

Analogy of the slow dynamics between the supercooled liquid and 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 with 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 α -relaxation times and nonergodicity parameters are controlled by the nontrivial static correlations $S(Q)$, as predicted by the mode coupling theory.

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It is well known that very different materials, such as silica, low-molecular-weight liquids (carbohydrates, alcohols), polymers, and 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 (TDOF), orientational (ODOF), or even internal degrees of freedom can be at the origin of the mobility of a specific substance and approaching the glass 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 investigate mainly ODOF during the freezing process. Indeed, some of the plastic crystals called *glassy crystals* [3], such as cyanoadamantane [4], ethanol [5], or orthocarborane [6], can be considered as true rotational analogs of canonical liquid glass formers since they show a step of the specific heat at T_g or a non-Arrhenius behavior 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 [5,7], 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 temperature pico to nanosecond regime, a fundamental question concerns the onset of the precursor cooperative mechanisms that lead to the glass transition at T_g . In the last two decades, much attention has been devoted to mode coupling theory (MCT) [11]. So far, it is the only theory that provides a microscopic description of supercooled atomic liquids. The intrinsic basis of MCT states that the behavior 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 validated in numerous experiments and molecular dynamics (MD) simulations [12] of systems whose dynamics are controlled by TDOF. Some of the most important tests of the theory originating from experiments on colloidal systems [13]. 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 shown in particular that some of the basic predictions of MCT still hold, due to TDOF/ODOF coupling. As revealed by a recent MD investigations [14] performed on orthoterphenyl (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 [4,15], we have 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 behavior of plastic crystals and molecular liquids.

In this article, we present results of a molecular dynamics 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 $\text{CFCl}_2\text{—CCCl}_2$ close to dumbbells extensively used in MD calculations as prototype of molecular glass-former liquids [16]. 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 [17]. Changes concerning the nature of dynamics in this system have been reported from NMR experiments, and Brillouin and dielectric spectroscopy, where it was suggested that the freezing process could be described on the basis of MCT [17].

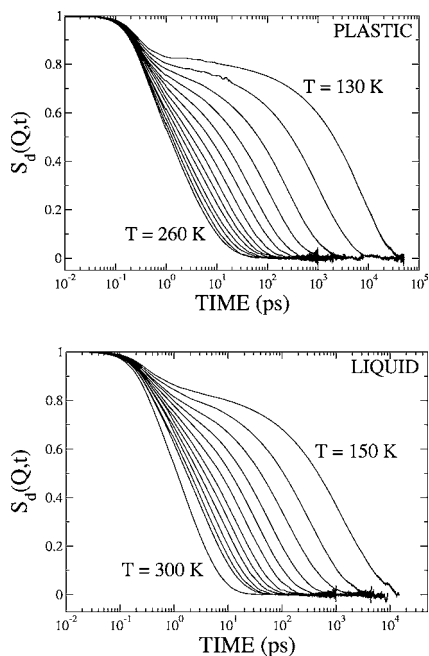


FIG. 1. Coherent intermediate scattering function $S_d(Q,t)$ at $Q = 1.54 \text{ \AA}^{-1}$ obtained for the plastic phase from $T=130$ to 260 K and the liquid phase from $T=150$ to 300 K. Scattering functions are normalized by their respective $S_d(Q,t=0)$ values.

MD simulations were performed for an orientationally disordered crystal sample of DFTCE at 14 different temperatures from $T=130$ to 260 K in steps of 10 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 [18,19].

The intermediate scattering function as it can be classically obtained from coherent neutron scattering experiments will be mainly considered: $S(\vec{Q},t) = \langle \rho_{\vec{Q}}(t) \rho_{\vec{Q}}^*(0) \rangle$, where $\rho_{\vec{Q}}(t)$ is the time-dependent density correlator; $\rho_{\vec{Q}}(t) = \sum_{\alpha} b_{\alpha} \exp[i\vec{Q} \cdot \vec{r}_{\alpha}(t)]$, where the sum is over all the atoms α of the system. b_{α} and \vec{r}_{α} are the coherent scattering length and the position of the α 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 [20]: $S(Q,t) = S_c(Q) + S_d(Q,t)$, where $S_c(Q) = |\langle \rho_{\vec{Q}} \rangle|^2$ is the coherent elastic scattering and $S_d(Q,t) = \langle \delta \rho_{\vec{Q}}(t) \delta \rho_{\vec{Q}}^*(0) \rangle$, where $\delta \rho_{\vec{Q}}(t) = \rho_{\vec{Q}}(t) - \langle \rho_{\vec{Q}} \rangle$ 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 nonzero value $S_c(Q)$. This behavior is found at all temperatures and it is associated with the crystalline order of the TDOF 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 behaviors.

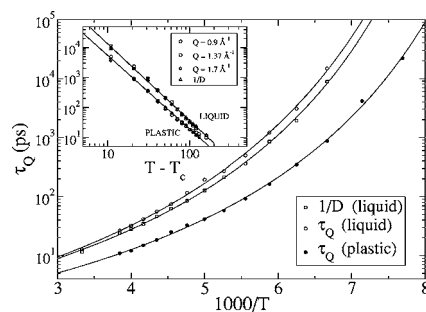


FIG. 2. Temperature dependence of the relaxation τ_Q at $Q = Q_{max} \approx 1.27 \text{ \AA}^{-1}$ for both the plastic and the liquid phases. Inverse of the diffusion constant D is also indicated. Solid lines show VFT fits (see text). Relaxation times τ_Q at $Q=0.9, 1.37,$ and 1.7 \AA^{-1} and diffusion constant D ($10^{-9} \text{ m}^2 \text{ s}^{-1}$) as function of the rescaled temperature $T - T_c$ are displayed in the inset. Solid lines show fits using power law dependence $(T - T_c)^{\gamma}$. ($T_c^l \approx 139$ K, $\gamma^l \approx 2.55$) and ($T_c^p \approx 129$ K, $\gamma^p \approx 2.45$) are found for the supercooled liquid and the supercooled plastic crystal, respectively. Relaxation times are shifted in order to demonstrate the overlap and the generic power law dependence.

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 [16]. For the plastic crystal phase of DFTCE, it is evident that ODOF dominates in $S_d(Q,t)$. For the liquid phase, the answer is not so clear. Inspired by the work of Lewis and Wahnström [21] on OTP, several partial intermediate scattering functions controlled by only ODOF or TDOF have been calculated. This preliminary investigation (not shown here) reveal that both degree of freedom are coupled as observed in [21] and that both TDOF and ODOF qualitatively behave in a similar way. 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 nonergodicity 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 τ_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 τ_Q at $Q = Q_{max}$ corresponding the first diffraction peak [see Fig. 3(c)]. In addition, for liquid DFTCE, the translational diffusion constant D has also been calculated from the mean square displacement $\langle r^2(t) \rangle$. τ_Q characteristic times and D are found to exhibit a very similar non-Arrhenius behavior. In order to quantify this similarity, 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 τ and K_{VFT} measures the kinetic fragility. We 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 τ_Q of the liquid and τ_Q of the plastic crystal, respectively. Results obtained from MD calculations are in fair

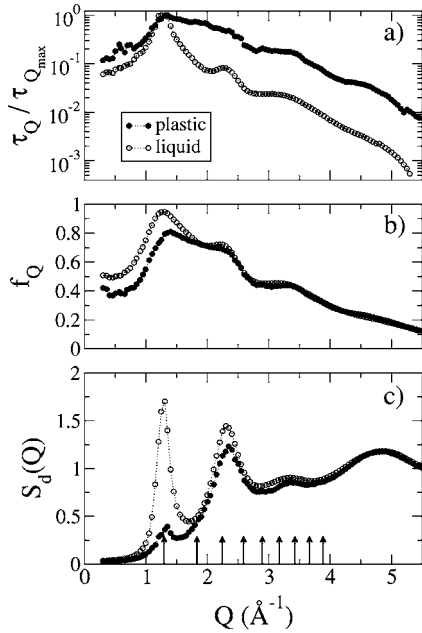


FIG. 3. Q -dependence of different parameters for the plastic (full circles) and the supercooled liquid (circles) phase at the temperature $T=160$ K. (a) The α -relaxation times $\tau_Q/\tau_{Q_{\max}}$, where $\tau_{Q_{\max}}$ is about 345 ps in the plastic phase and 4122 ps in the liquid phase at this temperature. (b) The nonergodicity parameter f_Q obtained from a fitting procedure using a von Schweidler law as derived from MCT including second-order corrections. (c) The diffuse scattering $S_d(Q)$. First Bragg peaks are also indicated with vertical arrows.

agreement with the parameters $K_{\text{VFT}}=0.13$ and $T_{\text{VFT}}=70$ K found from dielectric experiments of plastic DFTCE [17]. We have no clear explanation as to why the relaxation time for the liquid state is slower than for the plastic state. In order to fully compare both systems, a plot of both plastic and liquid relaxation times as function of a rescale temperature T_{ref}/T where T_{ref} is the temperature at which the relaxation times reach 10 ns has been performed (not shown here). It reveals a very similar behavior for both physical states. It should be noted that characteristic times, mostly τ_2 extracted from Raman or NMR experiments, exhibit no discontinuity at the liquid-plastic crystal transition (see many examples reported in [22]). Moreover, O'Dell and Berne [23] showed for a rough sphere fluid that rotational motion could be less hindered in the plastic phase just below the melting point. Both points seem consistent with our results.

In [15], 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 [15], 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 an independent fitting analysis per-

formed in the α 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. Some deviations from MCT predictions are observed at high temperatures. As reported in other papers [4,15], those could be attributed to the crossover from the mean-field regime to a landscape-influenced regime. Nevertheless, the good agreement with the T -dependent MCT predictions is also confirmed by other tests in the β regime wherein data were analyzed using a von Schweidler law including the second-order correction, which will be described elsewhere. Q -dependent 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 [24] or molecular liquids [25]. In order to check this behavior 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 nonergodicity parameter f_Q , the total prefactors $h^1(Q)$ and $h^2(Q)$, and the relaxation time τ_Q . A fitting procedure using a von Schweidler law as derived from MCT including second-order correction was employed [15]. Similarly to the intermediate scattering function, the static correlator can be decomposed into two components: $S(Q)=S_c(Q)+S_d(Q)$, where $S_d(Q)=\langle |\delta\rho_{\vec{Q}}|^2 \rangle = \langle |\rho_{\vec{Q}}|^2 \rangle - |\langle \rho_{\vec{Q}} \rangle|^2$ is the diffuse scattering. Owing to the high rotational disorder, plastic 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 [20]. Moreover, remarkable similarities of the structure factor between plastic and liquid phases of different systems have been observed [20,26]. Both $S_c(Q)$ and $S_d(Q)$ are displayed in Fig. 3(c) 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 . τ_Q and f_Q are also shown in Figs. 3(a) and 3(b), respectively. Both plastic and liquid DFTCE Q -dependence clearly exhibit very similar features. In the investigated Q -range $[0.3-5.5] \text{\AA}^{-1}$, $S_c(Q)$ shows a few Bragg peaks expected for a bcc crystalline structure with a cell parameter $a=6.82 \text{\AA}^{-1}$ (experimentally, $a=6.98 \text{\AA}^{-1}$). For $S_d(Q)$, four broad bumps are localized at 1.27, 2.30, 3.34, and 4.85\AA^{-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 τ_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. 3 exhibit the same behavior. The nonergodicity parameter or the total prefactor obtained from $S(Q)$ of the plastic phase also shows a modulation with Bragg peaks of the elastic scattering $S_c(Q)$ (not shown here). It should be mentioned that colliding infinitely thin needles distributed on a lattice are often considered as prototype of glassy crystals [27,28]. 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 [27,28]. The present work seems to illustrate some differences between real plastic crystals and the colliding needles on the origin of their respective ideal glass transitions.

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- [18] MD calculations were performed using the DL_POLY package (W. Smith and T. Forester, CCLRC, Daresbury Laboratory) on a system of $N=686$ ($7 \times 7 \times 7$ bcc crystalline cells) DFTCE molecules. Each molecule is described by its eight atoms and is 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 the literature and are given in [19]. 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-ray diffraction, neutron spin echo, and NMR experimental results. Newton's equations of motion were solved with a time step of $\Delta t=5$ fs. We worked in the NPT statistical ensemble with periodic boundaries conditions, where the simulating box is allowed to change in size and shape.
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