Experimental and numerical signatures of dynamical crossover in orientationally disordered crystals

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By means of NMR experiment and MD computer simulation we investigate the dynamical properties of a chloroadamantane orientationally disordered crystal. We find a plastic-plastic dynamical transition at $T_2 \simeq 330$ K in the pico-nanosecond regime. It is interpreted as the rotational analogue of the Goldstein crossing temperature between quasi-free diffusion and activated regime predicted in liquids. Below $T_x$, NMR experimental data are well described by a Frenkel model corresponding to a strongly anisotropic motion. At higher temperatures, a drastic deviation is observed toward quasi-isotropic rotational diffusion. Close to $T_x$, we observe that two-step relaxations emerge. An interpretation which is based on the present study of a specific heat anomaly detected by a recent calorimetric experiment is proposed.

The elusive nature of the glass formation relates to the sharp rise of the transport coefficients (viscosity or relaxation times) in a narrow temperature range above the calorimetric transition temperature $T_g$ [1]. Some of the recent active investigations focus on the existence of a dynamical crossover which could occur above $T_g$ in glass-forming liquids. The idealized version of the Mode Coupling Theory (MCT) [2] predicts that a dynamical decoupling occurs at a critical temperature $T_c > T_g$ [3]. It is however suspected that $T_c$ corresponds to or is close to the temperature $T_x$ at which the system also starts being sensitive to the energy landscape in its exploration of the configurational hyperspace [4–6]. Motions in liquids would thus be dominate at low temperature by activated processes between potential energy minima while free diffusion occurs at high temperatures. Such dynamical crossover was already argued by Goldstein thirty years ago [7]. In the last few years a significant effort has been undertaken to investigate experimentally and numerically the properties of glass-forming liquids in order to detect such dynamical changeover. However, most of the good glass-formers which allow easy investigations of the supercooled metastable state such as oterphenyl [8] are molecular liquids where contributions due to translational, orientational and internal degrees of freedom (TDOF, ODOF) are inextricably mixed. It makes the properties of the energy landscape topography, MCT predictions or detection of dynamical transitions extremely hard to investigate. A clear visualization of the different processes at the molecular level of simple model compounds is needed. The discovery that some orientationally disordered crystals exhibit the phenomenology of conventional glasses is therefore an exciting opportunity.

Indeed, some molecular crystals present a plastic phase in which the molecular centers of mass show a perfect average crystalline translational order while the orientations are dynamically disordered. Some plastic crystals, i.e. glassy crystals [9], can be undercooled and present many properties characteristic of conventional molecular-liquid glasses, both in the way the glass occurs (undercooling) and the thermodynamic signatures. Glassy crystals which are the very rotational analogue of liquid glass-formers offer an excellent opportunity to focus on the role of the ODOF. In [10], Barrat et al. investigated the rotational dynamics of a colliding hard needle model on a rigid lattice and have shown the emergence of a dynamical decoupling. Substituted adamantanes plastic crystals such as the cyanoadamantane [11] noted CNa in the following are good experimental candidates and some of them exhibit a glass transition signature. In [12], MD numerical simulations of a simple model inspired from the CNa molecular geometry allowed us to investigate both TDOF and ODOF properties. In this work a dynamical decoupling and two-step relaxations were found to be possible in a rotator phase.

In the present letter, we address the possibility of finding such a behaviour in a real system. We have found chloroadamantane C$_{10}$H$_{15}$Cl (Cla) to be a very favorable and relevant system for this investigation. It shows a plastic phase over a wide interval of temperature [442 – 442] K (see Fig. 1c) and a structure isomorphous to CNa [13]. The Cla molecule possesses a smaller substitute than does CNa. This gives rise to faster dynamics in the plastic phase where rotational motions are also suspected to change in nature as it is reported from earlier incoherent quasielastic neutron scattering experiments [14]. Our results show for the first time, for a rotator phase, using experimental NMR and numerical MD simulations, the evidence of a dynamical crossover between quasi-free rotational diffusion and activated motion occurring in the pico-nanosecond regime. It is also shown that this accident can explain the existence of a calorimetric anomaly (see Fig. 1f) recently detected in Cla by Oguni et al. [15].

NMR experiments were performed on Chloroadamantane on Bruker spectrometers ASX100 and AMX 400. $^1$H and $^{13}$C linewidths and relaxation times were measured. The experiments were carried out on powder sam-
amples sealed in glass tubes for $^1$H experiments or packed into zirconium rotors for $^{13}$C MAS experiments. The spinning speed of the sample was 4 kHz. The sample temperature was regulated to within ±0.5 K by a Bruker BVT 2000 temperature controller. The spin lattice relaxation times were measured using the inversion recovery pulse sequence, the recovery of the magnetization was always found to be exponential within experimental accuracy. The $^1$H spin lattice $T_1$ vs temperature is reported in Fig. 1a. The main feature of this curve is the occurrence of an abrupt change of the activation energy, from 1400 K to 3400 K, at a temperature close to $T_x \approx 330$ K which is far from both the melting temperature and the brittle to plastic transition.

Slow diffusive motions of the molecules are generally observed in plastic phases. In the present study, their contribution to the spin-lattice relaxation time $T_1$ was found to be negligible in the temperature range investigated. This fact was particularly evidenced by measurements of the dipolar order $T_{1D}$ (see Fig. 1b). The diffusional correlation time ($\tau_{d_{ff}} \approx 30,000$ s at room temperature) was found to be strongly temperature dependent with a very high activation energy $\approx 14000$ K. Self diffusion has thus to be discarded as the origin of the break observed in $T_1$. Previous neutron studies have suggested that two types of motion occur in the rotator phase of Cla: tumbling of the molecular $C_3$ axis among six fourfold crystallographic axes along the [100] direction, and fast uniaxial rotation about the threefold axis. It was shown that the motion around the molecular axes is very fast ($\approx 10^{-12}$ s at room temperature) with an activation energy of about 1240 K. Therefore, it takes place outside the time window where the dynamical crossover is detected at $T_x$. Dipolar tumbling motions are thus mainly involved in the evolution of the spin-lattice relaxation. Two separate temperature domains are clearly identified: below $T_x$, both NMR experimental proton and carbon data are well described by a Frenkel model assuming an Arrhenian behavior of tumbling and uniaxial rotations. Above $T_x$, it was not possible to describe the evolution of $T_1$ using the previous model. Hence, we expect that some hypotheses of this model in particular the finite number of equilibrium positions become irrelevant at high temperatures.

Anisotropy in the rotational motion can be precisely seen from the spin lattice relaxation times of the three different protonated carbons. Effectively the main relaxation process of the methylene and methine carbons is the dipole-dipole interaction between the $^{13}$C nuclei and their attached protons (see Fig. 1b). Relaxation times for carbon were measured as a function of temperature in the rotator phase. The ratio $T_1(C4)/T_1(C2)$ of the relaxation times for the methylene (C2, C4) is displayed in Fig. 1c. A strongly anisotropic motion is found below $T_x$ where the ratio of the carbon relaxational times is about 0.25. This latter value can be well reproduced by the previous Frenkel model. A drastic deviation from the anisotropic behaviour occurs at high temperatures where a ratio value of 0.7 is reached. Since free isotropic rotational diffusion processus would correspond to identical relaxational times for the methylene, this result reveals the influence of the residual crystalline field on the rotational dynamics. The experimental heat capacity obtained by Oguni et Al. in the Cla plastic phase is reported in Fig. 1c. The evolution of $C_p$ shows an anomalous hump which was reported to resemble somewhat to a Schottky anomaly. Owing to the nature of the Cla molecule which is mainly rigid, conformational changes have to be discarded for the origin of the Schottky anomaly. Clearly, the hump covers the entire temperature range where the dynamical crossover is seen in our NMR investigation. Its origin will be discussed in the light of the MD simulation results.

MD simulations have been performed at 29 different temperatures from $T = 220$ to 500 K for a sample corresponding to the crystalline fcc rotator phase on a simple model of Cla (see Fig. 2). A complete description of the model is given in [17, 18]. Owing to the very long MD runs, we succeeded in investigating truly equilibrated states of the system down to 220 K. The reorientational motions can be described by a set of correlation functions which are defined as: $C_l(t) = \frac{1}{N} \sum_{i=1,N} \langle \hat{\mu}_i(t) \hat{\mu}_i(0) \rangle$ where $P_l$ is the $l$-order Legendre polynomial and $\hat{\mu}_i$ is the individual dipolar moment of the molecule $i$. The nature of dynamical changes and anisotropy can be checked by
computing $C_{l=1,2}$ functions which can also be related to the information obtained from NMR relaxation measurements.

Fig. 3 shows the $C_2(t)$ time correlation function for all investigated temperatures above 220 K. Clearly, a two step relaxational behaviour classically seen in supercooled molecular liquids \[8, 19\] is shown in our simulations. When lowering the temperature, an intermediate plateau region emerges which proves the presence of an orientational caging between neighboring molecules. This is the rotational analogue of the translational cage effect observed in liquids. This transient regime is followed by a slow $\alpha$ process which can be associated in our system, as checked for CNa \[13\], with large tumbling motion between fourfold crystallographic directions where dipoles are preferably localized (see Fig. 2). A consequence is that the tumbling of one molecule is allowed only if an orientational rearrangement of its local neighbors occurs. This cooperative motion is clearly displayed using projections of the individual dipolar moments on one crystallographic plane in Fig. 2.

The $\tau_1$ and $\tau_2$ relaxational times are defined as the time it takes for their respective time correlation functions to decay $e^{-1}$ of their initial values. They are displayed in Fig. 4a. Clearly, close to $T_x \approx 330$ K, both $\tau_1$ and $\tau_2$ relaxational times start diverging simultaneously from the Arrhenian high temperature behaviour. Both high and low temperature apparent activation energies are found to be in good agreement with NMR experimental results. The nature of the rotational motions involved in this dynamical change is given by the ratio $\tau_1/\tau_2$ in Fig. 4b. This latter evolves from a value equal to 3 corresponding to free small-step rotational diffusion to a value of 1 classically associated to activated jump-like motion (see also Fig. 3) \[20, 21\]. These results prove for the first time the existence of a plastic-plastic transition which can be interpreted as the rotational analogue of the Goldstein crossing temperature in liquids. It could also be associated with a different process of exploring the energy landscape topography above and below $T_x$. As it has been recently \[10\] proposed, dynamics of the system can be viewed as hopping processes between separated inherent structures at sufficiently low temperatures.

![Fig. 2](image2.png)

**FIG. 2.** a. Snapshots of the $\vec{\mu}$ dipolar moments are projected on one $x_y$ plane at different instants in a run of 250 ps above (400 K) and below (220 K) $T_x \approx 330$ K. At $T = 220$ K, Some orientations are not populated since the system is not completely equilibrated over this duration. b. trajectory of the dipolar cosine angle $\theta$ of a target molecule at the same temperatures.

![Fig. 3](image3.png)

**FIG. 3.** Orientational correlation function $C_2$ as function of time $t$ at different temperatures from 220 to 500 K.

Specific heats have been directly extracted from the calculated enthalpy ($C_p = dH/dT$) and are shown in Fig. 4. Clearly, a pronounced hump is seen which extends over the low temperature part of the rotator phase below 350 K. It proves that our MD simulation captures the main features which are responsible to the anomaly found in calorimetric experiments by Oguni et Al. \[16\]. A good agreement with the experimental results is found for the area under the $C_p$ hump and its temperature extension while for the position of the maximum it is only fair. Obviously, the underlying absolute value of the specific heat is not reproduced in this computation owing to the simplicity of our model, where the internal vibrational contributions of the Cla molecule and the fast uniaxial rotations have not been taken into account. Thermodynamically, the anomalous hump requires an abrupt decrease and a sharp change in curvature of the entropy vs temperature evolution. Fig. 4 shows that as the temperature is lowered the $C_p$ hump begins to develop when dynamics change in nature. The strong localization of the dipole along the [100] directions (see Fig. 2) which develops below $T_x$, is thus the prime suspect for the drastic change of the configurational entropy.
The IDRIS where some of the simulations were carried out. This work was supported by the IN-TERREG II program (Nord Pas de Calais/Kent). The authors wish to acknowledge the use of the facilities of the IDRIS where some of the simulations were carried out.

FIG. 4. a, orientational α-relaxation time τ1 (circle) and τ2 (square) obtained by simulation as function of the temperature T. The quantity plotted is \( T \log(\tau_1 / \tau_0) \) where the time \( \tau_0 \) is obtained by fitting the relaxation times values for \( T = [400 \text{--} 500] \) K to an Arrhenius form. Deviation from the constant high-temperature value \( \approx 1418 \) K (dashed line) is observed around \( T_c \approx 330 \) K. Low temperature apparent activation energy is about 3109 K for \( \tau_1 \) and 3325 K for \( \tau_2 \) (solid line) in good agreement with NMR experimental data. b, the ratio of the relaxation times \( \tau_1 / \tau_2 \). c, calculated heat capacity as function of the temperature.

In conclusion, convincing experimental and numerical evidence for a dynamical crossover \( (T_x) \) in the rotator phase of chloroadamantane have been obtained, very much in keeping with recent views on structural glass-formers. It is seen as a transition from quasi-free rotational diffusion of the molecular dipoles to activated geared tumblings at low temperatures. This rotational localization is shown numerically to give rise to a specific heat hump as was recently measured \[14\]. The possible existence of such a calorimetric signature of a dynamical accident in liquids is highly debated and was unsuccessfully searched until now \[22, 23\]. Certainly, the underlying lattice and specificity of the orientational disorder contribute to make dynamical changes in the system much sharper than in liquids. We now feel confident that orientationally disordered crystals provide a valuable analog and alternative to the conventional liquid glass-formers. Results of the present study offer new interesting possibilities of testing the different theoretical approaches of the glass formation.

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[18] The simulated molecules are composed of two sites: one chlorine (Cl) and one super atom that models the adamantane group C10H15. Molecular dynamics calculations were performed on a system of \( N = 256 \) (4 × 4 × 4 fcc crystalline cells) modeled Cln molecules interacting through a short range site-site Lennard-Jones potential. Size effects have been checked and no significant structural or dynamical change has been found for a larger system made of 2048 molecules. The electrostatic interactions were handled by the Ewald method. Two partial charges (\( q = \pm 0.151 \) e) are localized on both sites in order to reproduce the dipolar moment \( \mu \) (2.39 Debyes). A time step of Δt = 5 fs was used. We worked in the NPT statistical ensemble with periodic boundary conditions.
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