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Microscopic origins of first order SmA-SmC phase behavior in de Vries smectic liquid crystals

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We explore the phase behavior of tilted hard rods as a model of de Vries smectic behavior and the first order smectic C (SmC) to smectic A (SmA) phase transition. The free energy cost of azimuthal rotation of a molecule away from the local tilt direction is calculated via umbrella sampling. This calculation is used to map the hard rod system onto a lattice spin system which shows a cross-over from a continuous to first order phase transition as the tilt of the rods is increased. This analysis offers a natural explanation of the first order SmA-SmC phase transition common to de Vries smectics.

Keywords: liquid crystal, smectic, de Vries, electroclinic effect, XY model

In 1977, de Vries reported a new type of liquid crystal SmA phase that showed a set of qualitatively different features from the conventional SmA phase [1–3]. Initially this phase was distinguished from other smectics by a first order SmA-SmC phase transition with an anomalously small reduction in layer spacing [4]. Subsequent work showed the characteristics of the de Vries SmA phase also includes large electroclinic responses [5], large field driven changes in birefringence in chiral materials [6], and a lack of a nematic phase in the phase sequence. One of de Vries’ early models, now called the hollow cone model, proposed that these phases are smectics with a molecular orientational distribution which is uniform in azimuthal angle ϕ but has a preferred tilt away from the layer normal, θ_A , sweeping out the surface of a cone, Figure 1. While this model remains controversial, it neatly explains the electro-optic response of chiral de Vries systems as well as the small layer contraction as the effects of averaging the molecular properties over azimuthal angle [7].

Although many of the features of the de Vries SmA phase can be explained by applying the hollow cone model, the observations of a first order SmA-SmC transition [1, 5] remain unexplained despite substantial study of these systems. In this paper we show using simulations and mean field theory that, much like the anomalous layer spacing and electro-optic response, the first order SmA-SmC phase transition seen in de Vries smectics can be understood as a direct result of the hollow cone model.

Materials exhibiting de Vries phases sparked interest for use in ferroelectric liquid crystal displays [8]. The small change in layer spacing makes these good candidates for ferroelectric liquid crystal (FLC) displays where large changes to that spacing can cause the formation of “zig-zag” defects during manufacturing [9]. In addition, the large electroclinic effect of de Vries SmA phases is well suited for sensitive chirality detection [5]. These potential applications have led to substantial research attempting to characterize and understand de Vries be-

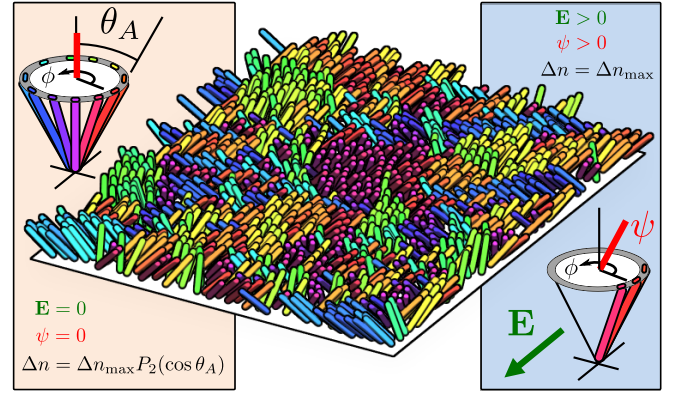


FIG. 1. (Color online) A snapshot from a Monte Carlo simulation of a single layer hard spherocylinder smectic with the hollow cone orientation distribution (color represents azimuthal orientation). This NPT simulation was performed with cone angle $\theta_A = 45^\circ$ and spherocylinder length $L/D = 5$ in the SmA phase near the SmA-SmC phase transition. Molecules in the hollow cone model have the orientation distribution in tilt, θ , and azimuthal angle, ϕ , of the form $f(\theta, \phi) = (2\pi)^{-1}g(\theta)$. The distribution is uniform in ϕ while $g(\theta)$ is narrowly peaked around the cone angle, θ_A , which we take as the delta function, $\delta(\theta - \theta_A)$. Hollow cone smectics show no global polar order in the SmA phase, but produce finite correlated regions. Macroscopic tilt, ψ , is the result of global bias of molecules to one side of the ϕ distribution.

havior which in turn has led to empirical exploration of the properties of de Vries materials. For instance, liquid crystal chemists discovered that chemical and structural motifs that promote layering, such as polyphilic or bulky tails, tend to produce de Vries-like behavior. This has given us some degree of predictive power in the design of de Vries mesogens [10]. The correlation between strong layering and de Vries materials also manifests as a direct isotropic to SmA phase transition, bypassing the nematic phase entirely. Meanwhile, high-resolution x-ray studies of the SmA-SmC phase transition have directly observed a discontinuous change in layer spacing in several ma-

terials [5, 11]. Exploration of the electro-optic behavior reveals a distinct sigmoidal polarization response, or double peaked polarization current response [7, 12–15] in a broad range of de Vries materials, also indicative of a first order SmA-SmC phase transition. This first order phase transition is in sharp contrast to the second order SmA-SmC transition common in conventional smectics [1, 16].

Several groups have performed theoretical studies of the de Vries SmA phase and the SmA-SmC transition at a phenomenological level. Bahr et al. used a simple Landau theory to model de Vries like electroclinic response seen in material C7 [12]. The mean field theory developed by Saunders et al. shows that coupling between tilt and biaxiality in smectics can produce a first order SmA-SmC phase transition, but doesn't point to a microscopic origin for this coupling [17, 18]. In a similar vein, work by Gorkunov et al. shows that the addition of higher order coupling terms into a mean field theory recreates the anomalously small change in layer spacing through the SmA-SmC phase transition, and shows how these couplings might arise based on a model of intermolecular interaction [19, 20]. At the microscopic level, Lagerwall et al. have proposed an alternate to the hollow cone model based on a conventional SmA with abnormally low nematic order [21].

Our work starts from the microscopic foundation of the hollow cone model and explores the implications of this model for de Vries smectics using Monte Carlo simulations, umbrella sampling, coarse graining, and mean field techniques. This bottom-up analysis culminates in the realization that the first order SmA-SmC transition can be viewed as a consequence of the hollow cone model via a defect condensation mechanism.

We begin by considering the behavior of a hollow cone fluid of a single smectic layer of hard spherocylinders. We performed NPT Monte Carlo simulations of a fluid of spherocylinders which are confined to the $z = 0$ plane and tilted from the layer normal by fixed cone angle θ_A , but allowed to freely rotate in azimuthal angle ϕ . This rigid realization of the hollow cone model where the distribution of spherocylinders in z and θ_A are explicitly delta functions is chosen to reduce the number of free parameters in the model. A more realistic model would include out-of-layer fluctuations and a finite distribution in angle θ centered around the cone angle, but such generalizations should not change the qualitative conclusions of the analysis.

The pressure in the simulation is equivalent to an effective mean attraction between the spherocylinders, mapping the hard core system onto a thermotropic system with temperature inversely proportional to pressure. At sufficiently large cone angles, simulations of this idealized system show a first order phase transition between a quasi-long ranged SmC-like phase at high pressure (low temperature) and a disordered phase at low pressure (high temperature) where finite ϕ -correlated domains

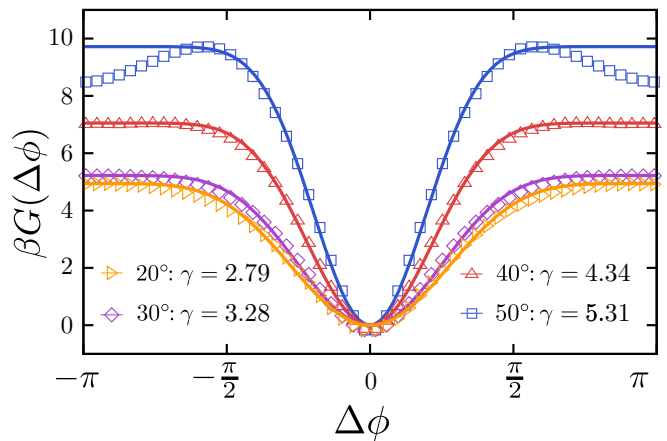


FIG. 2. (Color online) Umbrella sampling calculations of the Gibbs free energy of azimuthal rotation within a smectic layer of a single spherocylinder relative to the polarization vector averaged among surrounding spherocylinders within radius $a = 5\sigma$ where σ is the spherocylinder diameter. These calculations are performed within the SmC phase near the SmA-SmC phase transition at different cone angles, θ_A . At larger cone angles a secondary minimum appears at $\phi = \pi$. Superimposed are fits of the γ -potential, Equation 1, where the secondary minimum is excluded from the fitting procedure if present by separately fitting G_{\max} as demonstrated in the 50° fit. As the cone angle is increased the width of the well is reduced, or equivalently, γ increases.

average to SmA symmetry as demonstrated in Figure 1. These domains occur in hollow cone smectics due to the effective potential experienced by tilted spherocylinders interacting with their neighbors. The existence of these correlated domains predicts very different behavior from conventional SmA phases. Specifically, whereas fields on conventional SmA phases act on single molecules resulting in weak electroclinic coupling, the electroclinic effect due to reorienting the ϕ value of correlated domains around the cone is much larger. This is particularly noticeable near the SmA-SmC phase transition, which is consistent with experimental measurements of de Vries systems [5].

We measure the effective azimuthal potential by computing the Gibbs free energy cost of rotating a single spherocylinder by angle $\Delta\phi$ away from the local azimuthal order averaged over a domain of radius a in the fluid layer, $G(\Delta\phi)$. An umbrella sampling scheme ensures proper sampling over the full range of the rotational potential. We make iterative approximations to $G(\Delta\phi)$ in order to bias the system away from well sampled regions. Each iteration improves the approximation by using the sampled histogram, $\rho^{(i)}(\Delta\phi)$, via the equation

$$G^{(i)}(\Delta\phi) = -k_B T \ln(\rho^{(i-1)}(\Delta\phi)) \quad ,$$

where the superscripts denote the iteration. The free en-

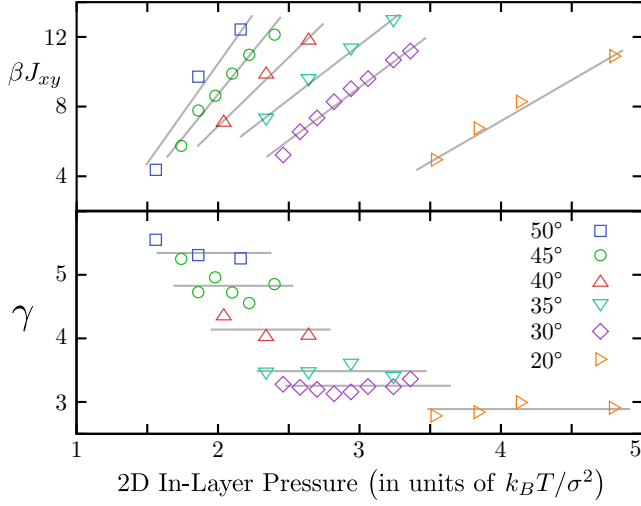


FIG. 3. (Color online) The mapping between the hard spherocylinder hollow cone system and the γ -potential XY model when using $a = 5\sigma$ as the coarse graining length scale where σ is the diameter of the spherocylinders. Spin coupling strength, J_{xy} , increases approximately linearly with pressure while the γ values are nearly independent of pressure but increases with larger cone angles, θ_A . While the specific values of J_{xy} and γ depend on a , these trends do not.

ergy profile, demonstrated in Figure 2 for various cone angles in the SmC phase near the SmA-SmC transition, shows a narrow minimum at $\Delta\phi = 0$ whose width decreases with increasing cone angle. This result is robust to changes in the hollow cone θ -distribution. For instance, defining a diffuse hollow cone via a harmonic potential in the θ coordinate produces qualitatively similar results.

Using the free energy profile and our observation that this system is well represented as a collection of ϕ -correlated domains, we define a coarse graining transformation which maps our off-lattice hollow cone smectic onto a generalized XY spin model with lattice constant a , the coarse graining length-scale. The average ϕ coordinate of the correlated domains within the smectic layer maps to the spin orientations in the XY model and the free energy profile maps to the in-layer nearest neighbor interaction. Motivated by this measured azimuthal free energy curve, we choose an in-layer potential of the form

$$U_{ij} = -J_{xy} \left[\frac{1}{2} (\cos(\phi_i - \phi_j) + 1) \right]^\gamma. \quad (1)$$

This potential, which we call the γ -potential, features an energy minimum at $\Delta\phi = 0$ whose width is tuned via parameter γ . The γ -potential fits well to the free energy profile at small to moderate cone angles near the SmA-SmC phase transition as shown in Figure 2. At larger cone angles we observe a secondary minimum at $\Delta\phi = \pi$ which we choose to exclude from the fitting procedure as our analysis suggests that the width of the minimum at $\Delta\phi = 0$ is the essential feature of the interaction. At sufficiently large cone angles, however, we predict that de Vries systems might additionally exhibit a smectic phase with two-dimensional nematic order of the c -director analogous to the phase reported in spin systems with a secondary minimum [22].

These fits provide us with a map, summarized in Figure 3, between our hard spherocylinder system governed by pressure, spherocylinder length, and cone angle to a spin system of lattice constant a governed by the angular width of the minimum in the neighbor interaction potential (encoded in γ) and the dimensionless energy ratio βJ_{xy} . With respect to pressure, the map reveals a roughly linear increase of the coupling strength, J_{xy} , and approximately constant γ independent of cone angle. We note that while the energy ratio βJ_{xy} corresponding to the transition shows no real trend with respect to cone angle, the value of γ shows a distinct increase as the angle increases.

The γ -potential can be viewed as a continuous version of the Potts model interaction, $u(\phi_i, \phi_j) = -J\delta_{\phi_i, \phi_j}$ where δ_{ϕ_i, ϕ_j} is the Kronecker delta over possible discrete ϕ states. Previous work by Domany et al. on two-dimensional spin systems used the γ -potential to explore the cross-over between the continuous Kosterlitz-Thouless phase transition of the planar rotor XY model with interaction $u(\phi_i, \phi_j) = -J \cos(\phi_i - \phi_j)$ at $\gamma = 1$ and the first order phase transition of the n -state standard Potts model where $n > 4$ [23].

Our de Vries system is composed of smectic layers which, like the two dimensional spin systems of Domany et al., are represented as planes of spin coupled by the γ -potential of strength J_{xy} in the x and y directions. The spins in these layers interact with adjacent layers in the z direction via a planar rotor style coupling of strength J_z . The Hamiltonian for this anisotropic cubic XY model is given by Equation 2 where we have assumed integer γ , expressed the γ -potential as a finite Fourier sum with known coefficients b_k , and sum the last term over all in-layer neighbors.

$$H = -pE \sum_i \cos(\phi_i) - J_z \sum_i \cos(\phi_i - \phi_{i+1}) - J_{xy} \sum_{(i,j)} \sum_{k=1}^{\gamma} b_k \cos(k(\phi_i - \phi_j)) \quad (2)$$

We characterize the phase behavior of our related

system using self-consistent variational mean field the-

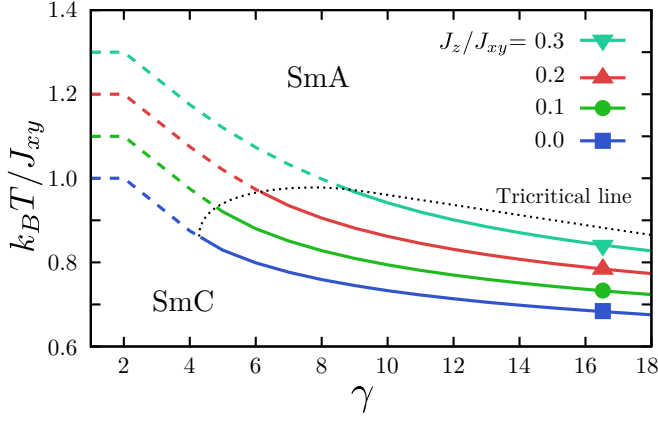


FIG. 4. (Color online) The $\gamma - T$ phase diagram of the γ -potential spin system showing tricritical behavior. The dashed and solid phase boundaries denote second and first order phase transitions, respectively. In the two dimensional system (■) and systems with weak inter-layer coupling, $J_z/J_{xy} < 0.1$, the phase transition crosses over from continuous to first order between $\gamma = 4$ and $\gamma = 5$. At stronger couplings, we see a sharp shift to larger values of γ as the cumulative potential begins to resemble the planar rotor.

ory [24]. In the mean field approximation we absorb the lattice's geometric factors into our coupling constants and combine the planar rotor inter-layer coupling with the first term of the in-layer coupling. We assume that the N -spin matrix can be written as the product of single-spin density matrices, Equations 3 and 4. Sets of order parameters, c_k , are found that satisfy the γ different self-consistency constraints in Equation 5. The stable phase is parametrized by the set of order parameters minimizing the mean free energy, Equation 6.

$$\rho_1 = \frac{1}{Z_1} \exp[\beta(pE + \sum_k J_k c_k \cos(k\phi))] \quad (3)$$

$$Z_1 = \int_0^{2\pi} \exp[\beta(pE + \sum_k J_k c_k \cos(k\phi))] d\phi \quad (4)$$

$$c_k = \int_0^{2\pi} \rho(\phi) \cos(k\phi) d\phi \quad (5)$$

$$F = \frac{1}{2} N \sum_k J_k c_k^2 - \frac{N}{\beta} \ln(Z_1) \quad (6)$$

The system shows a transition between the paramagnetic (SmA) phase and ferromagnetic (SmC) phase as shown in the $\gamma - T$ phase diagram in Figure 4. Much like Domany et al. we see a continuous phase transition at small γ and a first order transition at large γ . [23] Comparing with our parameter mapping, systems corresponding to smectics with large cone angles show first order SmA-SmC phase transitions while values of γ corresponding to small cone angles show continuous behav-

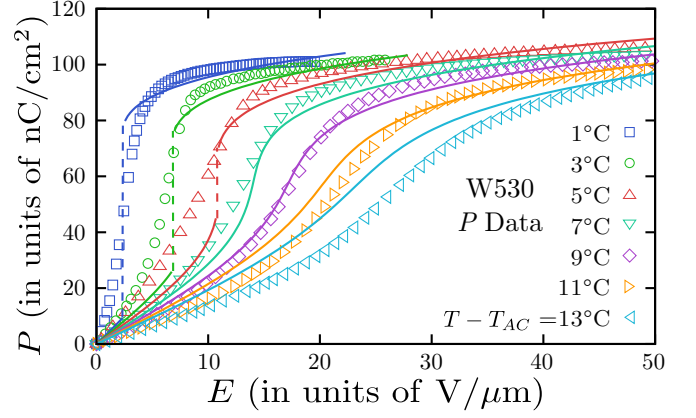


FIG. 5. (Color online) Comparison of the polarization density response of de Vries material W530 (symbols) when an electric field is applied across a liquid crystal cell with bookshelf alignment [13] and the model's predictions for $\gamma = 6$ (curves). The model's energy units at a given value of γ are set by equating the model's SmA-SmC transition temperature, T_{AC} , to the transition temperature for W530, 39°C. The polarization density saturation and susceptibility is scaled to demonstrate simultaneous qualitative agreement with several polarization curves near the SmA-SmC transition. At lower temperatures we predict a discontinuous change in P which is not seen experimentally. The continuous experimental behavior may be due to quenched surface disorder in the cell.

ior. Our analysis locates the tricritical point in the two-dimensional system between the γ values of 4 and 5 which corresponds to a cone angle of approximately 40° , though this is dependent on the coarse graining length scale. The phase behavior proves to be robust to weak inter-layer planar rotor interactions. To first order, the inter-layer coupling stabilizes the SmC phase to higher temperatures but doesn't significantly change the location of the tricritical point.

The first order phase transition within the spin system, and thus the spherocylinder system, can be understood in the context of defect or vacancy condensation much like phase transition in the standard Potts model [25]. The system free energy is reduced by overlapping disordered regions, producing a depletion-style attraction between disordered domains. This suggests that the first order phase transition seen in de Vries smectics also originates from a disorder condensation mechanism.

In addition to exploring the phase behavior of the system, we examined the polarization field response of the model. Figure 5 demonstrates the qualitative agreement between the spin model and a series of polarization response curves for de Vries material W530 measured via the polarization reversal current [13, 26]. These fits capture the basic sigmoidal behavior over a substantial range of temperatures above the SmA-SmC phase transition using only three free parameters.

In summary, we've shown that the implications of a

hollow cone smectic go further than the layer spacing and electro-optics to which it has been previously applied. The steric interactions inherent in a hollow cone smectic imply ϕ -correlated domains and, at sufficiently large cone angles, a first order SmA-SmC phase transition which leads to the observed sigmoidal field response.

Further simulation studies, for example an atomistic level investigation, are needed to understand the microscopic origins of hollow cone behavior itself. Our work, however, has shown that once hollow cone behavior is present, first order behavior emerges naturally as a consequence of excluded volume effects. Even without features such as out-of-layer fluctuations and an atomistic molecular model, we find that our minimal hollow cone model is a microscopic picture of de Vries smectics that encompasses most of the experimentally observed characteristics of the phase including the common first order phase transition and qualitative agreement with the electro-optics.

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