Anomalous glassy relaxation near the isotropic-nematic phase transition

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Dynamical heterogeneity in a system of Gay-Berne ellipsoids near its isotropic-nematic (I-N) transition and also in an equimolar mixture of Lennard-Jones spheres and Gay-Berne ellipsoids in deeply supercooled regime is probed by the time evolution of non-Gaussian parameter (NGP). The appearance of a dominant second peak in the rotational NGP near the I-N transition signals the growth of pseudonematic domains. Surprisingly such a second peak is instead observed in the translational NGP for glassy binary mixture. Localization of orientational motion near the I-N transition is found to be responsible for the observed anomalous orientational relaxation.

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The dynamics of liquid crystals [1] across the isotropic-nematic (I-N) phase transition displays an array of dynamical features that have been a subject of renewed interest in recent times [2, 3, 4, 5]. In particular, the emergence of multiple time scales in orientational relaxation has been demonstrated in the isotropic phase of a number of liquid crystals as the I-N transition temperature T_{IN} is approached from above [3, 4]. The long time exponential decay with a temperature dependent time constant has been observed to obey the Landau-de Gennes (LdG) theory [1]. This long time decay is ascribed to the orientational randomization of the so called pseudonematic domains. Although the isotropic phase is macroscopically homogeneous, near the I-N transition a local nematic-like order persists over a length scale $\xi(T)$ that characterizes these pseudonematic domains. The LdG theory predicts the *correlation length* $\xi(T)$ to grow as temperature T approaches T_{IN} from above: $\xi(T) = \xi_0 \left[T^\star/(T - T^\star)\right]^{1/2}$ where ξ_0 is a molecular length. It suggest that $\xi(T)$ eventually diverges at $T^\star$ which falls just below T_{IN} (typically, $T_{IN} - T^\star \sim 1\ K$) [1]. The concomitant slow down of orientational relaxation is so dramatic that it finds an *analog* in the phenomenal increase of the time scale of orientational dynamics in the molecular liquids with the glass transition temperature approached from above [2].

Recently Fayer and coworkers have carried out extensive optical Kerr effect (OKE) measurements which indicate that the analogy between the isotropic phase of liquid crystals and the supercooled liquids in orientational relaxation *persists over a rather wide range of time scales* [2, 3, 6]. A description, that involves a power law at short times and an exponential decay at long times with a second power law in the crossover region, has been found to conform well to the optical heterodyne detected OKE experimental data for a number of liquid crystals in the isotropic phase and supercooled liquids [2]. The resemblance suggests that a similar underlying microscopic mechanism for relaxation is operative in liquid crystals in the isotropic phase near T_{IN} and in the supercooled liquids even though the latter do not undergo a structural phase transition [2].

The goal of the present Letter is to explore the analogy following a different approach. The appearance of pseudonematic domains in the isotropic phase near T_{IN} is expected to result in heterogeneous dynamics. Such heterogeneity in dynamical behavior has been observed for glassy liquids in a large number of experimental and computer simulation studies [7, 8, 9], but, to the best of our knowledge, has not been studied near the I-N transition. We have therefore carried out extensive computer simulation studies to gain further insight into the apparent analogy between the dynamics of the isotropic phase of the liquid crystals near T_{IN} and that of the supercooled liquids from the perspective of heterogeneity with special emphasis on rotational degrees of freedom. To this end, we have investigated two systems: (1) a collection of 576 Gay-Berne ellipsoids (with aspect ratio $\kappa = 3$) along an isotherm at a series of densities across the I-N transition; (2) a binary mixture of 128 Lennard-Jones spheres and 128 Gay-Berne ellipsoids along an isochore at a series of temperatures down to the deeply supercooled regime. For our liquid crystal system, we have used the well-known Gay-Berne pair potential [10] with the most studied parametrization [11], that is known to undergo a rather sharp I-N transition on scanning the density along an isotherm [12]. In a recent simulation study [5], this system has been shown to exhibit a short time power law decay of the second rank orientational correlation function in single-particle as well as collective dynamics on approaching the I-N transition from the isotropic side. On the other hand, the binary mixture studied here is a *new* model introduced with an intention to study orientational dynamics in the supercooled regime. The choice of a binary system is motivated by the success of the Kob-Andersen binary mixture [13], that is widely used for computer simulations of supercooled liquids as the additional complexity of the system is sufficient to avoid crystallization. Here, the interaction potential between a sphere and an ellipsoid, which is chosen to be a prolate (with $\kappa = 2$), is given by following Cleaver and coworkers [14]. We have determined the set of energy and length parameters such that neither any phase separation occurs

nor any liquid crystalline phase with orientational order appears even at the lowest temperature studied at a high density [15]. For the present purpose, we concentrate on the dynamics of only ellipsoids in the binary mixture.

This Letter invokes non-Gaussian parameters [16] for the description of dynamical heterogeneity [13, 17]. The non-Gaussian parameter (NGP) for the translational degrees of freedom is defined for a three-dimensional system of N rigid bodies of the same kind by

$$\alpha_2^{(T)} = \frac{3 \ < \Delta\mathbf{r}(t)^4 >}{5 \ < \Delta\mathbf{r}(t)^2 >^2} - 1 \qquad (1)$$

where $< \Delta\mathbf{r}(t)^{2n} >= \frac{1}{N}\sum_{i=1}^{N} < |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^{2n} >$. Here $\mathbf{r}_i(t)$ is the position of the center mass of the ith body at time t. If $\mathbf{r}(t)$ is a Gaussian process, $\alpha_2^{(T)}$ vanishes for all time. The analog to this description for the rotational degrees of freedom can be obtained through the replacement of $\mathbf{r}_i(t)$ by the corresponding angular variable $\boldsymbol{\phi}_i$ [18], the change of which is defined in terms of angular velocity $\boldsymbol{\omega}_i$ by $\Delta\boldsymbol{\phi}_i(t) = \boldsymbol{\phi}_i(t) - \boldsymbol{\phi}_i(0) = \int_0^t dt'\boldsymbol{\omega}_i(t')$. For the symmetry of the ellipsoids, the definition for the rotational non-Gaussian parameter then reads as

$$\alpha_2^{(R)} = \frac{< \Delta\boldsymbol{\phi}(t)^4 >}{2 < \Delta\boldsymbol{\phi}(t)^2 >^2} - 1 \qquad (2)$$

where $< \Delta\boldsymbol{\phi}(t)^{2n} >= \frac{1}{N}\sum_{i=1}^{N} < |\boldsymbol{\phi}_i(t) - \boldsymbol{\phi}_i(0)|^{2n} >$.

Figure 1a shows the time dependence of the rotational NGP $\alpha_2^{(R)}(t)$ for a series of densities across the I-N transition. In this case, the transition density is at $\rho^*_{IN} = 0.315$ when temperature $T^* = 1$ [5]. Note the growth of a dominant peak following a shoulder on approaching the I-N transition from the isotropic side. *The appearance of a shoulder at small times in the rotational NGP is accompanied by a signature of a sub-diffusive regime in the temporal evolution of mean square angular deviation* (data not shown). Also, the time scale of the shoulder is found to nearly coincide with that of the onset of the sub-diffusive regime. The shoulder in the rotational NGP can therefore be ascribed to what may be called the rotational analog of *rattling within a cage*. Subsequent to the shoulder, the second peak appears around a time $t^\star_{max} \approx 20$, which shifts rather slowly to higher values with increasing density. We note that this time is comparable to the onset of diffusive motion for rotational degrees of freedom. We have further explored whether the time scale of the second peak of $\alpha_2^{(R)}(t)$ has any correlation in the relaxation of the second rank single particle orientational time correlation function $C_2^s(t)$. The latter is defined for a system of ellipsoids as

$$C_2^s(t) = \frac{\langle \sum_i P_2(\hat{\mathbf{e}}_i(0)\cdot\hat{\mathbf{e}}_i(t))\rangle}{\langle \sum_i P_2(\hat{\mathbf{e}}_i(0)\cdot\hat{\mathbf{e}}_i(0))\rangle}, \qquad (3)$$

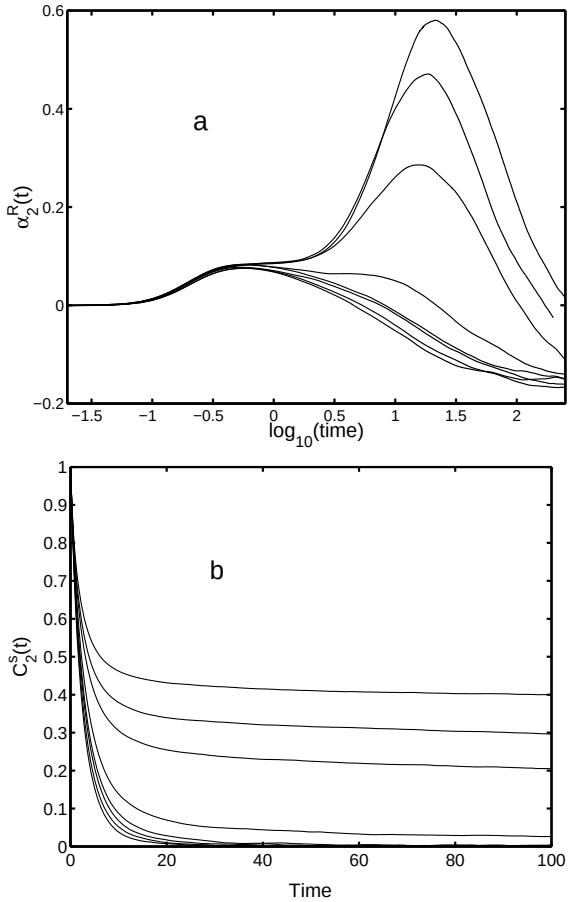

FIG. 1: (a) Semi-log plot of rotational NGP versus the reduced time near the I-N transition at different densities ranging from $\rho^* = 0.285$ to $\rho^* = 0.32$ in a grid of $\delta\rho^* = 0.005$ (arranged in the increasing order of density from bottom to top). (b) Single particle second rank orientational time correlation function versus reduced time for the corresponding densities arranged in the reverse order.

where $\hat{\mathbf{e}}_i$ is the unit vector along the principal axis of symmetry of the ellipsoid i, P_2 is the second rank Legendre polynomial and the angular brackets stand for statistical averaging. In **Figure 1b**, the time dependence of $C_2^s(t)$ is shown for several densities. We find that the time scale of the second peak also marks the *onset of slow relaxation* in $C_2^s(t)$. This suggests that the second peak is due to the heterogeneity in rotational dynamics arising from pseudonematic domains that have random local directors.

In **Figure 2**, we show the microscopic reason for the glassy relaxation of the nematogens with a display of single particle trajectories in the orientational space. This clearly demonstrates the onset of localization of the orientational motion in a preferred direction which is the direction of the director of a pseudonematic domain. The single particle trajectories give the direct evidence of rotational symmetry breaking in the dynamics near the I-N transition. Note that the interaction between the ellip-

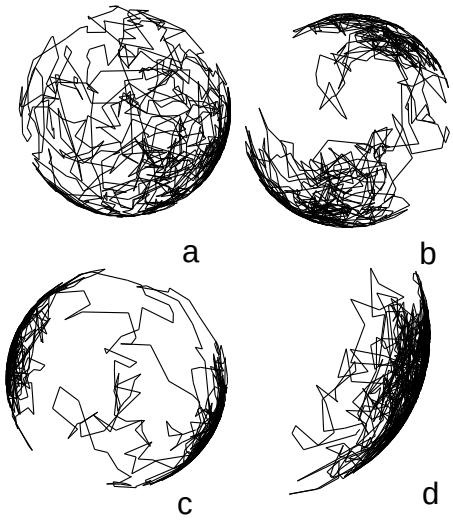

FIG. 2: Typical single particle trajectories of the unit orientation vector at four densities: (a) $\rho^* = 0.285$ (in the isotropic phase), (b) $\rho^* = 0.31$ (very close to the I-N transition), (c) $\rho^* = 0.315$ (at the I-N transition point), and (d) $\rho^* = 0.32$ (in the nematic phase).

soids still has the up-down symmetry; however, the dynamics of the director looses this symmetry in the nematic phase.

The above dynamical features have been found to have some correspondence with those revealed by the simulations of our binary system in the supercooled regime [19]. **Figures 3a** and **3b** show the temporal evolution of the rotational and translational NGPs, respectively, of the ellipsoids in the binary mixture for a series of temperatures close to the mode-coupling theory critical temperature. It is evident from **Figure 3a** that the growth of the rotational NGP to its maximum value $\alpha_{2max}^{(R)}$ before it starts decaying is rather smooth at all the temperatures studied and the inset shows that the maximum is reached on a time scale that characterizes the onset of diffusive motion for rotational degrees of freedom. This time $t_{max}^{(R)}$ gets lengthened with decreasing temperature. The time dependence of the translational NGP, however, differs in having a shoulder that resembles that of the rotational NGP near the I-N transition. Starting from $\alpha_2^{(T)}(t = 0) = 0$, translational NGP rises smoothly to a value $\alpha_{2max}^{(T)}$ on a time scale that characterizes the crossover from the ballistic to diffusive motion for translational degrees of freedom at high temperatures. It then starts falling off to reach the long time limit. As temperature drops, *a shoulder* or *a step-like feature* appears in between the initial rise and subsequent growth to its maximum value. We note that the shoulder appears as a sub-diffusive regime sets in between the ballistic and diffusive motion as evident from the time dependence of the mean square displacement shown in the inset of **Figure 3b**. It has been further observed (data not shown) that the shoulder in translational NGP appears on a time scale that coincides with the second maximum of the velocity autocorrelation function which shows oscillatory character, particularly at low temperatures. The above analysis suggests that the shoulder at small times in the translational NGP can be attributed to what is known as the *rattling within a cage* while the dominant peak appears on a time scale that characterizes the escape of a particle from the cage formed by its nearest neighbors. The absence of the step-like feature in the time dependence of the rotational NGP may be ascribed to the observation that the freezing in rotational degrees of freedom is less pronounced than it is in translational degrees of freedom [19].

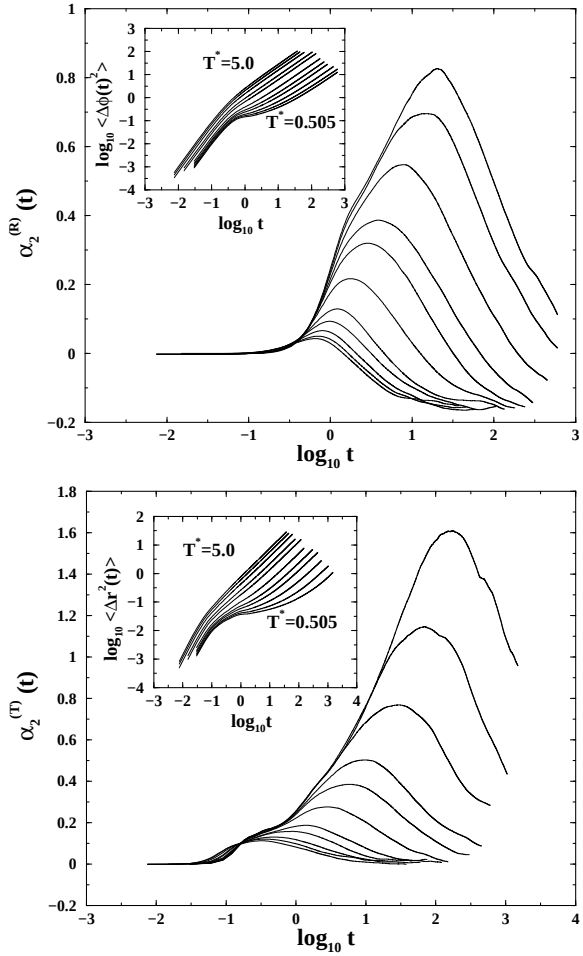

FIG. 3: (a) Semi-log plot of rotational NGP versus the reduced time for the ellipsoids in the binary mixture for all temperatures studied. From bottom to top the temperature decreases from $T^\star = 5$ to $T^\star = 0.505$. The inset shows the time evolution of the mean square angular deviation (msad) for the same set of temperatures in a log-log plot. (b) Semi-log plot for the corresponding translational NGP showing its time evolution. The inset displays the time dependence of the mean square deviation (msd) in a log-log plot.

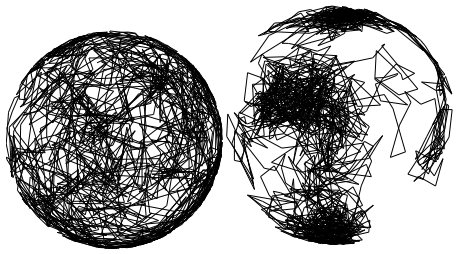

FIG. 4: Typical trajectories of the orientational unit vector of a single particle at the highest (left) and lowest (right) temperatures studied.

That the long time limit of the rotational NGP, defined by Eq. (2), is different from its translational counterpart requires further attention. Note that there is as yet no unique way of computing NGP for rotational degrees of freedom because the angular space is as such bounded while one needs the rotational analog of $\mathbf{r}_i(t)$ to be an unbounded one. Here we have followed a procedure that has been used previously to compute rotational diffusion [18], but there is no earlier report of rotational NGP in a three-dimensional system (to the best of our knowledge). Although the prefactor of 1/2 in Eq. (2), which is the appropriate one for there being two rotational degrees of freedom for the ellipsoids within the linear molecule approximation, can capture the expected zero time limit, it does show a deviation from the long time limit which one would desire to be zero.

In **Figure 4**, we display single particle trajectories of the ellipsoids in the binary mixture in the orientational space. While the dynamics is ergodic at high temperatures, the signature of non-ergodicity is evident at the lowest temperature studied. A comparison between Figures 2 and 4 reveals both the similarities and the differences between the rotational dynamics of the nematogens (near the I-N transition) and the ellipsoids in the binary mixture. For the liquid crystal system "nonergodic-like" behavior is driven by the rotational anisotropy that emerges near the I-N transition. Note the large scale angular displacement near the I-N transition which is similar to the one observed in the supercooled regime [19].

Mode coupling theory (MCT) may provide valuable insight into the origin of the slow down in both the cases. MCT predicts that near the I-N transition, the low frequency rotational memory kernel should diverge in a power law fashion [3].

$$M_R(z) \approx \frac{A}{z^{\alpha}} \tag{4}$$

with $\alpha \simeq 0.5$. This leads to the power law in the temporal decay of the orientational time correlation function at intermediate times. Note, however, that the above singularity is not robust in the sense that it assumes a divergence of static orientational pair correlation function at small wavenumbers ($k \simeq 0$), which never occurs because the I-N transition intervenes before that [20]. For density fluctuations in the supercooled liquid, the relevant memory function is that of the longitudinal current and this function also develops a power-law singularity of the same type as Eq. (4) [21, 22]. However, the origin of this singularity is due to the formation of pronounced local order at molecular length scale (first peak of the static structure factor). Considering the analogous dynamical behavior revealed in recent studies, an attempt to explore the difference in physical origin within the framework of MCT would definitely be a worthwhile undertaking, particularly the crossover from the power law to the LdG exponential relaxation near the I-N transition.

Perhaps the difference is best understood by looking at the free energy landscape. While the free energy with respect to orientational density fluctuations becomes increasingly flat as the I-N transition is approached, the free energy surface becomes rugged for the supercooled liquid. The confining mean potential for the orientation is a symmetric double well separated by an angle of π at the I-N transition. This point, however, deserves further study.

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