

Anomalous Diffusion and Cage Effects in the Isotropic Phase of a Liquid Crystal

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The translational motion of 4-*n*-hexyl-4'-cyanobiphenyl (6CB) in its isotropic phase has been studied by atomistic molecular dynamics simulation from 280 to 330 K. The mean square displacement shows evidence of a subdiffusive dynamics, with a plateau that becomes very apparent at the lowest temperatures. A three-time self-intermediate scattering function reveals that this plateau is connected with a homogeneous dynamics that, at longer times, becomes heterogeneous and finally exponential. These features are shared by, for example, a high-density system of hard spheres, which supports the universal character of the translational dynamics of liquids in their supercooled condition. As predicted by the idealized version of the mode-coupling theory (MCT), the diffusion coefficient dependence upon temperature is well described by a power law, with a critical temperature very close to that obtained by experimental measurements on orientational relaxation. This agreement might indicate a complete freezing of both rotational and translational intradomain dynamics. The time–temperature superposition principle also holds. The shape of the cage that surrounds a 6CB molecule has been reconstructed, and this analysis suggests a preferential side-by-side arrangement of molecules, which locally tend to align their long axes even in the isotropic phase.

Recent experimental studies have suggested a close analogy between the reorientational dynamics of supercooled molecular liquids and liquid crystals in their isotropic phase.^{1–4} For the latter, the temperatures selected for the optical Kerr effect (OKE) measurements cover a range of ~40–50 K up from the clearing temperature, that is, the temperature of the nematic to isotropic transition T_{N-I} . It has been observed that the OKE signal decays according to power laws for a very wide (some decades) time window starting from ~1 ps until the exponential decay sets in after some 100 ns, as predicted by Landau–de Gennes theory.

The experimental findings¹ show that the scaling relationships derived from the mode-coupling theory (MCT)^{5,6} can be applied equally well to the description of the orientational relaxation of supercooled molecular liquids and isotropic liquid crystals.

In particular, the OKE measurements mentioned,^{1,2} examined in terms of MCT, indicate the presence of a single critical temperature, T_c , for supercooled molecular liquids and two for liquid crystals. In the latter case, both T_c 's are predicted to occur below T_{N-I} ; therefore, the phase transition rules out any possibility of experimentally approaching them.

The MCT, originally developed to describe supercooled systems in their approach to the glass transition, has been successfully applied to a mixture of supercooled Lennard-Jones particles,^{7–9} a triatomic model of the fragile glass-former orthoterphenyl,^{10,11} and also to a disordered crystal¹² and ionic liquids.¹³

For mesogenic systems, most of the peculiar properties stem from the orientational degrees of freedom, and most attention had been focused on them; therefore, the question as to whether their translational dynamics also can be rationalized in terms of the MCT is still to be answered.

Among the liquid crystals examined through OKE¹ and dielectric relaxation measurements,¹⁴ there are members of the 4-*n*-alkyl-4'-cyanobiphenyl (nCB) series, namely, 5CB and 8CB. For the nCB series, we developed a force field from ab initio calculations that provides a satisfactory description of various properties of these systems, for example, transition temperatures T_{N-I} and orientational order parameters, with a semiquantitative agreement with measured values.¹⁵

In the following, we report on some results that can be used to characterize the dynamics of the center of mass of our model 6CB molecule in its isotropic phase. We studied by molecular dynamics (MD) a system of 192 molecules at various temperatures, starting from 330 K and decreasing it in steps of 10 K down to 280 K. The latter is well below the T_{N-I} of our model (300 ± 10 K,¹⁵ versus an experimental value of 302 K). The simulations were carried out in the NVE ensemble at the experimental density,¹⁶ as not to affect the dynamics of the systems. At the same time, this procedure prevents volume fluctuations and the occurrence of dishomogeneities and keeps the systems in the isotropic phase throughout the runs, as proved by the low value (≈ 0.1) of the orientational order parameters. The simulations span some tens of nanoseconds at each temperature.

Below, we define the tools used to analyze the center of mass dynamics of our model of 6CB. Perhaps the most basic property is the mean square displacement, defined as $MSD(t) =$

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$\langle [\mathbf{R}(t) - \mathbf{R}(0)]^2 \rangle$, where $\mathbf{R}(t)$ is the position of the center of mass of a molecule at time t . From its long time limit, the self-diffusion coefficient D can be extracted via the standard Einstein relation

$$D = \lim_{t \rightarrow \infty} \text{MSD}(t)/6t.$$

The self-part of the intermediate scattering function $F_s(k, t)$ is defined as

$$F_s(k, t) = \frac{1}{N} \left\langle \sum_{j=1}^N \exp[i\mathbf{k} \cdot (\mathbf{R}_j(t) - \mathbf{R}_j(0))] \right\rangle \quad (1)$$

Following Heuer,^{17,18} we introduce a three-time intermediate self-scattering function $F_s(k, t, t_3)$

$$F_s(k, t, t_3) = \frac{1}{N} \left\langle \sum_{j=1}^N \exp[i\mathbf{k} \cdot (\mathbf{R}_j(2t) - \mathbf{R}_j(t))] \cdot \exp[i\mathbf{k} \cdot (\mathbf{R}_j(t) - \mathbf{R}_j(0))] \right\rangle \quad (2)$$

which can provide information on the physical mechanism underlying the deviations from exponential decay, namely, whether this is due to a dynamics strongly effected by the presence of “cages” (the homogeneous case) or to the superposition of processes with a distribution of diffusion rates (the heterogeneous case).

For $F_s(k, t)$'s, we chose seven k 's ranging from ≈ 0.6 to $\approx 1.3 \text{ \AA}^{-1}$, which correspond to the first and second maximum of the computed static structure factor, $S(k)$, of the system. These values of k mark the distances at which the spatial correlations among the molecules are more significant. We observed that the results for $k = 0.6$ and 0.91 \AA^{-1} , the first minimum of $S(k)$, are very similar at all temperatures. Hence, we chose the latter k for the plots in view of its favorable time scale.

We first checked the amount of rototranslational coupling through the calculation of the covariance that measures the coupling between translational and rotational kinetic energies.¹⁹ It turns out that the normalized function at $T = 310 \text{ K}$ reaches its maximum value of $\sim 4\%$ after 0.2 ps and then decays rather quickly into the noise, with an overall shape that closely resembles that obtained for a liquid of diatomic Lennard-Jones molecules.¹⁹ Analogous behavior has been observed at the other temperatures, and so, the center of mass dynamics can be considered uncoupled to the rotational (and internal) degrees of freedom. Presumably, this supports the point of view that it makes sense to compare our MD results for a fairly complex molecular system with the MCT predictions for simple liquids.

In Figure 1 and, even more clearly, in Figure 2, we can note that both $\text{MSD}(t)$'s and $F_s(k, t)$ develop a plateau at intermediate times (10^0 – 10^1 ps), which becomes more and more apparent and extended in time as the temperature decreases.

In the time range corresponding to the plateau, the molecule has moved over a rather short distance, from $\sim 0.5 \text{ \AA}$ at 280 K to $\sim 0.8 \text{ \AA}$ at 330 K . This distance is significantly smaller than the nearest neighbor separation, $\sim 5 \text{ \AA}$,¹⁵ indicating that the tagged molecule can only perform a small amplitude rattling within its cage. Irrespective of temperature, only after a time on the order of nanoseconds can a truly diffusive behavior be achieved, which manifests itself by the linear dependence of $\text{MSD}(t)$ on time and the exponential decay of $F_s(k, t)$. Thus, we identify as subdiffusive the regime of $\text{MSD}(t)$ ranging from the end of the pure ballistic dynamics (hundreds of femtosec-

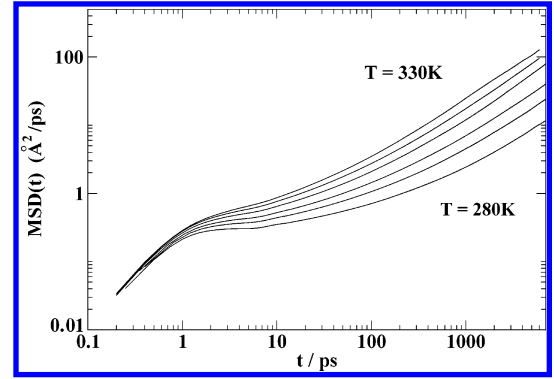


Figure 1. Log–log plot of $\text{MSD}(t)$ at temperatures from 280 (bottom) to 330 K (top) in steps of 10 K.

TABLE 1: Temperature Dependence of the Translational Diffusion Coefficient and the Relaxation Time of $F_s(k, t)$ ($k \approx 0.91 \text{ \AA}^{-1}$)

$T \text{ (K)}$	$D \text{ (} 10^{-6} \text{ cm}^2/\text{s})$	$\tau_k \text{ (ns)}$
280	0.074 ± 0.014	1.76 ± 0.3
290	0.15 ± 0.041	0.66 ± 0.15
300	0.28 ± 0.12	0.33 ± 0.09
310	0.56 ± 0.13	0.16 ± 0.037
320	0.78 ± 0.17	0.11 ± 0.02
330	1.1 ± 0.07	0.071 ± 0.0045

onds) to the onset of the linear behavior, which occurs on a nanosecond time scale.

A closer analysis of the subdiffusive dynamics and useful insights into its physical origin is provided by the behavior of the three-time intermediate scattering function, $F_s(k, t, t_3)$, compared to that of $F_s(k, 2t)$ and $F_s(k, t)^2$, shown in Figure 2.

We can see that at short times (up to roughly 100 ps), $F_s(k, t, t_3) \approx F_s(k, t)^2$, which points to a mainly homogeneous dynamics, connected with the idea of molecules trapped in a cage. At longer times, the three-time intermediate scattering function gradually drifts from $F_s(k, t, t_3) \approx F_s(k, t)^2$ to $F_s(k, t, t_3) \approx F_s(k, 2t)$, which shows that the dynamics is becoming heterogeneous. At still longer times, the hydrodynamic regime is eventually achieved, and $F_s(k, t)$'s tail is well fitted with an exponential so that $F_s(k, t) = \exp(-Dk^2t)$. In other words, at very long times, we observe particles escaped from their cage with the same characteristic time.

The translational dynamics of 6CB, as outlined above, exhibit a remarkably analogous behavior to that of such diverse systems as high-density hard spheres,¹⁸ supercooled (atomic and molecular) liquids,^{8,9} polymers,²⁰ and macromolecular compounds.²¹ This is clear evidence to support the truly universal character of the processes governing this kind of dynamics. Moreover, it suggests the possibility of testing the prediction of the ideal mode-coupling theory on a fairly complex system as 6CB.

In particular, with the data we have collected so far, it is possible to carry out a more quantitative test of some of the MCT predictions, namely, (i) that the diffusion coefficient scales with temperature as a power law, $D(T) \propto (T - T_c)^\nu$, as the relaxation time relevant to the α regime of $F_s(k, t)$ also does, $\tau_k(T) \propto (T - T_c)^{-\nu}$; (ii) the factorization property holds, according to which it is possible to select two arbitrary times (t_1 and t_2) in the β regime and observe that the following relation is satisfied at each temperature and k

$$\Omega(t) = \frac{F_s(k, t) - F_s(k, t_1)}{F_s(k, t_2) - F_s(k, t_1)}$$

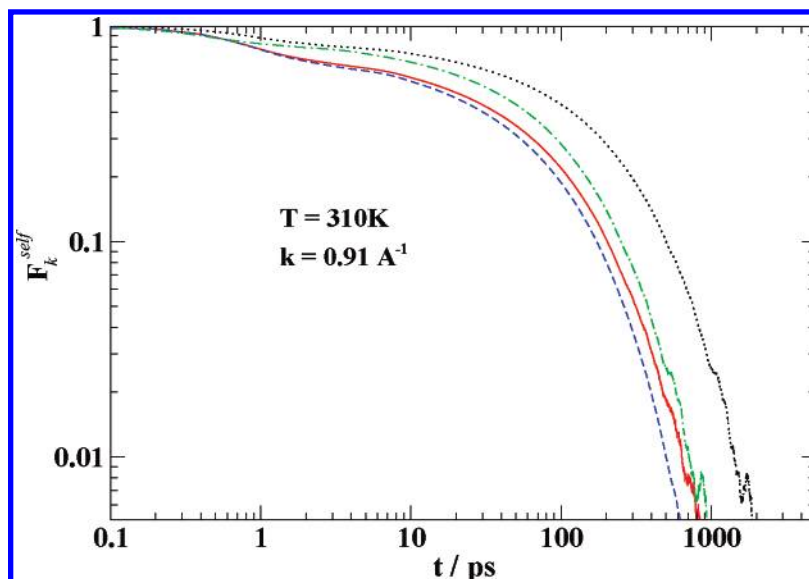


Figure 2. Log–log plot of $F_s(k, t)$ (dotted, black), $F_s(k, 2t)$ (dashed-dotted, green), $F_s(k, t, t)_3$ (solid line, red), and $F_s(k, t)^2$ (dashed, blue). The curves correspond to $k = 0.91 \text{ \AA}^{-1}$ and $T = 310 \text{ K}$.

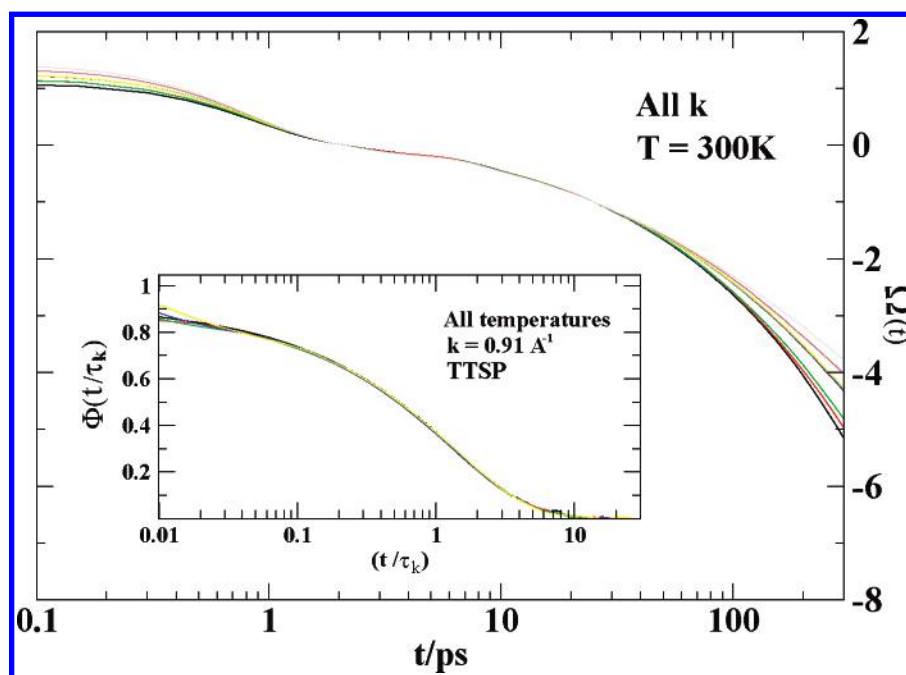


Figure 3. The master curve representing $\Omega(t)$; t_1 and t_2 are 2 and 25 ps, respectively. A different choice of t_1 and t_2 in the β regime does not affect the curve. Note that the superposition lasts for 2 decades in time. ($T = 300 \text{ K}$, and all k have been used). The inset shows that the TTSP holds for almost all rescaled times spanned. Here, we represent curves for $k \approx 0.91 \text{ \AA}^{-1}$ at all temperatures.

and (iii) the time–temperature superposition principle (TTSP) holds, which states that all $F_s(k, t)$'s at the same k but different temperatures should coincide, if time is properly scaled

$$\Phi(t) = F_s(k, t/\tau_k)$$

In this case, τ_k is chosen as the time required for $F_s(k, t)$ to reach e^{-1} .

In other words, if MCT holds, $\Omega(t)$ results k independent and $\Phi(t)$ must fall onto a master curve.

The diffusion coefficients, D , reported in Table 1 have been obtained fitting $\text{MSD}(t)/6t$ with a stretched exponential, $D + A\exp[-(t/\tau)^\beta]$. This fit reproduces the asymptotic behavior at long times very well, even when applied to a relatively restricted window (about 2 ns for the lowest temperature).

The MD results of D for 6CB are in the correct range of values, as can be estimated from the experimental data for the

smaller homologue 5CB in its isotropic phase at 320 K ($\sim 0.75 \times 10^{-6} \text{ cm}^2/\text{s}$).²² It turns out that a power law $[c(T - T_c)^\gamma]$ fits quite satisfactorily both the $D(T)$ and $\tau_k(T)^{-1}$ values (see Table 1) at all k 's considered. For these functions, a simple exponential law performs very poorly. The critical temperature we obtain is $T_c = 265 \pm 10 \text{ K}$, and the exponent is $\gamma = 2 \pm 0.3$. The analysis of the experimental OKE data for orientational relaxation in 5CB and 8CB¹ allowed the authors to identify two different critical temperatures, one, T_{CH} , very close to $T_{\text{N-I}}$ and a second, significantly lower one, T_{CL} . The first is related to the freezing of local nematic domains that exist even in the isotropic phase near $T_{\text{N-I}}$, while at T_{CL} , the intradomain dynamics also freezes. From the dynamical point of view, the intradomain relaxation of both orientational and translational degrees of freedom occurs on a short time scale compared to the lifetime of the nematic domains. It is precisely this shorter

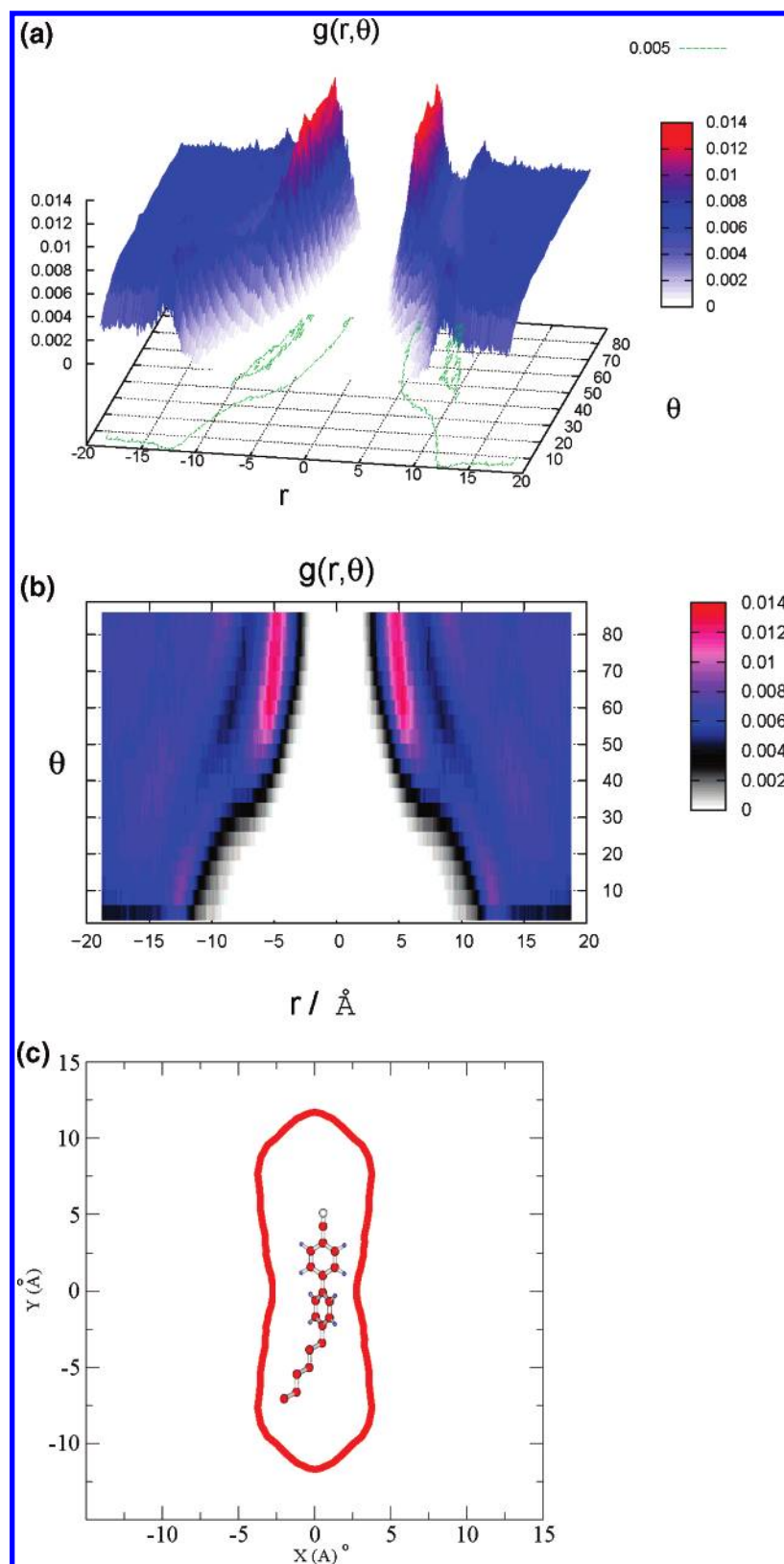


Figure 4. (a) Normalized angular-dependent radial distribution function of the center of mass, $g(|\mathbf{R}_{ij}|, \theta)$, (see text). Green level curves indicate the first significant nonzero values of $g(|\mathbf{R}_{ij}|, \theta)$ (innermost curves) and the minimum in the transverse direction, $\theta \approx 90^\circ$. (b) 2-D contour plot of the same distribution as in a. (c) The cage that surrounds a 6CB molecule, with a molecule inside drawn on the same scale. The blank region is not empty but just free of the centers of mass of other molecules.

time scale that our simulation can probe; hence, it is encouraging that the critical temperature we obtain (265 ± 10 K) is close to the experimental T_{CL} for 5CB, that is, 268 ± 2 K.¹ This close agreement might well be accidental; however, it might also suggest that translational and orientational degrees of freedom

freeze at basically the same temperature, as observed in a simulation of a supercooled liquid of diatomic molecules.²³

Figure 3 demonstrates that the MCT predictions of points (ii) and (iii) are fulfilled. At $T = 300$ K and all k values, we observe that, from a few to tens of picoseconds, the $F_s(k, t)$'s

fall onto the same $\Omega(t)$ function, confirming that t_1 and t_2 have been picked up in the correct β regime (estimated to be between 2 and 40 ps). In the inset of Figure 3, we show that the TTSP holds; from 280 to 330 K, all of the curves fall onto $\Phi(t)$ for about four decades in time.

A central idea of MCT is that the presence of a long-lived cage surrounding a target particle delays the occurrence of the diffusive regime; when a particle is trapped (β regime), its displacement is restricted, and a plateau appears in many correlation functions, while only in the α regime, that is, after the particle has escaped from the cage, does the dynamics begin to be diffusive.

Even in an isotropic phase, the strongly anisotropic shape of the 6CB molecule induces some extent of local order. Therefore, we calculated the angular-dependent pair distribution function $g(|\mathbf{R}_{ij}|, \theta)$, where \mathbf{R}_{ij} is the vector joining the center of mass of molecule j and i and $\theta = \cos^{-1}(\mathbf{u}_i \cdot \mathbf{R}_{ij})$, with \mathbf{u}_i as the long axis of molecule i . Thus, we chose a polar coordinate system (r, θ, α), whose origin is on the center of mass of the molecule, and investigated the dependence of g on $|\mathbf{R}_{ij}| = r$ and on the polar angle θ . Assuming symmetry, the calculation has been restricted to $0^\circ < \theta < 90^\circ$. First, we note that the maximum (the most probable distance of finding a neighbor) is for $3.5 < r < 5.5$ Å and $70^\circ < \theta < 90^\circ$. These are the same r values found for the first peak of the usual $g(r)$ ¹⁵ and, as the angles suggest, is due to molecules arranged side by side. On the other hand, when the distance \mathbf{R}_{ij} between a pair of molecules is aligned to the long axis of the tagged molecule in a (mostly) end-to-end configuration ($\theta \sim 0^\circ$), no neighbor is found for $r < 12$ Å. Figure 4a and b also allows a second weak peak to be observed at $r \approx 7.5$ Å, at large θ . This peak shifts to larger distances with the decreasing of θ and vanishes for $\theta \approx 30^\circ$. This shows that the local ordering extends more in the direction perpendicular to \mathbf{u}_i with a well-defined first shell of molecules and a second diffuse one, while along \mathbf{u}_i , only a broad and weak band is visible.

The information provided by $g(r, \theta)$ has been used to obtain a schematic, pictorial view of the cage that surrounds a molecule. In Figure 4c, we plot $x = r \cos \theta$, $y = r \sin \theta$, where r is the first distance at which nonzero values of $g(r, \theta)$ are found. The reconstructed shape of the cage presents a narrowing around the $x, y \approx 0$ (the zone perpendicular to \mathbf{u}_i) and a maximum around $\theta \approx 0^\circ$ or, equivalently, $x \approx 0$ (the zone parallel to \mathbf{u}_i). A model of the 6CB molecule has been inserted in the cage, represented by a red contour (see Figure 4). The blank space inside the cavity is actually "populated" by the alkyl chains or the terminal CN groups of the neighbors; therefore, it actually defines the excluded volume for the centers of mass of the other molecules.

In conclusion, evidence of a subdiffusive translational dynamics has been found both in $\text{MSD}(t)$ and $F_s(k, t)$ for the isotropic phase of a model of 6CB. The range of temperature explored (330–280 K) extends well below the isotropic to nematic transition T_{N-I} of the model, 300 K versus the experimental value of 302 K. As the system has been kept homogeneous and isotropic, these low temperatures have made

the deviation from "normal" diffusive dynamics much more apparent and allowed a semiquantitative test of some predictions of the MCT.

In particular, we found that the temperature dependence of the diffusion coefficient is well described by a power law with an exponent $\gamma = 2 \pm 0.3$ and a critical temperature $T_c = 265 \pm 10$ K. In view of the time scale probed, the latter has been tentatively related to T_{CL} , the lower critical temperature experimentally found for the intradomain orientational relaxation of similar molecules, such as 5CB (268 ± 2 K) and 8CB (277 ± 2 K).¹ The TTSP has been shown to hold for all of the (rescaled) times.

A homogeneous scenario underlies the nonexponential decay of $F_s(k, t)$ for $0 \leq t \leq 200$ –500 ps at the k value of the first minimum of $S(k)$. At longer times, a heterogeneous environment sets in, this transition occurring earlier at larger k 's. The physical model at the base of the homogeneous scenario assumes the presence of cages, whose lifetimes grow as temperature is lowered, and that more and more hinder the translational dynamics of the trapped molecule. A static picture of such a structure has been reconstructed by computing an angular-dependent $g(r, \theta)$. This analysis supports the idea of molecules preferentially disposed in a side-by-side arrangement, which might provide the seed for the transition to a phase with a truly long-range orientational order.

The successful outcome of the semiquantitative test of some predictions of MCT in its idealized form, for a fairly complex material such as 6CB, emphasizes the universal character of the translational dynamics of systems in their "supercooled" liquid condition.

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