How glassy are orientational dynamics of rodlike molecules near the isotropic-nematic transition?

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In an attempt to quantitatively characterize the recently observed slow dynamics in the isotropic and nematic phase of liquid crystals, we investigate the single-particle orientational dynamics of rodlike molecules across the isotropic-nematic transition in computer simulations of a family of model systems of thermotropic liquid crystals. Several remarkable features of glassy dynamics are on display including non-exponential relaxation, dynamical heterogeneity, and non-Arrhenius temperature dependence of the orientational relaxation time. In order to obtain a quantitative measure of glassy dynamics in line with the established methods in supercooled liquids, we construct a relaxation time versus scaled inverse temperature plot, and demonstrate that one can indeed define a 'fragility index' for thermotropic liquid crystals, that depends on density and aspect ratio. The values of the fragility parameter are surprisingly in the range one observed for glass forming liquids. A plausible correlation between the energy landscape features and the observed fragility is discussed.

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INTRODUCTION

Thermotropic liquid crystals exhibit exotic phase behavior upon temperature variation. The nematic phase is rich with a long-ranged orientational order but lacks translational order. The isotropic-nematic (I-N) phase transition, which is believed to be weakly first order in nature with certain characteristics of the continuous transition, has been a subject of immense attention in condensed matter physics and material sciences [1, 2]. In contrast, the dynamics of thermotropic liquid crystals have been much less studied, the focus being mostly on the long-time behavior of orientational relaxation near the I-N transition [1]. A series of optical Kerr effect (OKE) measurements have, however, recently studied collective orientational relaxation in the isotropic phase near the I-N transition over a wide range of time scales [3]. The dynamics have been found to be surprisingly rich, the most intriguing feature being the power law decay of the OKE signal at short-to-intermediate times [3]. The relaxation scenario appears to be strikingly similar to that of supercooled molecular liquids [4], even though the latter do not undergo any thermodynamic phase transition. Although the analogous dynamics have been investigated in subsequent studies [5, 6], a quantitative estimation of glassy dynamics of rodlike molecules near the I-N transition still eludes us.

The prime objective of this paper is to provide a quantitative measure of glassy dynamics near the I-N transition. To this end, we have undertaken molecular dynamics simulations of a family of model systems consisting of rodlike molecules across the I-N transition in search of glassy behavior. Given the involvement of the phase transition to an orientationally ordered mesophase upon lowering the temperature, we choose to probe the single-particle orientational dynamics. We have defined a 'fragility index' and explored plausible correlation of the features of the underlying energy landscape with the observed fragility in analogy with supercooled liquids.

MODEL AND DETAILS OF THE SIMULATION

The systems we have studied consist of ellipsoids of revolution. The Gay-Berne (GB) pair potential [7], that is well established to serve as a model potential for systems of thermotropic liquid crystals, has been employed. The GB pair potential, which uses a single-site representation for each ellipsoid of revolution, is an elegant generalization of the extensively used isotropic Lennard-Jones potential to incorporate anisotropy in both the attractive and the repulsive parts of the interaction [7, 8]. In the GB pair potential, the interaction between two ellipsoids of revolution is given by

$$U_{ij}^{GB}(r_{ij}, e_i, e_j) = 4\epsilon(r_{ij}^{-12} - r_{ij}^{-6})$$

where

$$r_{ij} = \frac{r_{ij} - \sigma(\hat{r}_{ij}, e_i, e_j) + \sigma_{ss}}{\sigma_{ss}}.$$  

(2)
Here $\sigma_{ss}$ defines the thickness or equivalently, the separation between the two ellipsoids of revolution in a side-by-side configuration, $r_{ij}$ is the distance between the centers of mass of the ellipsoids of revolution $i$ and $j$, and $\hat{r}_{ij} = r_{ij}/r_{ij}$ is a unit vector along the intermolecular separation vector $r_{ij}$. The molecular shape parameter $\sigma$ and the energy parameter $\epsilon$ both depend on the unit vectors $e_i$ and $e_j$ as well as on $\hat{r}_{ij}$ as given by the following set of equations:

$$\sigma(\hat{r}_{ij}, e_i, e_j) = \sigma_0 \left[ 1 - \frac{\chi}{2} \left\{ \frac{(e_i \cdot \hat{r}_{ij} + e_j \cdot \hat{r}_{ij})^2}{1 + \chi (e_i \cdot e_j)} + \frac{(e_i \cdot \hat{r}_{ij} - e_j \cdot \hat{r}_{ij})^2}{1 - \chi (e_i \cdot e_j)} \right\} \right]^{-1/2}$$

(3)

with $\chi = (\kappa^2 - 1)/(\kappa^2 + 1)$ and

$$\epsilon(\hat{r}_{ij}, e_i, e_j) = \epsilon_0 [\epsilon_1(e_i, e_j)]^{\mu} [\epsilon_2(\hat{r}_{ij}, e_i, e_j)]^{\nu}$$

(4)

where the exponents $\mu$ and $\nu$ are adjustable parameter, and

$$\epsilon_1(e_i, e_j) = \left[ 1 - \chi^2 (e_i \cdot e_j)^2 \right]^{-1/2}$$

(5)

and

$$\epsilon_2(\hat{r}_{ij}, e_i, e_j) = 1 - \frac{\chi'}{2} \left[ \frac{(e_i \cdot \hat{r}_{ij} + e_j \cdot \hat{r}_{ij})^2}{1 + \chi' (e_i \cdot e_j)} + \frac{(e_i \cdot \hat{r}_{ij} - e_j \cdot \hat{r}_{ij})^2}{1 - \chi' (e_i \cdot e_j)} \right]$$

(6)

with $\chi' = (\kappa'^{1/\mu} - 1)/(\kappa'^{1/\mu} + 1)$. Here $\kappa = \sigma_{ee}/\sigma_{ss}$ is the aspect ratio of the ellipsoid of revolution with $\sigma_{ee}$ denoting the separation between two ellipsoids of revolution in a end-to-end configuration, and $\sigma_{ss} = \sigma_0$, and $\kappa' = \epsilon_{ss}/\epsilon_{ee}$, where $\epsilon_{ss}$ is the depth of the minimum of the potential for a pair of ellipsoids of revolution aligned in a side-by-side configuration, and $\epsilon_{ee}$ is the corresponding depth for the end-to-end alignment. $\epsilon_0$ is the depth of the minimum of the pair potential between two ellipsoids of revolution aligned in cross configuration. The GB pair potential defines a family of models, each member of which is characterized by the values chosen for the set of four parameters $\kappa, \kappa', \mu$, and $\nu$, and is represented by GB($\kappa, \kappa', \mu, \nu$). Three systems, namely GB(3, 5, 2, 1), GB(3.4, 5, 2, 1), and GB(3.8, 5, 2, 1), that differ in the aspect ratio have been investigated. Molecular dynamics simulations have been performed with each of these systems, consisting of 500 ellipsoids of revolution, in a cubic box with periodic boundary conditions. Each of these systems has been studied along three isochors ($\rho = 0.31, 0.32$, and $0.33$ for $\kappa = 3.0$; $\rho = 0.25, 0.26$, and $0.27$ for $\kappa = 3.4$; $\rho = 0.215, 0.225$, and $0.235$ for $\kappa = 3.8$) at several temperatures, starting from the high-temperature isotropic phase down to the nematic phase across the I-N phase boundary. All quantities are given in reduced units defined in terms of the Gay-Berne potential parameters $\epsilon_0$ and $\sigma_0$: length in units of $\sigma_0$, temperature in units of $\frac{k_B}{\sigma_0}$, and time in units of $(\frac{\sigma_0 m}{k_B})^{1/2}$, $m$ being the mass of the ellipsoids of revolution. The mass as well as the moment of inertia of each of the ellipsoids of revolution have been set equal to unity. The intermolecular potential is truncated at a distance $r_{cut}$ and shifted such that $U(r_{ij} = r_{cut}) = 0$, $r_{ij}$ being the separation between two ellipsoids of revolution $i$ and $j$. The equations of motion have been integrated using the velocity-verlet algorithm with integration time step $dt = 0.0015$. Equilibration has been done by periodic rescaling of linear and angular velocities of particles. This has been done for a time period of $t_q$ following which the system has been allowed to propagate with a constant energy for a time period of $t_e$ in order to ensure equilibration upon observation of no drift of temperature, pressure, and potential energy. The data collection has been executed in a microcanonical ensemble. At each state point, local potential energy minimization has been executed by the conjugate gradient technique for a subset of 200 statistically independent configurations. The landscape analysis has been done with a system size of 256 ellipsoids of revolution, which is big enough for having no qualitative change in the results due to the system size. Minimization has been performed with three position coordinates and two Euler angles for each particle, the third Euler angle being redundant for ellipsoids of revolution.

RESULTS AND DISCUSSION

The single-particle second rank orientational time correlation function (OTCF) $C^2_2(t)$ is defined by

$$C^2_2(t) = \frac{\langle \sum_i P_2(\hat{e}_i(t) \cdot \hat{e}_i(0)) \rangle}{\langle \sum_i P_2(\hat{e}_i(0) \cdot \hat{e}_i(0)) \rangle},$$

(7)

where $P_2$ is the second rank Legendre polynomial, $\hat{e}_i$ is the unit vector along the long axis of $i$th ellipsoid of revolution, and the angular brackets stand for ensemble averaging.
Figure 1 shows the time evolution of the single-particle second rank OTCF for one of the three systems considered here as the temperature is lowered along an isochor from the high-temperature isotropic phase down to the nematic phase across the I-N phase boundary. In the inset, the average orientational order parameter \( \langle S \rangle \) is shown as a function of temperature along the isochor \([11]\). The variation of \( \langle S \rangle \) with temperature serves to locate the I-N phase boundary. In the present study, the I-N transition temperature \( T_{I-N} \) is taken as the temperature at which \( \langle S \rangle \) of the system is 0 \([35]\).

For each aspect ratio, three isochors at different densities have been considered. The qualitative behavior has been found to be the same for all the three systems along all the isochors studied (data not shown). The emergence of the power law decay in the isotropic phase near the I-N transition is evident in all the cases as a universal characteristic of I-N transition \([12]\). As the I-N phase boundary is crossed upon cooling, the advent of two power law decay regimes separated by an intervening plateau at short-to-intermediate times imparts a step-like feature to the temporal behavior of the second rank OTCF. Such a feature bears remarkable similarity to what is observed for supercooled liquids as the glass transition is approached from the above \([13, 14]\). While for the supercooled liquid the emergence of step-like feature in the OTCF is well understood as a consequence of \( \beta \) relaxation, the origin of such a feature observed for liquid crystal defined of reliable explanation.

We estimate the orientational correlation time \( \tau \) as the time taken for \( C_2^S(t) \) to decay by 90%, i.e., \( C_2^S(t = \tau) = 0.1 \). Figure 2(a) shows \( \tau \) in the logarithmic scale as a function of the inverse temperature along the three isochors for each of the three systems considered. We have scaled the temperature by \( T_{I-N} \) in the spirit of Angell's plot, that displays the shear viscosity (or the structural relaxation time, the inverse diffusivity, etc.) of glass-forming liquids as a function of the inverse of the scaled temperature, the scaling being done in the latter case by the glass transition temperature \( T_g \) \([15, 16]\). For all the three systems, two distinct features are common: (i) in the isotropic phase far away from the I-N transition, the orientational correlation time \( \tau \) exhibits the Arrhenius temperature dependence, i.e., \( \tau(T) = \tau_0 \exp[E/(k_B T)] \), where the activation energy \( E \) and the pre-factor \( \tau_0 \) are both independent of temperature; (ii) in the isotropic phase near the I-N transition, the temperature dependence of \( \tau \) shows marked deviation from the Arrhenius behavior and can be well described by the Vogel-Fulcher-Tammann (VFT) equation \( \tau(T) = \tau_0 \exp[B/(T - T_{VFT})] \), where \( \tau_0 \), \( B \), and \( T_{VFT} \) are constants, independent of temperature. Again these features bear remarkable similarity with those observed for fragile glass-forming liquid. A non-Arrhenius temperature behavior is taken to be the signature of fragile liquids. For fragile liquids, the temperature dependence of the shear viscosity follows the Arrhenius behavior far above \( T_g \) and can be fitted to the VFT functional form in the deeply supercooled regime near \( T_g \) \([15, 16]\).

The striking resemblance in the dynamical behavior described above between the isotropic phase of thermotropic liquid crystals near the I-N transition and supercooled liquids near the glass transition has prompted us to attempt a quantitative measure of glassy behavior near the I-N transition. For supercooled liquids, one quantifies the dynamics by a parameter called fragility index which measures the rapidity at which the liquid’s properties (such as viscosity) change as the glassy state is approached. In the same spirit \([17]\) that offers a quantitative estimation of the fragile
behavior of supercooled liquids, we here define the fragility index $m$ of a thermotropic liquid crystalline system as

$$m = \frac{d \log \tau(T)}{d \left( \frac{T_{I-N}}{T} \right)} \Bigg|_{T=T_{I-N}}.$$  \hfill (8)

Figure 2(b) shows the density dependence of the fragility index for the three systems with different aspect ratios. For a given aspect ratio, the fragility index increases with increasing density, the numerical values of the fragility index $m$ being comparable to those of supercooled liquids. The change in the fragility index for a given density difference $(\Delta \rho)$ increases with the decrease in the aspect ratio.

Another hallmark of fragile glass-forming liquids is spatially heterogeneous dynamics \cite{18} reflected in non-Gaussian dynamical behavior \cite{19}. It is intuitive that the growth of the pseudo-nematic domains, characterized by local nematic order, in the isotropic phase near the I-N transition would result in heterogeneous dynamics in liquid crystals. We have, therefore, monitored the time evolution of the rotational non-Gaussian parameter (NGP) \cite{26}, $\alpha^R_2(t)$, which in the present case is defined as

$$\alpha^R_2(t) = \frac{\langle \Delta \phi^4(t) \rangle}{2 \langle \Delta \phi^2(t) \rangle^2} - 1,$$  \hfill (9)

where

$$\langle \Delta \phi^{2n}(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} < |\phi_i(t) - \phi_i(0)|^{2n} > .$$  \hfill (10)

Here $\phi_i$ is the rotation vector like the position vector $r_i$, appears incase of translational NGP of ith ellipsoid of revolution, the change of which is defined by $\Delta \phi_i(t) = \phi_i(t) - \phi_i(0) = \int_0^t dt' \omega_i(t')$, $\omega_i$ being the corresponding angular velocity \cite{13, 14}, and $N$ is the number of ellipsoids of revolution in the system. NGP will have value equal to zero when system dynamics is spatially homogeneous and will have a non-zero value when the system dynamics is spatially heterogeneous. As a typical behavior, Fig. 3(a) shows the time dependence of the rotational NGP for one of the systems at several temperatures across the I-N transition along an isochor. On approaching the I-N transition upon cooling, a bimodal feature starts appearing with the growth of a second peak, which eventually becomes the dominant one, at longer times.

We further investigate the appearance of this bimodal feature in NGP plot. To this end we calculate mean square angular deviation (MSAD) of the system at different temperatures starting from high temperature isotropic phase to low temperature nematic phase. The appearance of the bimodal feature in the rotational NGP is accompanied by
FIG. 3: (a) Time evolution of the rotational non-Gaussian parameter $\alpha_R^2(t)$ in a semi-log plot for the system with aspect ratio $\kappa = 3$. The time dependence is shown at several temperatures across the isotropic-nematic (I-N) transition along an isochor at density $\rho = 0.33$. (b) On a different scale along the vertical axis (appearing on the right), time evolution of the mean square angular deviation $<\Delta \phi^2(t)>$ is shown in a log-log plot for three temperatures: the highest temperature studied in the isotropic phase and the other two temperatures that are nearest to the I-N transition in the from both side along with the time evolution of $\alpha_R^2(t)$, and (c) On a different scale along the vertical axis (appearing on the right), the time evolution of the single-particle second rank orientational time correlation function $C_s^2(t)$ is shown in a log-log plot for the two temperatures that are closest to the I-N transition on either side along with the time evolution of $\alpha_R^2(t)$.

Mode coupling theory analysis

This striking similarities of the dynamics between liquid crystals near I-N transition and supercooled liquid near glass transition are also supported by the use of Mode Coupling Theory (MCT) to explain the dynamics of both the systems. While MCT was used first for the supercooled liquid, recently it has been used for liquid crystals also. MCT theory devloped by Gottke et al. [20] predicts that near I-N transition, the low frequency rotational memory kernel
should diverge in a power law fashion.

\[ M_R(z) \approx \frac{A}{z^\alpha} \]  

(11)

Mean field treatment gives \( \alpha = 0.5 \). Invoking the rank \((l)\) dependence of the memory function, the single particle OTCF can be written as \[21, 22, 23, 24\]

\[ C^*_l(z) = \left[ z + \frac{l(l + 1)k_B T}{I(z + \Gamma_l(z))} \right]^{-1} \]  

(12)

The above equation can be Laplace inverted to obtain a short-to-intermediate power law decay in \( C^*_2(t) \) which is a universal characteristic of the I-N transition for several model liquid crystals \[3, 4, 12\]. Recently, Li et al. \[25\] have shown that it is also possible to formulate a schematic model that combines short-to-intermediate time relaxation with long time relaxation. In their model, they have expressed the total memory function \((M(t))\) as the sum of mode coupling memory function \((M_{MCT}(t))\) and Landau-de Gennes memory function \((M_{LdG}(t))\).

\[ M(t) = M_{MCT}(t) + M_{LdG}(t) \]  

(13)

where

\[ M_{MCT}(t) = \Omega^2 K(t) \]  

(14)

\( \Omega \) is the characteristic frequency and \( K(0) = 1 \). Time dependence of \( K(t) \) can be written expressed in terms of the memory function \( m(t) \) \[25\] and \( m(t) \) has the following form

\[ m(t) = \kappa \phi(t) \phi_1(t) \]  

(15)

Where \( \phi(t) \) is the autocorrelation function of the anisotropy of the polarizability and \( \phi_1(t) \) is the solution of a \( F_{12} \) schematic model for what is referred to as the density correlator. \( \kappa \) being the coupling constant between them. Now, \( M_{LdG}(t) \) can be written as

\[ M_{LdG}(t) = \Gamma \delta(t) \]  

(16)

Here \( \Gamma^{-1} \) is the relaxation time \((\Gamma^{-1} = \tau_{LdG})\) and it diverges as \((T - T^*)^{-1}\) as the critical temperature \( T^* \) of the I-N transition is approached from the above. Following the calculation of Ref. \[25\], one can get two important relaxation equations.

\[ \ddot{\phi}_1(t) = -\Omega^2_1 \phi_1(t) - \mu_1 \dot{\phi}_1(t) - \Omega^2 \int_0^t dt' m_1(t - t') \dot{\phi}_1(t') \]  

(17)

With the initial conditions \( \phi_1(0) = 1 \) and \( \dot{\phi}_1(0) = 0 \) and

\[ \ddot{\phi}(t) = -(\Omega^2 + \mu \Gamma) \phi(t) - (\mu + \Gamma) \dot{\phi}(t) - \Omega^2 \int_0^t dt' m(t - t') \phi(t') - \Omega^2 \Gamma \int_0^t dt' m(t - t') \phi(t') \]  

(18)

with the initial conditions \( \phi(0) = 1 \) and \( \dot{\phi}(0) = -\Gamma \cdot \mu_1 \) and \( \mu \) are the damping constants. Eq. 17 is identical to one gets from the MCT analysis of the supercooled liquids. Difference between this schematic model and one applied for the supercooled liquid is in Eq. 18. If \( \Gamma \) is set equal to 0 in Eq. 18, the supercooled model is recovered. Eq. 18 is the orientational correlation function coupled to the density correlation function with specific new terms that account for the long-time portion of the relaxation profile that has been previously described by LdG theory.

**Energy landscape analysis**

Several studies have attempted to interpret the fragility of glass-forming liquids in terms of the features of the underlying energy landscapes \[26, 27, 28, 29, 30, 31\]. Energy landscape analysis gives the potential energy, which devoids of any kind of thermal motions, of inherent structures of the parent liquid and hence provide a better understanding of the structure and dynamics of the parent liquid. A recent study on thermotropic liquid crystals
The energy landscapes as explored by the system with the aspect ratio 3 on variation of temperature along three isochors. (a) The average inherent structure (IS) energy per particle as a function of the inverse temperature at different densities. The solid line, dashed line, and dot-dashed lines are the linear fits to the data at the densities \( \rho = 0.31, 0.32, 0.33 \), respectively. (b) The displaced average IS energy per particle versus a scaled inverse temperature along the same three isochors. If the Gaussian model for the number density of the IS energy with a given energy is validated, a collapse of the data for all densities is expected onto a straight line with negative unit slope, that is drawn. The data are shown over the temperature regimes in which the average IS energy is on a decline.

has reported the temperature dependent exploration of the energy landscapes of a family of the Gay-Berne model systems across the mesophases \[10\]. The average inherent structure (IS) energy \( \langle e_{IS} \rangle \) has been found to fall as \( \langle S \rangle \) grows across the I-N phase boundary and through the nematic phase in contrast to its insensitivity to the temperature in the high-temperature isotropic phase and the low-temperature smectic-B phase \[10\]. Such a fall in the average IS energy is consistent with a Gaussian form for the number density of inherent structures with energy \( e_{IS} \), that predicts a linear variation of \( \langle e_{IS} \rangle \) with the inverse temperature:

\[
\langle e_{IS} \rangle (T) = e_{0IS} - \frac{\sigma^2}{2Nk_B T},
\]

where \( e_{0IS} \) and \( \sigma \) are parameters independent of temperature and \( k_B \) is the Boltzmann constant \[29\]. Note that this has been observed for a glassy system \[29\], where the average IS energy also falls over a temperature range \[27\]. In Fig. 4(a), we demonstrate with the original and the most studied parameterization for the GB pair potential GB(3, 5, 2, 1) that the prediction holds good over the temperature range where \( \langle e_{IS} \rangle \) is on a decline along all the three isochors studied. It then follows that a plot of \( \langle e_{IS} \rangle (T) - e_{0IS} \) versus \( \sigma^2/(2Nk_B T) \) would result in a collapse of the \( \langle e_{IS} \rangle \) data for all densities onto a straight line with negative unit slope. This is indeed found to be true, as shown in Fig. 4(b), implying the validity of the Gaussian model in this case as well. It may be noted that when the distribution of IS energy is Gaussian, the fragility of glass-forming liquids has been shown to depend on the total number of inherent structures, the width of the Gaussian, and the variation of the basin shape with the average IS energy \[29\].

CONCLUSION

The origin of the glassy orientational dynamics, both single particle and collective, of nematogens near the isotropic-nematic transition has been addressed in several publications in recent years \[3, 4, 5, 10\]. In these studies, the similarity between dynamics of supercooled glassy liquid and liquid crystals has been discussed in detail, but no quantitative measure of the similarity was provided. The fragility index introduced here serves to remove that lacuna. It is indeed surprising that even the values of the fragility parameter are in the range observed for glassy liquids as well. This is in agreement with the repeated observation by Fayer and coworkers that the values of the power law exponents observed in the two systems are quite similar. Further understanding of the relaxation mechanism has been obtained from a closure look on the heterogeneous dynamics. As figure 3 demonstrates, the rotational non-Gaussian parameter shows a dramatic enhancement of heterogeneous dynamics as the I-N phase boundary is approached. Unlike what is found near the gas-liquid critical point \[32\], the single-particle dynamics near the I-N phase boundary are observed to be strongly affected by the approaching thermodynamic singularity. We have discussed mode coupling theory approaches introduced to understand anomalous dynamics observed in this problem.
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