Fluctuations and clinicity in tilted smectic liquid crystals

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The overwhelming majority of tilted smectic liquid crystals exhibit synclinic (Sm-C) ordering (a uniform tilt direction in all smectic layers) rather than anticlinic (Sm-C_A) ordering (a tilt direction that alternates from layer to layer). We propose that polar molecular-scale fluctuations of the interface between smectic layers provide a general entropic mechanism favoring synclinic ordering, and present evidence from simulations of the hard spherocylinder system in support of this hypothesis. We find that the entropy of the synclinic state of $L/D=5$ spherocylinders is higher than that of the anticlinic state for large tilt angles, and show that this entropy difference can be directly traced to molecular-scale fluctuations of the layer interface. This entropic mechanism may be suppressed in materials exhibiting anticlinic ordering due to a bent molecular conformational preference that quenches interface fluctuations.

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Among tilted smectic liquid crystals (LCs), anticlinic ordering (a tilt direction that alternates from layer to layer) is a rare and recently discovered phenomenon. To date, only ~400 anticlinic Sm-C_A LCs have been found, as compared with ~10 000 known synclinic Sm-C LCs [1], and the majority of these are structural variants of the first reported anticlinic material, MHPOBC [2,3]. Since the discovery of anticlinic LCs, a number of molecular models for the Sm-C_A phase have been advanced (for a recent review see Ref. [4]). Based on extensive quantum chemical and atomistic simulation studies of MHPOBC [5,6], we recently proposed that the entropy content of molecular-scale fluctuations of the interface between smectic layers (''out-of-layer'' molecular fluctuations) provides a general thermodynamic mechanism that uniquely favors synclinic ordering, and that the suppression of out-of-layer fluctuations in MHPOBC and similar materials, due to their unusual conformational behavior, permits the appearance of anticlinic ordering [7]. Evidence for a correlation between out-of-layer fluctuations and clinicity has been found previously by Fukuda and co-workers, who observed distinct higher-order Bragg reflections in x-ray diffraction measurements on several antiferroelectric liquid crystals [8]. This result suggests that out-of-layer fluctuations in Sm-C_A materials are significantly smaller than in conventional smectics, which in most cases exhibit only a first-order Bragg reflection. In this paper, we critically examine the general thermodynamic mechanism outlined above by assessing the contribution of molecular-scale interface fluctuations to the relative free energy of synclinic and anticlinic states of the hard spherocylinder system by means of Monte Carlo simulation.

The essence of this thermodynamic mechanism is captured by a simple conceptual model, the ''sawtooth'' model, shown schematically in Fig. 1. In this model, out-of-layer displacements of molecules in tilted smectic layers are assumed to impart a polar, or ''sawtooth,'' character to fluctuations of the layer interface (a necessary consequence of the symmetry of the interface). When two adjacent layers are tilted in the same direction, the sawteeth mesh, leading to an efficient filling of space. If adjacent layers are tilted in opposite directions, however, the sawteeth do not mesh, and space is not filled efficiently. Under constant-volume conditions, the system fills space either by quenching out-of-layer fluctuations or by increasing the in-layer molecular density (or both). In either case, there is an entropic penalty (the entropy of the anticlinic state is lower than that of the synclinic state), so the entropy associated with out-of-layer fluctuations uniquely favors the synclinic state.

To test this hypothesis, we have carried out a series of simulations of the hard spherocylinder system to directly probe the contribution of out-of-layer fluctuations to the free energy difference between synclinic and anticlinic states. We performed constant-volume, variable cell shape Monte Carlo simulations of periodic systems of hard spherocylinders in the Sm-A phase. Systems consisting of 480 spherocylinders

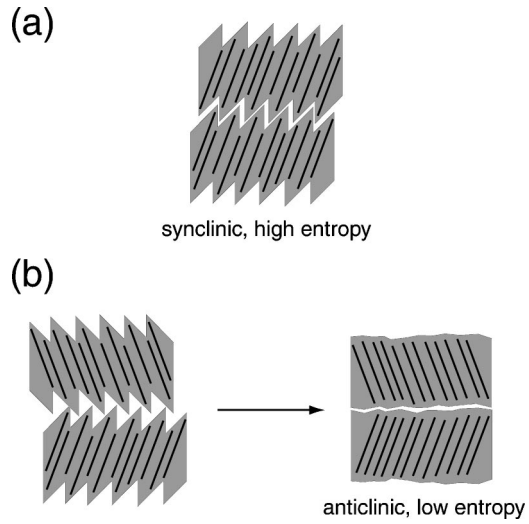

FIG. 1. Sawtooth model for interlayer tilt coupling. A synclinic structure (a) can accommodate large interface fluctuations while filling space efficiently. In an anticlinic arrangement (b), the sawtoothlike interface fluctuations do not mesh, and interface fluctuations are suppressed (with an accompanying loss of entropy) to fill space efficiently.

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in four smectic layers with length/breadth ratio $L/D=5$ were simulated at a density of $\rho/\rho_{CP}=0.6$, where ρ_{CP} is the close-packed density. This state point is in the middle of the Sm-*A* phase range [9,10].

Although the hard spherocylinder system does not exhibit tilted smectic phases, we can measure the free energy difference between synclinic and anticlinic states of this system using the umbrella sampling (biased sampling) technique of Torrie and Valleau [11], making use of biasing potentials that depend on the tilt and relative clinicity of adjacent smectic layers. The contribution of out-of-layer fluctuations to the synclinic/anticlinic free energy difference is probed by repeating the free energy calculations in the absence of out-of-layer fluctuations. We also measure the entropy content of out-of-layer fluctuations in the Sm-*A* phase, using a biasing potential that depends on the root-mean-square out-of-layer displacement.

Umbrella sampling makes use of a biasing potential to measure the probability distribution of a quantity Q,

$$P(Q)=\langle \delta(Q-Q(\mathbf{r}^N))\rangle = \frac{1}{Z}\int d\mathbf{r}^N \delta(Q-Q(\mathbf{r}^N))\exp[-\beta U(\mathbf{r}^N)], \quad (1)$$

for values of Q for which $P(Q)$ is small. Here, δ is a Dirac delta function, N is the number of particles, $\mathbf{r}^N$ denotes the set of particle coordinates, $\beta=(k_BT)^{-1}$, where k_B is Boltzmann's constant and T is the absolute temperature, $U(\mathbf{r}^N)$ is the potential energy, and Z is the configurational partition function. The biasing potential $U'(Q)$ is applied to constrain Q to some specifed range of values. The distribution of Q in the presence of a biasing potential is

$$P'(Q)=\frac{1}{Z'}\int d\mathbf{r}^N \delta(Q-Q(\mathbf{r}^N))\exp[-\beta(U(\mathbf{r}^N)+U'(Q))] = \frac{Z}{Z'}\exp[-\beta U'(Q)]P(Q), \quad (2)$$

where Z' is the partition function for the biased Hamiltonian. From this it follows that

$$P(Q)=\frac{Z'}{Z}\exp[\beta U'(Q)]P'(Q). \quad (3)$$

Thus, the distribution function $P(Q)$ can be obtained (to within a multiplicative constant) from a measurement of the biased distribution $P'(Q)$. The Helmholtz free energy F as a function of Q can then be obtained (to within an additive constant) from [12]:

$$F(Q)=-k_BT\ln[P(Q)]. \quad (4)$$

By piecing together distributions measured using a number of biasing potentials, it is possible to construct $P(Q)$ [and thus $F(Q)$] over any specified range of Q. Histograms obtained with individual biasing potentials are combined to minimize the variance in the overall $P(Q)$ using the weighted histogram analysis method [13].

To measure the free energy of the hard spherocylinder system as a function of tilt angle, we constrain the cosine of the tilt angle of the nematic director with respect to the layer normal ($\cos\Theta$) with a harmonic biasing potential,

$$U'(\cos\Theta)=\frac{1}{2}k_\Theta(\cos\Theta-\cos\Theta_0)^2, \quad (5)$$

where $\cos\Theta=\mathbf{v}\cdot\mathbf{z}$, $\mathbf{z}$ is a unit vector normal to the smectic layers, and $\mathbf{v}$ is the largest-eigenvalue eigenvector of the ordering tensor

$$Q_{\alpha\beta}=\frac{1}{N}\sum_{i=1}^{N}\left(\frac{3}{2}u'_{i\alpha}u'_{i\beta}-\frac{1}{2}\delta_{\alpha\beta}\right). \quad (6)$$

Here, $\mathbf{u}'_i$ is the ''modulated'' director of molecule i,

$$\mathbf{u}'_i=\mathbf{R}_\mu\mathbf{u}_i, \quad (7)$$

where $\mathbf{u}_i$ is a unit vector along the long axis of molecule i (the molecular director), μ is the index of the layer to which molecule i belongs, and $\mathbf{R}_\mu$ is a rotation matrix that rotates the director of every molecule in layer μ by an angle $\phi_\mu=\mu\Delta\phi$ about $\mathbf{z}$. For finite Θ_0, choosing $\Delta\phi=0$ biases the system towards a synclinic state, $\Delta\phi=\pi$ towards an anticlinic state, and $\Delta\phi=2\pi/n$ towards a period-n clock state.

To measure the free energy (entropy) content of interface fluctuations in the untilted (Sm-*A*) state, we carry out a separate series of simulations with a biasing potential of the form

$$U'(\Delta)=\frac{1}{2}k_\Delta(\Delta-\Delta_0)^2, \quad (8)$$

where

$$\Delta=\left[\frac{1}{N}\sum_{i=1}^{N}(z_i-z_{0\mu})^2\right]^{1/2} \quad (9)$$

is the instantaneous root-mean-square out-of-layer displacement. Here, z_i is the projection of the position of molecule i along $\mathbf{z}$, and $z_{0\mu}$ is the z coordinate of the layer to which molecule i belongs.

In Fig. 2 we show the reduced Helmholtz free energy $\beta F/N=-S/Nk_B$ as a function of $\cos\Theta$ for synclinic and anticlinic states of the hard spherocylinder system, produced by imposition of orientational biasing potentials with $\Delta\phi=0$ and $\Delta\phi=\pi$, respectively. Also shown is the free energy as a function of Θ (inset), and several representative configurations from this series of simulations. It is important to note that the biasing potential acts on overall (modulated or unmodulated) nematic director of the system, not on individual molecules, and so is minimally perturbative. In particular, the biasing potential does not, *a priori*, suppress director fluctuations. As anticipated, we measure a small but significant difference in free energy between synclinic and anticlinic states. The synclinic state has lower free energy (higher entropy) than the anticlinic state for large tilt angles ($\Theta>15°$), consistent with the simple sawtooth model. For $\Theta=25°$, for example, the free energy difference between

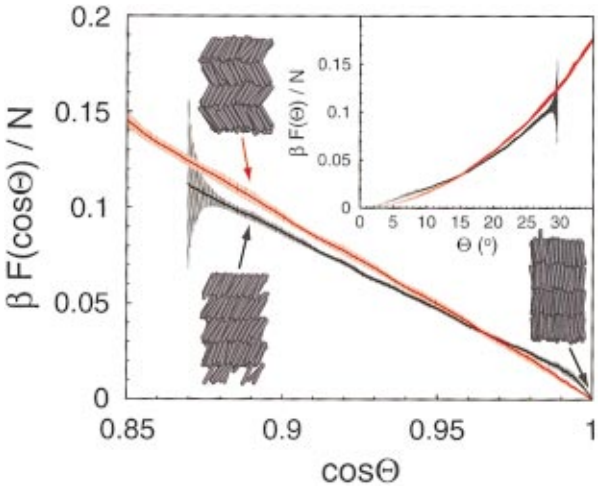

FIG. 2. (Color) Helmholtz free energy as a function of the cosine of the tilt angle for synclinic (black) and anticlinic (red) states of the hard spherocylinder system. Also shown is the free energy as a function of tilt angle (inset) for both states, and several representative configurations of the system. Error bars are indicated by vertical lines.

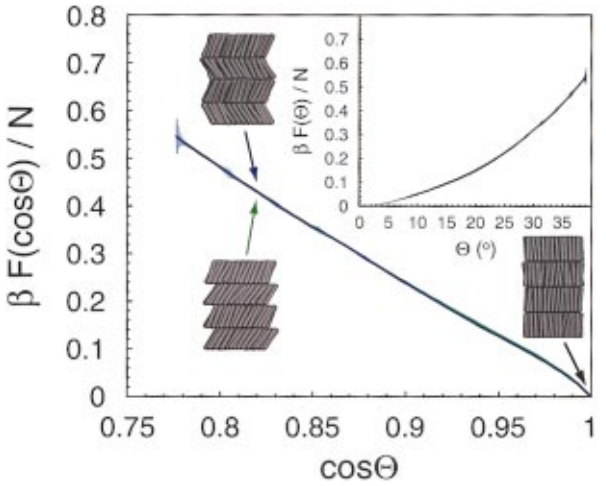

FIG. 3. (Color) Helmholtz free energy as a function of the cosine of the tilt angle for synclinic (green) and anticlinic (blue) states of the hard spherocylinder system, from a series of simulations in which out-of-layer fluctuations were suppressed. Also shown is the free energy as a function of tilt angle (inset) for both states and several representative configurations of the system. Error bars are indicated by vertical lines.

anticlinic and synclinic states is $\beta(F_{\mathrm{anti}}-F_{\mathrm{syn}})/N=(S_{\mathrm{syn}}-S_{\mathrm{anti}})/Nk_B=0.0069\pm0.0025$. Surprisingly, the free energy of the anticlinic state is lower than that of the synclinic state for small tilt angles ($\Theta<15°$), a result at variance with the simple sawtooth model. Note that the data for the synclinic state only extends up to tilt angles of $\sim30°$. Beyond this point, the orientation of the layer normal spontaneously changes via edge dislocation nucleation and migration.

To test the hypothesis that the observed free energy difference is associated with out-of-layer fluctuations, we have measured the reduced Helmoltz free energy of synclinic and anticlinic states of the hard spherocylinder system in which out-of-layer fluctuations are suppressed. The measured free energies are shown in Fig. 3, together with representative molecular configurations from the simulations. In the absence of out-of-layer fluctuations, there is no significant free energy difference between synclinic and anticlinic states. This is a compelling evidence that the entropy associated with out-of-layer molecular fluctuations accounts for the free energy difference seen in Fig. 2.

To further test this hypothesis, we have measured the root-mean-square out-of-layer displacement Δ as a function of Θ for both anticlinic and synclinic states, shown in Fig. 4. As expected, the amplitude of out-of-layer fluctuations in the anticlinic state is smaller than in the synclinic state for large tilt angles ($\Theta>15°$), but is larger for tilt angles smaller than 15°. For $\Theta=25°$, we find $\Delta_{\mathrm{syn}}-\Delta_{\mathrm{anti}}=0.065$.

To carry this analysis a step further, we can assess the entropic cost of quenching out-of-layer displacements by measuring the free energy as a function of Δ in the untilted state of the hard spherocylinder system, as shown in Fig. 5. The free energy is minimized for $\Delta=0.535$. Reducing Δ by 0.117 from its equilibrium value (to $\Delta=0.418$) leads to a decrease in entropy equal to the measured entropy difference between synclinic and anticlinic states at $\Theta=25°$. This is of the same order as, but somewhat larger than, the measured difference in Δ between synclinic and anticlinic states at $\Theta=25°$ (0.065), suggesting that the variation in free energy with Δ is more pronounced in tilted states than in the untilted state. Nevertheless, this analysis demonstrates that the entropy content of molecular-scale fluctuations of the interface between smectic layers is sufficient to account for the observed entropy difference between synclinic and anticlinic states. It is interesting to note that the free energy cost of tilt is more than a factor of 2 smaller in the unconstrained system than in the system in which out-of-layer fluctuations are suppressed. For example, the free energy cost of a 25° tilt is $\beta F/N=0.2255$ in the absence of out-of-layer fluctuations and $\beta F/N=0.0823$ (synclinic) or $\beta F/N=0.0892$ (anticlinic)

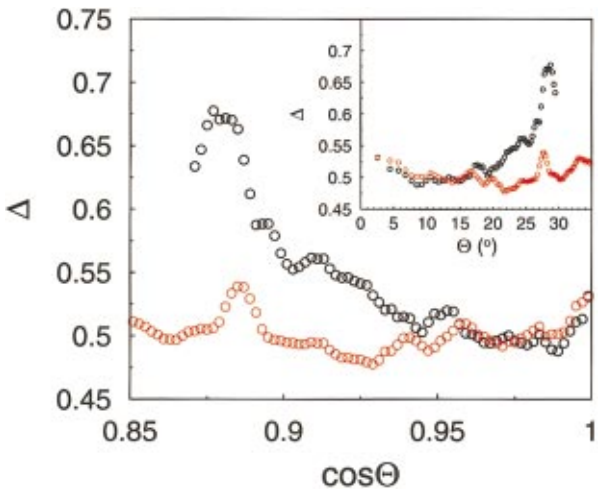

FIG. 4. (Color) Root-mean-square out-of-layer displacement Δ as a function of the cosine of the tilt angle for synclinic (black) and anticlinic (red) states of the hard spherocylinder system. Also shown is the Δ as a function of tilt angle (inset) for both states.

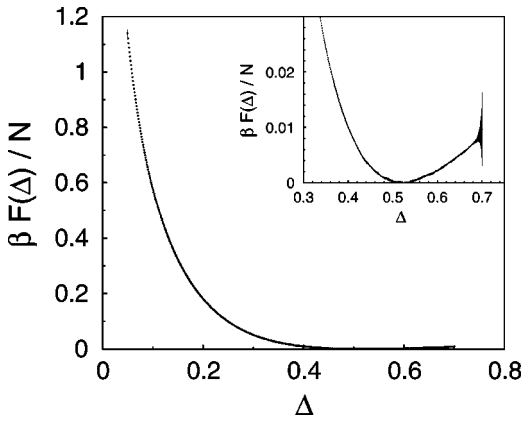

FIG. 5. Helmholtz free energy as a function of root-mean-square out-of-layer displacement Δ for the hard spherocylinder system. An expanded view of the region near the minimum is shown in the inset. Error bars are indicated by vertical lines.

in the presence of out-of-layer fluctuations. This is largely due to the fact that the entropy associated with out-of-layer fluctuations depends on the amplitude of molecular displacements along the molecular director (of order $\Delta/\cos\Theta$) rather than that of displacements along the layer normal (of order Δ). Assuming that Δ is independent of Θ, a simple free volume estimate of the entropy difference between unconstrained and constrained systems gives $(S_{\mathrm{uncon}}-S_{\mathrm{con}})/Nk_B = -\ln(\cos\Theta)$, under the further assumption that the in-layer free area per molecule is the same for both constrained and unconstrained systems at a given Θ. This accounts for most of the free energy difference between constrained and unconstrained systems, yielding, for example $(S_{\mathrm{uncon}}-S_{\mathrm{con}})/Nk_B = 0.0984$ at $\Theta = 25°$.

In summary, we have shown that the entropy associated with molecular-scale fluctuations of the interface between smectic layers governs clinicity in the hard spherocylinder system, and that such fluctuations uniquely favor synclinic ordering for large tilt angles. This entropic mechanism may account for the preponderance of synclinic (Sm-C) ordering among tilted smectic LCs, and may be absent in materials that exhibit anticlinic (Sm-C_A) ordering, perhaps owing to the suppression of out-of-layer fluctuations due to an intrinsic preference for bent molecular conformations [14,17]. Suppression of out-of-layer fluctuations due to molecular shape may play a role in the occurrence of other rare varieties of smectic liquid crystals, including ''de Vries'' smectics [15], in the observation of a filament morphology for smectic domains growing from the isotropic melt for certain materials [16], and in the remarkable ambivalence of bow-shaped mesogens with respect to their relative tilt and polar ordering in adjacent smectic layers [17].

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