Analogy of the slow dynamics between the supercooled liquid and the supercooled plastic crystal states of difluorotetrachloroethane

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Slow dynamics of difluorotetrachloroethane in both supercooled plastic crystal and supercooled liquid states have been investigated from Molecular Dynamics simulations. The temperature and wave-vector dependence of collective dynamics in both states are probed using coherent dynamical scattering functions \(S(Q, t)\). Our results confirm the strong analogy between molecular liquids and plastic crystals for which \(\alpha\)-relaxation times and non-ergodicity parameters are controlled by the non trivial static correlations \(S(Q)\) as predicted by the Mode Coupling Theory. The use of infinitely thin needles distributed on a lattice as model of plastic crystals is discussed.

It is well known that very different materials such as: silica, low-molecular-weight liquids (carbohydrates, alcohols), polymers or even proteins are able to exhibit a very intriguing feature called glass transition \[1\]. This latter is characterized by an extraordinary decrease of several orders of magnitude of the mobility in a narrow temperature range. Translational, orientational or even internal degrees of freedom (TDOF, ODOF or IDOF) can be at the origin of the mobility of a specific substance and approaching the glass transition transition temperature \(T_g\), all of them are inextricably coupled. Most of the investigations performed on glassy materials considered molecular liquids and focused on TDOF so far. The precise role of the ODOF remains particularly unclear as demonstrated by the so-called low-temperature translation-rotation paradox \[2\]. Plastic crystals \(i.e\) molecular crystals composed of orientationally disordered molecules offer an interesting solution in order to mainly investigate ODOF during the freezing process. Indeed, some of the plastic crystals called glassy crystals \[3\] such as cyanoadamantane \[4\], ethanol \[3\] or orthocarborane \[4\] can be considered are true rotational analogs of canonical liquid glassformers since they show a step of the specific heat at \(T_g\) or a non-Arrhenius behaviour of the rotational relaxation times. Only a few substances show the extraordinary property to exhibit a glass transition from both the plastic and the liquid phase: ethanol \[3, 4\], cyclohexene \[8\], PMS \[9\] or 2-bromothiophene \[10\]. An investigation of such materials is particularly interesting to understand the fundamental microscopic mechanisms of the glass transition and the precise interplay between the different degrees of freedom.

In the high temperatures pico-nanosecond regime (ps-ns), a fundamental question concerns the onset of the precursor cooperative mechanisms which lead to the glass transition at \(T_g\). In the last two decades, much attention has been devoted to the mode coupling theory (MCT) \[11\]. So far, it is the only theory which provides a microscopic description of supercooled atomic liquids. The intrinsic basis of MCT states that the behaviour of any time-dependent correlators describing the dynamics of the system is only controlled by its static density correlator \(i.e\) \(S(Q)\) and predicts the existence of a critical temperature \(T_c\). Scaling properties predicted by MCT approaching \(T_c\) have been successfully validated in numerous experiments and molecular dynamics (MD) simulations \[12\] of systems whose dynamics are controlled by TDOF. Recently, some extensions of MCT called molecular mode coupling theory (MMCT) \[12\] have been proposed to take ODOF into account: one diatomic probe molecule in an atomic liquid, liquids made of linear molecules or water to cite only a few. The authors have particularly shown that some of the basic predictions of MCT still hold owing TDOF/IDO coupling. As revealed by a recent MD investigations \[13\] performed on orthoterphephenyl (OTP), coupling of the rotational dynamics to the center-of-mass motion can be very complex. No microscopic theory has been developed for plastic crystals so far. However, in \[4, 14\], we have particularly shown from NMR and Raman experiments, and MD computer simulations that some predictions of the idealized version of the MCT (critical temperature \(T_c\) and time scaling laws) were able to describe relatively well rotational dynamics of different plastic crystals. This intriguing previous result call for new investigations to clarify the similarity between slow dynamics behaviour of plastic crystals and molecular liquids.

In this Letter, we present results of a Molecular Dynamics (MD) comparative numerical study of the supercooled plastic and the supercooled liquid phases of difluorotetrachloroethane (DFTCE). It should be noted that the supercooled state of liquid DFTCE is obtained owing the hyperquenching rate of the MD simulation. This compound is composed of simple molecules CFCl\(_2\) – CFCl\(_2\) close to dumbbells extensively used in MD calculations as prototype of molecular glass-formers liquids \[15\]. DFTCE plastic crystal has been experimentally widely studied and exhibits a glass transition of the overall rotation of the molecules at \(T_g = 86\) K \[16\].
Changes concerning the nature of dynamics in this system has been reported from NMR experiments, Brillouin and dielectric spectroscopy where it was suggested that the freezing process could be described on the basis of MCT. 

In order to obtain a general, the atoms per temperatures from ρ and the position of the atom. Measurements will be mainly considered: the freezing process could be described on the basis of MCT [16].

The intermediate scattering function as it can be classically obtained from coherent neutron scattering experiments will be mainly considered: $S(Q, t) = \langle \rho_Q(t) \rho_Q(0) \rangle$ where $\rho_Q(t)$ is the time-dependent density correlator: $\rho_Q(t) = \sum_\alpha b_\alpha \exp[iQ \cdot r_\alpha(t)]$ where the sum is over all the atoms $\alpha$ of the system. $b_\alpha$ and $r_\alpha$ are the coherent scattering length and the position of the $\alpha$ atom respectively. An average over isotropically distributed $Q$-vectors having the same modulus $Q$ is performed in order to obtain $S(Q, t)$ for a polycrystalline sample. In general, $S(Q, t)$ can be expressed as [19]: $S(Q, t) = S_v(Q) + S_d(Q, t)$ where $S_v(Q) = \langle |\rho_Q|^2 \rangle$ is the coherent elastic scattering and $S_d(Q, t) = \langle \delta\rho_Q(t)\delta\rho_Q(0) \rangle$ where $\delta\rho_Q(t) = \rho_Q(t) - \langle \rho_Q \rangle$ is the fluctuation of the time-dependent density operator. For plastic crystals, $S(Q, t)$ is identical to $S_d(Q, t)$ except for $Q$-vectors corresponding to Bragg peaks for which the long time limit of $S(Q, t)$ reaches the non-zero value $S_v(Q)$. This behaviour is found at all temperatures and it is associated to the crystalline order of the TDIF and not the freezing process of the ODOF. Therefore, in the following, $S_d(Q, t)$ will be preferred to $S(Q, t)$ in order to be able to compare directly molecular liquids and plastic crystal behaviours.

MD simulations were performed for an orientationally disordered crystal sample of DFTCE at 14 different temperatures from $T = 130$ to 260 K and a supercooled liquid sample at 13 different temperatures from $T = 150$ to the melting temperature $T_m \approx 300$ K in steps of 10 K. The same model was used for both phases and it is completely described in [17, 18].

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Upon cooling, as shown in Fig. 1, both plastic and liquid $S_d(Q, t)$ display a two-step decay as classically observed in supercooled systems [13]. The long time α-relaxation of both plastic and liquid $S_d(Q, t)$ is separated from short time regime (β) by a plateau-like region. This latter can be associated to the so-called cage effect corresponding to the trapping of molecules. The nature of this cage is of translational origin for liquids and of rotational origin (steric hindrance) for plastic crystals [4]. The height of this plateau is usually called the non-ergodicity parameter and will be noted $f_Q$ in the following. In order to probe the long time regime, we also defined the characteristic α-relaxation time $\tau_Q$ of the rotational dynamics as the time it takes for $S_d(Q, t)$ to decay from 1 to 0.1. In Fig. 2, we plot the relaxation time $\tau_Q$ at $Q = Q_{\text{max}}$ corresponding the first diffraction peak (see Fig. 3). In addition, for liquid DFTCE, the translational diffusion constant $D$ has also been calculated from the mean square displacement $\langle r^2(t) \rangle$. $\tau_Q$ characteristic times and $D$ are found to exhibit a very similar non-Arrhenius behavior.
we used a Vogel-Fulcher-Tammann (VFT) law written as \( \tau = \tau_\infty \exp[1/K_{VFT} (T/T_{VFT} - 1)] \) where \( T_{VFT} \) is the temperature of apparent divergence of \( \tau \) and \( K_{VFT} \) measures the kinetic fragility. We particularly obtained \( K_{VFT} \approx 0.18, 0.16 \) and 0.20 and \( T_{VFT} \approx 92.5, 90.4 \) and 86.9 K from the inverse of the diffusion coefficient, \( \tau_Q \) of the liquid and \( \tau_Q \) of the plastic crystal, respectively. It should be noted that results obtained from MD calculations are in fair agreement with the parameters \( K_{VFT} = 0.13 \) and \( T_{VFT} = 70 \) K found from dielectric experiments of plastic DFTCE [16].

In [14], we suggested that some common microscopic mechanisms, relatively well described by MCT, are involved in both orientationally disordered crystals and molecular liquids. Therefore, in the following, we discuss in the MCT framework the wave-vector and temperature dependence of dynamics for both plastic and liquid DFTCE. MCT predictions on the scaling features \( \tau_Q(T) = A(Q)(T - T_c)^{-\gamma} \) in the long time decay have been carefully checked using a procedure completely described in [14] and results are displayed in Fig. 2. For plastic crystal DFTCE it was possible to extract the critical temperature \( T_c^p \approx 129 \) K and scaling exponent \( \gamma_p \approx 2.45 \) from independent fitting analysis performed in the \( \alpha \) regime at different \( Q \). Using the same method, \( T_c^l \approx 139 \) K and \( \gamma_l \approx 2.55 \) were found for the supercooled liquid DFTCE. This good agreement with the \( T \)-dependence MCT predictions is also confirmed by other tests in the \( \beta \) regime where data were analyzed using a von Schweidler law including the second order correction which will be described elsewhere. \( Q \)-dependence MCT predictions are presented in the following. A fundamental property of MCT or MMCT stresses that dynamics are driven by the static density correlator \( S(Q) \). This has been confirmed in several numerical and experimental studies for simple [20] or molecular liquids [21]. In order to check this behaviour in plastic crystals, we calculated the static density correlator \( S(Q) = S(Q,t = 0) \) at different temperatures and wave vectors as well as the non-ergodicity parameter \( f_Q \), the total prefactors \( h^1(Q) \) and \( h^2(Q) \) and the relaxation time \( \tau_Q \). A fitting procedure using a von Schweidler law as derived from MCT including second order correction was employed [14]. Similarly to the intermediate scattering function, the static correlator can be decomposed into two components: \( S(Q) = S_c(Q) + S_d(Q) \) where \( S_d(Q) = \langle |\delta \rho_Q|^2 \rangle = \langle |\rho_Q|^2 \rangle - \langle |\rho_Q|^2 \rangle^2 \) is the diffuse scattering. Owing the high rotational disorder, plastics crystals yield only a few diffraction peaks but exhibit intense and highly structured diffusive scattering which provide useful information to characterize rotational motions and most probable orientations [19]. Moreover, remarkable similarities of the structure factor between plastic and liquid phases of different systems have been particularly observed [10, 22]. Both \( S_c(Q) \) and \( S_d(Q) \) are displayed in Fig. 3a as function of the wave vector \( Q \). At the largest \( Q \)-vectors, both plastic and liquid \( S_d(Q) \) merge since the intramolecular structure is probed by the wave vector \( Q \). \( \tau_Q \) and \( f_Q \) are also shown in Fig. 3b and c respectively. Both plastic and liquid DFTCE \( Q \)-dependence clearly exhibit very similar features. In the investigated \( Q \)-range \( [0.3 - 5.5] \) Å\(^{-1}\), \( S_c(Q) \) shows a few Bragg peaks expected for a bcc crystalline structure with a cell parameter \( a = 6.82 \) Å\(^{-1}\) (experimentally, \( a = 6.98 \) Å\(^{-1}\)). For \( S_d(Q) \), four broad bumps are localized at 1.27, 2.30, 3.34 and 4.85 Å\(^{-1}\) both in the supercooled plastic and liquid phases. The first sharp diffraction peak of the liquid particularly corresponds to the first and most intense Bragg peak of the plastic phase. Clearly, we see that \( f_Q \) and \( \tau_Q \) obtained for plastic or liquid phases are mainly correlated with \( S_d(Q) \) as predicted by MCT. The total prefactors not displayed in Fig. 3c exhibit the same behaviour. The non-ergodicity parameter or the total pre-factor obtained from \( S(Q) \) of the plastic phase also shows a modulation with Bragg peaks of the elastic scattering \( S_c(Q) \) (not shown in the present Letter). It should be mentioned that colliding infinitely thin needles distributed on a lattice are often considered as prototype
of glassy crystals \cite{23, 24}. Two-step relaxation processes are observed and an ideal glass transition can be obtained when the length of the rods (the analog of the temperature for these systems) reaches a critical value. If the thickness of the rods are chosen infinitely thin, all static correlations vanish and thus, following MCT predictions, no glass transition is expected \cite{23, 24}. The present work clearly illustrates the strong difference between real plastic crystals and the colliding needles on the origin of their respective ideal glass transition.

In this Letter, collective dynamics of both supercooled plastic crystal and supercooled liquids states of DFTCE have been investigated using MD simulations. From the calculation of the total intermediate scattering functions S(Q, t) at different wave vectors Q and temperatures T, our results confirm the strong analogy between two systems made of the same molecules but for which dynamics are controlled by different degrees of freedom. The authors hope that the present investigation could contribute to develop a theoretical framework for orientationally disordered crystal based on MCT.

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\begin{thebibliography}{25}
\bibitem{1} P. G. Debenedetti and F. H. Stillinger, Nature \textbf{410}, 259 (2001).
\bibitem{2} F. R. Blackburn, C.-Y. Wang, and M. Ediger, J. Phys. Chem. \textbf{100}, 18249 (1996).
\bibitem{3} H. Suga and S. Seki, J. of Non-Cryst. Solids \textbf{16}, 171 (1974).
\bibitem{4} F. Affouard, J.-F. Willart, and M. Descamps, J. of Non-Cryst. Solids \textbf{307-310}, 9 (2002).
\bibitem{5} S. Benkhof, A. Kudlik, T. Blochowicz, and E. Rössler, J. Phys.: Condens. Matter \textbf{10}, 8155 (1998).
\bibitem{6} M. Winterlich, G. Diezemann, H. Zimmermann, and R. Böhmer, Phys. Rev. Lett. \textbf{91}, 235504/1 (2003).
\bibitem{7} M. A. Miller, M. Jimenez-Ruiz, F. J. Bermejo, and N. O. Birge, Phys. Rev. B \textbf{57}, R13977 (1998).
\bibitem{8} O. Haida, H. Suga, and S. Seki, Bulletin of the Chemical Society of Japan \textbf{50}, 802 (1977).
\bibitem{9} H. Fujimori, M. Mizukami, and M. Oguni, J. of Non-Cryst. Solids \textbf{204}, 38 (1996).
\bibitem{10} H. Fujimori and M. Oguni, Journal of Physics and Chemistry of Solids \textbf{54}, 271 (1993).
\bibitem{11} W. Götze, in \textit{Liquids Freezing and the Glass Transition}, J. P. Hansen, D. Levesque and J. Zinn-Justin (North-Holland, 1990).
\bibitem{12} R. Schilling, in \textit{Collective Dynamics of Nonlinear and Disordered Systems}, G. Radons, W. Just, and P. Haeussler (Springer, 2003).
\bibitem{13} S.-H. Chong and F. Sciortino, Europhys. Lett. \textbf{64}, 197 (2003).
\bibitem{14} F. Affouard and M. Descamps, Phys. Rev. Lett. \textbf{87}, 035501 (2001).
\bibitem{15} S. Kämmerer, W. Kob, and R. Schilling, Phys. Rev. E \textbf{56}, 5450 (1997).
\bibitem{16} J. K. Krüger, J. Schreiber, R. Jimenez, and K.-P. Bohn, J. Phys.: Condens. Matter \textbf{6}, 6947 (1994).
\bibitem{17} MD calculations were performed using the DL\_POLY package (W. Smith and T. Forester, CCLRC, Daresbury Laboratory) on a system of N = 686 (7 × 7 × 7 bcc crystalline cells) DFTCE molecules. Each molecule is described by its 8 atoms and considered as rigid. The system is made of a constant 50% ratio of both trans and gauche conformers. The very slow trans-gauche transformation has been neglected in our simulation. Molecules only interact through a Buckingham short range atom-atom potential whose parameters are taken from literature and given in \cite{18}. The electrostatic contributions have been neglected since the DFTCE molecule possesses a weak dipolar moment. Both structure and dynamics of the DFTCE plastic phase obtained from MD were found in good agreement with X-rays diffraction, Neutron Spin Echo (NSE) and NMR experimental results. Newton’s equations of motion were solved with a time step of Δt = 5 fs. We worked in the NPT statistical ensemble with periodic boundaries conditions where the simulating box is allowed to change in size and shape.
\bibitem{18} F. Affouard, E. Cochin, R. Decressain, M. Descamps, and W. Haeussler, in \textit{Slow Dynamics in Complex Systems}, M. Tokuyama and I. Oppenheim (American Institute of Physics, 2004).
\bibitem{19} G. Dolling, B. M. Powell, and V. F. Sears, Mol. Phys. \textbf{37}, 1859 (1979).
\bibitem{20} W. Kob and H. C. Andersen, Phys. Rev. E \textbf{52}, 4134 (1995).
\bibitem{21} S. Mossa, G. Ruocco, and M. Sampoli, Phys. Rev. E \textbf{64}, 021511 (2001).
\bibitem{22} R. Fayos, F. J. Bermejo, J. Davidowski, H. E. Fischer, and M. A. Gonzalez, Phys. Rev. Lett. \textbf{77}, 3823 (1996).
\bibitem{23} C. Renner, H. Löwen, and J.-L. Barrat, Phys. Rev. E \textbf{52}, 5091 (1995).
\bibitem{24} R. Schilling and G. Szamel, Europhys. Lett. \textbf{61}, 207 (2003).
\end{thebibliography}