical temperature \( T_c \approx 225 \pm 8 \text{ K} \) for all correlators.

In the \( \alpha \) regime, we defined the relaxation time \( \tau_q \) as the time it takes to the different correlators to decay from 1 to 1. It is assumed that any characteristic times belonging to the \( \alpha \) regime show asymptotically the same temperature dependence \( \tau_q \sim \tau \). The \( \tau_1 \) and \( \tau_2 \) relaxation times are defined similarly for the orientational correlation functions \( C_{l=1,2} \). For a direct comparison, orientational self intermediate scattering functions have been rescaled with the EISF as \( \left[ F_0^\alpha (q) - A_0 (q) \right] / \left[ 1 - A_0 (q) \right] \) in order to decay with time from 1 to zero. According to MCT, the \( \alpha \) relaxation times \( \tau_q^{-1/\gamma} (T) \) should yield straight lines intersecting the abscissa at \( T = T_c \). Fig. 3 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 \( T_c \approx 225 \pm 8 \text{ K} \) consistent with the \( \beta \)-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 certainly due to hopping processes. Furthermore, the time-temperature superposition principle has been also checked and we found that all correlators fall onto a master curve in the \( \alpha \) time domain when plotted as function of the rescaled time \( t/\tau_q \) (not display in the present Letter).

At present, we have no clear interpretation of this feature. Nevertheless, as it has been nicely demonstrated by Sastry et al. [3] for a binary Lennard-Jones MD simulation, we obtained here for plastic crystal a strong indication of the existence of a ‘landscape-influenced’ regime occurring in the temperature range \( [T_C - T_x] \). The dynamics should be ‘landscape-dominated’ only below \( T_c \).

In conclusion, for the first time, this study reveals that dynamics of one orientationally disorder crystal can be relatively well described by the idealized version of the MCT. It is noteworthy to remark that such an agreement was expected for those systems where dynamics are almost completely controlled by rotations, since some very recent extensions of MCT to molecular systems [6, 18, 19] have particularly shown that the asymptotic predictions of the idealized version of MCT still hold. For Cia plastic crystal, the same critical temperature \( T_C \approx 225 \text{ K} \) can be extracted in the \( \alpha \) and \( \beta \) regime which strongly supports the MCT description. Furthermore, this investigation confirms the existence of a second remarkable dynamical crossover at the temperature \( T_x > T_c \) consistent with previous calorimetric [20] and NMR and MD.
Fig. 5: $\alpha$ relaxation time $\tau_0^{-1/\gamma}$ as function of temperature for all investigated correlators (see Fig. 3). The exponent $\gamma = 2.02$ has been extracted from the MCT analysis in the $\beta$ regime. Solid lines indicate MCT-fit using the linear law $	au_0^{-1/\gamma} \sim (T - T_c)$. Deviation from the MCT prediction is found at $T > T_x \simeq 350$ K where $\tau_q$ can be fitted with a simple Arrhenius law.

This allows us to determine precisely the temperature range $[T_x - T_c]$ of the influenced-landscape’ regime in this rotator system as defined recently by Sastry et al. [2, 3] for a model glass forming liquid. Our results obtained for C1 call for new investigations: (i) It will be of great interest to study the q dependence of the different parameters $f_c$, $h^{(1)}_q$, or $\tau_0$ which has not been performed in the present Letter for C1 due to the limited number of investigated wave vectors. (ii) Experimental and numerical extensions of the present study to other well documented orientationally disordered crystals such as cyclooctanol 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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[15] Our system is made of molecules composed of two sites: one chlorine and one super atom that models the adamantane group C$_{10}$H$_{15}$. Molecular dynamics calculations were performed on a system of $N = 256$ (4 x 4 x 4 fcc crystalline cells) molecules interacting through a short range site-site Lennard-Jones potential. The electrostatic interactions were handled by the Ewald method with two partial charges ($q = \pm 0.151$ e) localized on both sites which reproduce the experimental dipolar moment $|\vec{\mu}| \simeq 2.39$ Debyes. A time step of $\Delta t = 5$ fs was used to integrate the Newton’s equations of motion. We worked in the NPT statistical ensemble with periodic boundary conditions.
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