Anisotropic translational diffusion in the nematic phase: Dynamical signature of the coupling between orientational and translational order in the energy landscape

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We find in a model system of thermotropic liquid crystals that the translational diffusion coefficient parallel to the director $D_\parallel$ first increases and then decreases as temperature drops through the nematic phase, and this reversal occurs where the smectic order parameter of the underlying inherent structures *becomes significant*. We argue, based on an energy landscape analysis, that the coupling between orientational and translational order can play a role in inducing the nonmonotonic temperature behavior of $D_\parallel$. Such a view is likely to form the foundation of a theoretical framework to explain the anisotropic translation diffusion.

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Anisotropic translational diffusion of nonspherical molecules enjoys immense interdisciplinary interests because of its importance in physical (liquid crystals), chemical (micelles), and biological (lipids) systems [1–5]. It is particularly important in the uniaxial nematic phase, where the diffusion description invokes $D_\parallel$ and $D_\perp$, the principal components of the second-rank diffusion tensor, for translational motion parallel and perpendicular, respectively, to the macroscopic director [1]. A variety of experimental techniques probe the anisotropic translational diffusion in the nematic phase [2,3,5]. However, a consensus regarding an appropriate dynamical model is still lacking. In particular, the role of coupling between the orientational and translational order parameters appears to be overlooked.

On the contrary, the interplay between orientational and translational order has been extensively discussed in the context of the nematic-smectic-*A* (NSm*A*) phase transition over three decades [1,6–13]. The de Gennes-McMillan (dGM) coupling, which refers to the occurrence of the smectic (one-dimensional translational) ordering being intrinsically coupled with increase in the nematic (orientational) ordering [1,6,7], could drive, within a mean-field approximation, an otherwise continuous NSm*A* transition first order for a narrow nematic range [6]. Halperin, Lubensky, and Ma later invoked the coupling between the smectic order parameter and the transverse director fluctuations in their theoretical treatment that predicted NSm*A* transition to be at least a weak first order [8].

Intuitively, $D_\parallel$ appears to be well placed to capture the dynamical signature of the coupling between orientational and translational order. Therefore, we here investigate anisotropic translational diffusion in a model system of thermotropic liquid crystals. The observed diffusion behavior of the system is correlated with the features of its underlying potential energy landscape [14]. In this paper, we show that the coupling between orientational and translational order can lead to the nonmonotonic temperature behavior of $D_\parallel$ being reported here.

We have investigated a system of 256 ellipsoids of revolution along two isochors at a series of temperatures. We have used the well-established Gay-Berne (GB) pair potential [15], which explicitly incorporates anisotropy in both the attractive and the repulsive parts of the interaction with a single-site representation for each ellipsoid of revolution [16]. The GB pair potential gives rise to a family of models, each member of which is characterized by the values chosen for the set of four parameters (κ,κ',μ,ν) [17]. Here κ defines the aspect ratio, that is the ratio of molecular length to breadth, of the ellipsoid of revolution and κ' is the energy anisotropy parameter defined by the ratio of the depth of the minimum of the potential for a pair of molecules aligned parallel in a side-by-side configuration to that in an end-to-end configuration while μ and ν are two adjustable exponents that also control the anisotropy in the well depth [17]. We have employed the original and most studied parametrization: $\kappa=3$, $\kappa'=5$, $\mu=2$, $\nu=1$ [15,17]. The isochors have been so chosen that the range of the nematic phase along these varies considerably.

Figure 1(a) shows the inverse temperature dependence of the principal components of the diffusion tensor (in the logarithmic scale) of the Gay-Berne system with the aspect ratio 3 along the two isochors considered [18]. $D_\parallel$ and $D_\perp$ are obtained from the slopes at long times of the respective mean square displacements versus time plots: $D_\parallel=\frac{1}{2}\lim_{t\to\infty}\frac{d}{dt}\langle\Delta r_\parallel^2(t)\rangle$, $D_\perp=\frac{1}{2}\lim_{t\to\infty}\frac{d}{dt}\langle\Delta r_\perp^2(t)\rangle$, where $\langle\Delta r_\parallel^2(t)\rangle=\langle[r_\parallel(t)-r_\parallel(0)]^2\rangle$ and $\langle\Delta r_\perp^2(t)\rangle=\langle[r_\perp(t)-r_\perp(0)]^2\rangle$ [19]. Here the subscripts refer to the Cartesian components, resolved in a system of axes based on the director defined at each time origin. For the finite size of the system, the average orientational order parameter S has a nonzero value even in the isotropic phase [20]. This allows us to compute $D_\parallel$ and $D_\perp$ also in the isotropic phase. It is evident from Fig. 1(a) that both $D_\parallel$ and $D_\perp$, which have nearly identical values in the isotropic phase, exhibit an Arrhenius temperature dependence in this phase. On crossing the isotropic-nematic (I-N) phase boundary as temperature drops, $D_\parallel$ first *increases and* then *decreases* while $D_\perp$ continues to undergo a monotonic decrease following an Arrhenius temperature behavior across the nematic phase. From the Arrhenius fits to the $D_\perp$ data, we find that the activation energy for the diffusive translational motion perpendicular to the director remains effectively unchanged on either side of the I-N transition.

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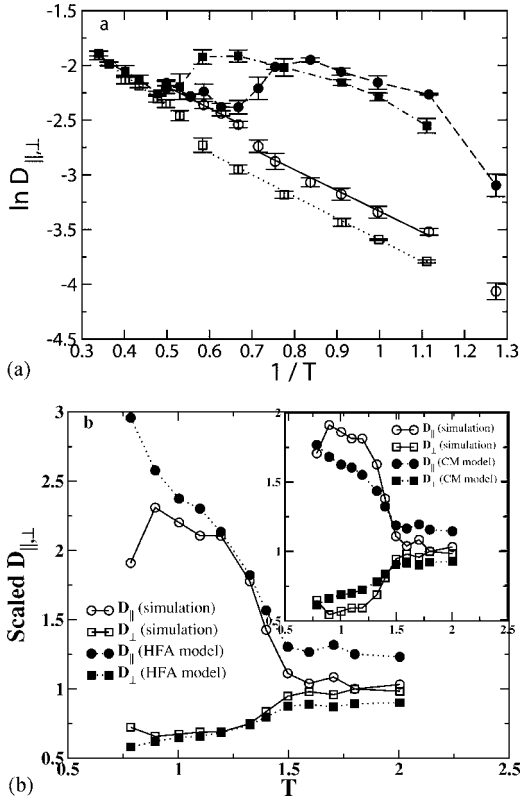

FIG. 1. (a) The self-diffusion coefficients $D_{\parallel}$ and $D_{\perp}$ in the logarithmic scale versus the inverse temperature along two isochors at densities $\rho=0.32$ (circles) and 0.33 (squares), respectively. The dot-dashed and long-dashed lines are guides for the eye for the $D_{\parallel}$ data (filled symbols) and the solid lines and the dotted lines are the Arrhenius fits to the $D_{\perp}$ (empty symbols) data for $\rho=0.32$ and 0.33, respectively. $D_{\perp}$ data have been considered separately across the isotropic phase and the nematic phase for the Arrhenius fits. (b) The comparison of the scaled $D_{\parallel}$ and $D_{\perp}$ data obtained from our simulations with those predicted by the Hess-Frenkel-Allen (HFA) model (main frame) and the Chu and Moroi (CM) model (inset). For the comparison with the HFA model the scaling is done by $\langle D\rangle_g$, while for the CM model it is done by $\langle D\rangle$.

A quantitative, albeit indirect, approach to capture the dynamical signature of the coupling between orientational and translational order is to compare the $D_{\parallel}$ and $D_{\perp}$ data obtained from our simulations with those predicted by the existing dynamical models, which ignore such coupling. In Fig. 1(b), we do so by considering two theoretical models [21,22], that have been applied to trace experimental and molecular dynamics simulation data of anisotropic translational diffusion in the nematic phase of liquid crystalline systems [3,21–24]. The main frame displays the comparison with the HFA model while the inset shows the same with the CM model. The latter gives relatively simple expressions for $D_{\parallel}$ and $D_{\perp}$ in terms of *only* the orientational order parameter S and the shape factor $g=\pi/(4\kappa)$: $D_{\parallel}=\langle D\rangle[1+2S(1-g)/(2g+1)]$ and $D_{\perp}=\langle D\rangle[1-S(1-g)/(2g+1)]$, where the isotropic average is defined by $\langle D\rangle=(2D_{\perp}+D_{\parallel})/3$. The HFA model invokes the concept of affine transformation from the space of isotropic hard spheres and yields the following expressions: $D_{\parallel}=\langle D\rangle_g\alpha[\kappa^{4/3}-2/3\kappa^{-2/3}(\kappa^2-1)(1-S)]$ and

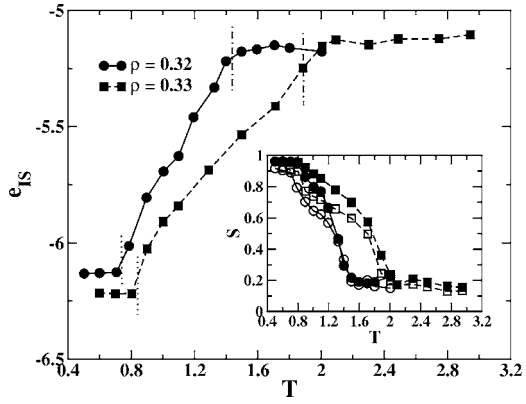

FIG. 2. The temperature dependence of the average inherent structure energy per particle along the two isochors at densities $\rho=0.32,0.33$. The inset shows the evolution of the average orientational order parameter S with temperature both for the inherent structures (filled) and the corresponding prequenched ones (empty). The two sets of data are for the same two densities as in Fig. 1(a). The vertical dot-dashed and dotted lines in the main frame show the locations of the isotropic-nematic and nematic-smectic phase boundaries, respectively.

$D_{\perp}=\langle D\rangle_g\alpha[\kappa^{-2/3}+1/3\kappa^{-2/3}(\kappa^2-1)(1-S)]$, where $\alpha=[1+2/3(\kappa^{-2}-1)(1-S)]^{-1/3}[1+1/3(\kappa^2-1)(1-S)]^{-2/3}$ and the geometric average is defined by $\langle D\rangle_g=D_{\perp}^{2/3}D_{\parallel}^{1/3}$. For the purpose of comparison, we plot scaled $D_{\parallel}$ and $D_{\perp}$ data. It follows from Fig. 1(b) that both the models cannot capture the nonmonotonic temperature behavior of $D_{\parallel}$. We next demonstrate directly by performing a landscape analysis that the nonmonotonic temperature behavior of $D_{\parallel}$ could be due to the coupling between orientational and translational order.

In the landscape formalism, the potential energy surface is partitioned into a large number of "basins," each defined as the set of points in the multidimensional configuration space such that a local minimization of the potential energy maps each of these points to the same local minimum [14]. The inherent structure corresponds to the minimum configuration [25]. As a result of this partitioning of the configuration space, the time-dependent position $\mathbf{r}_i(t)$ of a particle i can be resolved into two components: $\mathbf{r}_i(t)=\mathbf{R}_i(t)+\mathbf{S}_i(t)$, where $\mathbf{R}_i(t)$ is the spatial position of the particle i in the inherent structure for the basin inhabited at time t, and $\mathbf{S}_i(t)$ is the intrabasin displacement away from that inherent structure [26]. That the replacement of the real positions $\mathbf{r}_i(t)$ by the corresponding inherent structure positions in the Einstein relations yields an equivalent diffusion description, as has been theoretically argued and also verified in simulations [26,27], is the key to our analysis presented here.

Figure 2 displays the average inherent structure energy as the drop in temperature drives the system across the mesophases along two different isochors [28,29]. In the inset of Fig. 2, we show the concomitant evolution of the average orientational order parameter S both for the inherent structures and the corresponding prequenched ones. While the average inherent structure energy remains fairly insensitive to temperature variation in the isotropic phase and also in the smectic phase, it undergoes a steady fall as the orientational

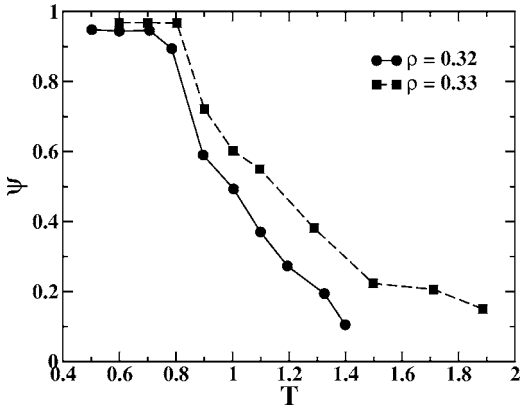

FIG. 3. The evolution of the smectic-order parameter Ψ for the inherent structures with temperature at two densities.

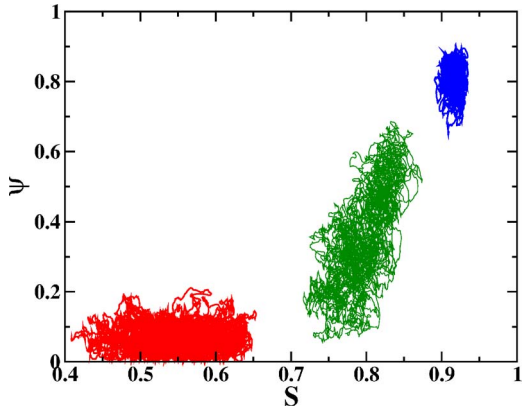

FIG. 4. (Color online) The coupling between the orientational order and the translational order in the Gay-Berne system with the aspect ratio $\kappa=3$ at three state points along the isochor at density $\rho=0.32$: at the nematic phase ($T=1.194$; red, left), at the smectic phase ($T=0.502$; blue, right), and at the nematic-smectic transition region ($T=0.785$; green, middle). Here S and Ψ denote the respective order parameters for instantaneous configurations.

order grows through the nematic phase. We find that $D_{\parallel}$ starts increasing near the I-N phase boundary at a temperature that marks the onset of the growth of the depth of the potential energy minima explored by the system.

The onset of the growth of the orientational order in the vicinity of the I-N transition induces a translational order in a layer in the underlying quenched configurations [29]. The smectic-order parameter Ψ provides a quantitative measure of the one-dimensional translational order [30]. In Fig. 3, we show the evolution of the average smectic order parameter Ψ of the inherent structures, obtained by averaging over the quenched configurations, with temperature [30]. A steady increase in Ψ with the concomitant growth of S in the underlying inherent structures is apparent across the nematic phase.

The interplay between the orientational order and the translational order, shown in Fig. 3, is reminiscent of the dGM coupling which was originally conceived to be present near the nematic-smectic phase boundary in the parent system. Figure 4 confirms this with an explicit demonstration of the coupling between the smectic-order parameter Ψ and the nematic-order parameter S near the nematic-smectic transition region. While the fluctuation of S is large at the nematic-phase, it is the fluctuation of Ψ that is rather large in the smectic phase. A strong coupling between the two is evident at the nematic-smectic transition region where configurations with larger S values tend to have larger Ψ values.

Upon scrutiny of Figs. 1 and 3, we find that the reversal in the temperature behavior of $D_{\parallel}$ in the nematic phase as temperature drops occurs when the smectic-order parameter in the underlying inherent structures becomes significant (above 0.3). The smectic-order parameter is a measure of the translational order which appears in a layer perpendicular to the director. The induction of such a translational order makes translational motion parallel to the director much more difficult, resulting in a reducing effect on $D_{\parallel}$. From the viewpoint of the energy landscape analysis, the translational order in the underlying inherent structures, therefore, appears to play a key role in the nonmonotonic temperature dependence of $D_{\parallel}$. The latter can therefore be taken as a dynamical signature of the de Gennes-McMillan coupling augmented in the potential energy landscape.

System size in the present study has been optimal, given that the landscape studies have often been restricted to a smaller system size while long wavelength fluctuations in the vicinity of a phase transition suggest a bigger one to be undertaken. The system size we have chosen here is, however, large enough so that the system tracks the phase diagram reported earlier [17]. Nevertheless, in order to check possible system size effects on our results, we have further considered systems with 500 ellipsoids of revolution along the isochor at density $\rho=0.32$. *No qualitative change* in the results has been observed (data not shown).

We have further studied effects of varying the aspect ratio κ and the energy anisotropy parameter κ' separately to explore the robustness of our results and analysis. In particular, we have considered the aspect ratio $\kappa=3.8$ along the isochor at $\rho=0.235$, for which a stable Sm-*A* phase appears between a wide nematic and low-temperature Sm-*B* phase. The temperature behavior of $D_{\parallel}$ in the nematic phase has been found to be qualitatively similar to what has been observed with the aspect ratio $\kappa=3$, for which the Sm-*A* phase appears only in the underlying inherent structure [29]. It is particularly interesting to consider a case where the smectic phase is absent and contrast the behavior. To this end, we have considered $\kappa'=1$, for which no smectic phase appears even at low temperatures and the underlying inherent structures for the nematic phase also do not have on the average any translational order [29]. In this case, we find that the signature of the nonmonotonic behavior in the temperature dependence of $D_{\parallel}$ is rather weak and is even missing in the scaled data (data not shown)—the dynamical models considered here also provide a better description of the anisotropic translational diffusion data. This further substantiates the importance of the coupling between orientational and translational order in the anisotropic translation diffusion in the nematic phase.

In summary, the present work throws light on the plausible role of the coupling between orientational and translational order in inducing a nonmonotonic temperature behav

ior of $D_{\|}$ in the nematic phase. While the competition between the alignment and thermal effects can also give rise to a nonmonotonic behavior, the importance of such coupling cannot be ignored particularly when a low-temperature smectic phase exists. A comparison of the simulated $D_{\|}$ data with those predicted by two well-known theoretical models shows the inadequacy of these models to capture the observed nonmonotonic temperature dependence of $D_{\|}$. The energy landscape analysis presented here suggests the necessity of a theoretical treatment that includes the coupling between orientational and translational order, which has an augmented manifestation in the underlying energy landscape. Such a suggestion is likely to form the foundation of a theoretical framework to explain the features anisotropic translational diffusion.

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