

Energy landscape view of phase transitions and slow dynamics in thermotropic liquid crystals

Dwaipayan Chakrabarti and Biman Bagchi*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

Edited by H. Eugene Stanley, Boston University, Boston, MA, and approved March 17, 2006 (received for review September 23, 2005)

Thermotropic liquid crystals are known to display rich phase behavior on temperature variation. Although the nematic phase is orientationally ordered but translationally disordered, a smectic phase is characterized by the appearance of a partial translational order in addition to a further increase in orientational order. In an attempt to understand the interplay between orientational and translational order in the mesophases that thermotropic liquid crystals typically exhibit upon cooling from the high-temperature isotropic phase, we investigate the potential energy landscapes of a family of model liquid crystalline systems. The configurations of the system corresponding to the local potential energy minima, known as the inherent structures, are determined from computer simulations across the mesophases. We find that the depth of the potential energy minima explored by the system along an isochor grows through the nematic phase as temperature drops in contrast to its insensitivity to temperature in the isotropic and smectic phases. The onset of the growth of the orientational order in the parent phase is found to induce a translational order, resulting in a smectic-like layer in the underlying inherent structures; the inherent structures, surprisingly, never seem to sustain orientational order alone if the parent nematic phase is sandwiched between the high-temperature isotropic phase and the low-temperature smectic phase. The Arrhenius temperature dependence of the orientational relaxation time breaks down near the isotropic–nematic transition. We find that this breakdown occurs at a temperature below which the system explores increasingly deeper potential energy minima.

inherent structure

The spectrum of static and dynamical features exhibited by thermotropic liquid crystals on transit across the nematic phase from the isotropic to the smectic phase upon cooling has been a subject of immense fundamental and practical interests over the years (1, 2). Although the phase transitions from the isotropic to the nematic and then to the smectic phase in thermotropic liquid crystals have been studied extensively, certain fundamental issues like the role of fluctuations (3) and the order of these transitions (4–6) are far from being completely resolved. The de Gennes–McMillan coupling (1, 5), which refers to the occurrence of the smectic ordering being intrinsically coupled with an increase in the nematic ordering, is known to provide a mechanism that can drive an otherwise continuous nematic to smectic-A (NA) phase transition first order when the NA transition is sufficiently close to the isotropic–nematic (I-N) transition. However, the present understanding suggests that the I-N transition as well as the N-A transition are weakly first order. On the other hand, much of the interests in dynamics in liquid crystals have centered on the long-time decay of orientational relaxation across the I-N transition (1). Recent optical Kerr effect (OKE) measurements (7) with ultrashort laser pulses, however, have revealed signatures of complex dynamics over a wide range of time scales from ultrafast to slow, rather similar to the relaxation scenario observed in supercooled molecular liquids (8–10), even though the latter do not undergo any phase transition. The most intriguing feature of the complex dynamics

is the power-law decay observed at short-to-intermediate times (7, 8).

An approach that explores the potential energy surface of a system has provided a wealth of information about complex dynamics in supercooled liquids as well as in proteins (11–15). In this approach, 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. The configuration corresponding to the minimum is known as an “inherent structure” (IS) (11). In an appealing landscape study of a binary Lennard–Jones mixture, it was found that the onset of nonexponential relaxation in the supercooled regime corresponded to a temperature below which the dynamics of the system was influenced by its energy landscape (15).

Here, we explore the evolution of the IS of a family of model liquid crystalline systems across the mesophases in an attempt to understand the interplay between orientational and translational order and the plausible correlation of the manner of exploration of the underlying energy landscape with some of the dynamical features observed. To this end, we have studied a system of 256 ellipsoids of revolution along three isochors at a series of temperatures and also along two isotherms at a series of densities. We have used the Gay–Berne pair potential (16), which is an elegant generalization of the extensively used isotropic Lennard–Jones potential, to explicitly incorporate anisotropy in both the attractive and the repulsive parts of the interaction with a single-site representation for each ellipsoid of revolution. The Gay–Berne pair potential, which is well established to serve as a model potential for systems of thermotropic liquid crystals, defines a family of models, each member of which is characterized by the values chosen for the set of four parameters $\{\kappa, \kappa', \mu, \nu\}$ (17). In the Gay–Berne model potential, κ defines the aspect ratio, which 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, whereas μ and ν are two exponents that are adjustable (16–18). It follows that κ provides a measure of the shape anisotropy, which is essential for the existence of the mesophases, whereas a measure of the anisotropy in the well depth is provided by κ' . The anisotropy in the well depth also is controlled by the other two parameters, μ and ν (17). We have used the original and the most-studied parameterization $\{\kappa = 3, \kappa' = 5, \mu = 2, \nu = 1\}$ (17). The isochors and isotherms have been so chosen that the range of the nematic phase along these varies considerably. Apart from the isotropic phase, this system is known to exhibit nematic and smectic-B phases (but no smec-

Conflict of interest statement: No conflicts declared.

This paper was submitted directly (Track II) to the PNAS office.

Abbreviations: I-N, isotropic–nematic; IS, inherent structure(s).

*To whom correspondence should be addressed. E-mail: bbagchi@sscu.iisc.ernet.in.

© 2006 by The National Academy of Sciences of the USA

made with a system size of 864 when checked for some of the state points along the same isochor (data not shown).

Because the I-N transition is sharper along an isotherm for density variation for the system under consideration than it is along an isochor with temperature variation (17), we explored the corresponding evolution of the average IS energy along two isotherms at temperatures $T = 1.0$ and 1.1 (data not shown). The average IS energy is on a slow decline even in the isotropic phase. The rate of this decrease with density change now exhibits a maximum, which marks the I-N transition.

To check the generality of our results within the family of the Gay-Berne models, we considered variation of κ and κ' . We explored the evolution of the average IS energy along an isochor corresponding to a density $\rho = 0.235$ for the Gay-Berne system with $\{3.8, 5, 2, 1\}$. The aspect ratio $\kappa = 3.8$ is so chosen as a smectic-A phase, then appears in between the nematic phase, which persists over a wider range of temperatures, and the low-temperature smectic-B phase (18). However, a similar observation has been made regarding the manner of exploration of the potential energy minima and the characteristics of the underlying IS for the parent nematic phase (see Fig. 5, which is published as supporting information on the PNAS web site), as found with the Gay-Berne system of ellipsoids of revolution having aspect ratio 3. Such observation precludes the possibility that the results reported here are due to crystallite formation in the two-phase region close to the solid phase. Given that the Gay-Berne pair potential has the propensity to smectic order controlled by the energy anisotropy parameter κ' (16), it would be quite illuminating to investigate how the exploration of the energy landscape evolves as κ' is reduced (21). We therefore studied two Gay-Berne systems, one with $\{3, 2.5, 2, 1\}$ and the other with $\{3, 1, 2, 1\}$, each along the isochor at density $\rho = 0.32$. Although the manner in which the system explores the potential energy landscape on its transit across the nematic phase remains essentially similar for both systems (see Figs. 6 and 7, which are published as supporting information on the PNAS web site), the IS for the system with $\kappa' = 1$ no longer have a translational order when the parent phase is nematic. We note that no smectic phase appears for the Gay-Berne system with $\{3, 1, 2, 1\}$, even at low temperatures at density $\rho = 0.32$.

Let us now summarize the main results of the present study on the energy landscape view of phase transitions and slow dynamics in thermotropic liquid crystals. We determined the IS of a family of Gay-Berne model systems as these systems are cooled along isochors from the high-temperature isotropic phase. We found that the depth of the potential energy minima explored by a system on an average grows through the nematic phase as temperature drops along an isochor. This finding is to be contrasted to its observed insensitivity in the isotropic phase and the low-temperature smectic-B phase. The onset of the growth of the orientational order in the parent phase is found to induce a translational order, resulting in a smectic-like layer in the underlying IS. This striking result is found to be valid whenever the systems sustain a thermodynamically stable low-temperature smectic phase. This finding is confirmed for the most-studied parameterization of the family of Gay-Berne model systems $\{3, 5, 2, 1\}$ and the variants $\{3.8, 5, 2, 1\}$ and $\{3, 2.5, 2, 1\}$ with respect to the aspect ratio κ and the energy anisotropy parameter κ' , respectively. It is of particular interest to consider the Gay-Berne system with the parameterization $\{3, 1, 2, 1\}$. In this case, we could not find a low-temperature smectic phase at the density studied. Simultaneously, the translational order in a smectic layer was found to be missing from the IS when the parent phase is nematic. The two contrasting observations on the structural features of the IS together suggest that the underlying IS do not sustain orientational order alone if the parent nematic phase is sandwiched between the high-temperature isotropic phase and the low-temperature smectic phase. We further found that the

breakdown of the Arrhenius temperature dependence of the orientational relaxation time near the I-N phase transition occurs at a temperature below which the system explores increasingly deeper potential energy minima.

The similarity in the manner of the exploration of the potential energy landscape in the present system and in a model system of glass-forming liquids (15) is remarkable, even though the latter does not undergo a phase transition. In ref. 15, which dealt with only translational degrees of freedom, it was shown that the temperature, below which the depth of the potential energy minima explored by the system started growing, marked the onset of the breakdown of the Arrhenius behavior in the temperature dependence of the structural relaxation time. We found, surprisingly, a similar result here for single-particle orientational relaxation times. The striking resemblance might imply a unique underlying landscape mechanism for slow dynamics in condensed-matter physics. Although a Gaussian distribution for the density of the potential energy minima (22) may give rise to temperature-dependent average IS energy as observed here across the nematic phase, it is likely that the breakdown of the Arrhenius behavior is correlated with some other feature of the landscape (12). It would be interesting to explore whether connectivity among the basins plays a role. However, unlike in supercooled liquids (15), the temperature-dependent exploration of the underlying potential energy landscape in the present system is found to remain unchanged (within the limit of the statistical error) with varying cooling rates (see Fig. 8, which is published as supporting information on the PNAS web site). The lack of the cooling rate dependence of the average IS energy data suggests that equilibrium for the configuration space in the parent system is maintained in the present case within the molecular dynamics time scale.

It certainly would be of considerable fundamental and practical importance if the nematic phase cannot sustain an IS of its own kind. We find it striking that the onset of the growth of the orientational order in the parent phase induces a one-dimensional translational order in the underlying IS if the parent nematic phase is sandwiched between the high-temperature isotropic phase and the low-temperature smectic phase. An explicit demonstration of the coupling between the orientational order parameter and the smectic order parameter ψ , the latter being a measure of one-dimensional translational order (23), is shown in Fig. 9, which is published as supporting information on the PNAS web site, obtained from our simulations at the nematic-smectic transition region. That such a coupling is evident in the underlying IS with the advent of the nematic phase itself might be the demonstration of the critical role of the entropy in stabilizing the nematic phase at higher temperatures.

Materials and Methods

Molecular dynamics simulations were performed with $N = 256, 500,$ and 864 Gay-Berne ellipsoids of revolution contained in a cubic box with periodic boundary conditions. All quantities are given in reduced units defined in terms of the Gay-Berne potential parameters ε_0 and σ_0 : length in units of σ_0 , temperature in units of ε_0/k_B , where k_B is the Boltzmann constant, and time in units of $(\sigma_0^2 m / \varepsilon_0)^{1/2}$, where m is the mass of the ellipsoids of revolution. As is customary (18), we set the mass as well as the moment of inertia of the ellipsoids equal to unity. The intermolecular potential U was truncated at a distance $r_{\text{cut}} = (\kappa + 1)\sigma_0$ and shifted such that $U(r_{ij} = r_{\text{cut}}) = 0$, where r_{ij} is the separation between two ellipsoids of revolution i and j , as in the previous work (18). The equations of motion were integrated by using the velocity-Verlet algorithm (24) with integration time steps of $\delta t = 0.0015$. Equilibration was done by periodic rescaling of linear and angular velocities of particles. This equilibration was done for a time period of t_q that defines the cooling rate together with the change in

temperature. After this rescaling, the system was allowed to propagate with a constant energy for a time period of t_c to ensure equilibration upon observation of no drift of temperature, pressure, and potential energy. The data collection was in a microcanonical ensemble. At each state point, local potential energy minimization was executed by the conjugate gradient technique for a subset of 200 statistically independent configurations or, equivalently, for configurations taken from a run length of 50 times the structural relaxation time.

Minimization was performed with three position coordinates and two Euler angles for each particle, the third Euler angle being redundant for ellipsoids of revolution.

We thank P. Bhimalapuram and S. Sastry for useful discussion and/or comments. This work was supported in parts by grants from the Department of Science and Technology (India) and the Council of Scientific and Industrial Research (India). D.C. received a Research Fellowship from the University Grants Commission (India).

1. de Gennes, P. G. & Prost, J. (1993) *The Physics of Liquid Crystals* (Clarendon, Oxford).
2. Chandrasekhar, S. (1992) *Liquid Crystals* (Cambridge Univ. Press, Cambridge, U.K.).
3. Yethiraj, A. & Bechhoefer, J. (2000) *Phys. Rev. Lett.* **84**, 3642–3645.
4. de Gennes, P. G. (1972) *Solid State Commun.* **10**, 753–756.
5. McMillan, W. L. (1971) *Phys. Rev. A* **4**, 1238–1246.
6. Halperin, B. I., Lubensky, T. C. & Ma, S.-K. (1974) *Phys. Rev. Lett.* **32**, 292–295.
7. Gottke, S. D., Cang, H., Bagchi, B. & Fayer, M. D. (2002) *J. Chem. Phys.* **116**, 6339–6347.
8. Cang, H., Li, J., Novikov, V. N. & Fayer, M. D. (2003) *J. Chem. Phys.* **118**, 9303–9311.
9. Chakrabarti, D., Jose, P. P., Chakrabarty, S. & Bagchi, B. (2005) *Phys. Rev. Lett.* **95**, 197801.
10. Jose, P. P., Chakrabarti, D. & Bagchi, B. (2005) *Phys. Rev. E* **71**, 30701(R).
11. Stillinger, F. H. & Weber, T. A. (1983) *Phys. Rev. A* **28**, 2408–2416.
12. Wales, D. J. (2003) *Energy Landscapes* (Cambridge Univ. Press, Cambridge, U.K.).
13. Stillinger, F. H. (1995) *Science* **267**, 1935–1939.
14. Heuer, A. (1997) *Phys. Rev. Lett.* **78**, 4051–4054.
15. Sastry, S., Debenedetti, P. G. & Stillinger, F. H. (1998) *Nature* **393**, 554–557.
16. Gay, J. G. & Berne, B. (1981) *J. Chem. Phys.* **74**, 3316–3319.
17. de Miguel, E. & Vega, C. (2002) *J. Chem. Phys.* **117**, 6313–6322.
18. Brown, J. T., Allen, M. P., del Río, E. M. & de Miguel, E. (1998) *Phys. Rev. E* **57**, 6685–6699.
19. Zannoni, C. (2000) in *Advances in the Computer Simulations of Liquid Crystals*, eds Pasini, P. & Zannoni, C. (Kluwer Academic, Dordrecht, The Netherlands), pp. 17–50.
20. Strandburg, K. J., ed. (1992) *Bond-Orientational Order in Condensed Matter Systems* (Springer, New York).
21. de Miguel, E., del Río, E. M., Brown, J. T. & Allen, M. P. (1996) *J. Chem. Phys.* **105**, 4234–4249.
22. Wales, D. J. & Doye, J. P. K. (2001) *Phys. Rev. B* **63**, 214204.
23. Polson, J. M. & Frenkel, D. (1997) *Phys. Rev. E* **56**, R6260–R6263.
24. Ihnyskiy, J. M. & Wilson, M. R. (2002) *Comput. Phys. Commun.* **148**, 43–58.