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Molecular model for de Vries type smectic A - smectic C phase transition in liquid crystals

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We develop a theory of Smectic A - Smectic C phase transition with anomalously weak smectic layer contraction. We construct a phenomenological description of this transition by generalizing the Chen-Lubensky model. Using a mean-field molecular model, we demonstrate that a relatively simple interaction potential suffices to describe the transition. The theoretical results are in excellent agreement with experimental data.

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Thermotropic smectic liquid crystals exhibit layered orientationally ordered phases. In the simplest smectic A (SmA) phase, the long molecular axis director $\mathbf{n}$ is normal to the smectic layers and the phase is uniaxial. But in the smectic C (SmC) phase, the director is inclined at an angle $\Theta$ to the layer normal, and the phase is biaxial. More complex smectic order has also been observed. Analogous tilted smectic order is observed in other soft-matter systems, such as block copolymers, lamellar $L_\alpha$ materials, biological membranes and tilted phases of Langmuir-Blodgett films. The origin of the tilt in the SmC phase has long been the subject of some controversy, and several different mechanisms of the SmA–SmC transition have been proposed.

Elementary pictures of the tilt transition assume almost perfect translational and orientational order. The transition here corresponds to a collective tilt of the orientationally ordered molecules. The closest analogy is a structural transformation, and the nature of the ordering in the two phases is essentially the same. The tilt has a geometrical rather than statistical definition, and the layer spacing $d$ decreases with tilt as $\cos \Theta$. Recently, however, materials have been discovered with diverse molecular structures, in which the SmC layer spacing is virtually constant.

A few such materials have long been known, but regarded as exceptional. A qualitative explanation, due to de Vries, requires that the SmA molecules are not oriented along the layer normal, but rather on a cone surface around it. The transition now involves an ordering of the molecular azimuthal angles, which results in a macroscopic average tilt. This model is inconsistent with high orientational order. Recent experiments do indeed indicate that the nematic order parameter is abnormally low in de Vries smectics.

However, different materials exhibit various degrees of layer contraction in the SmC phase. Neither of the extreme limits above is correct for real systems. Indeed the accumulated experimental data permit a study of a continuous range of materials between de Vries-type and normal smectics. The problem of why some materials do not show a layer contraction and why others do, is of considerable importance. The underlying physical mechanism is both of fundamental physical interest and of key practical importance. Chiral tilted smectic ferro-, antiferro- and helielectric materials are extremely promising for the new generation of fast electro-optic displays as well as various non-display applications. Layer contraction causes the emergence of chevron structures and ‘zig-zag’ defects, which present serious obstacles for the commercialization of such devices. However, novel de Vries-type materials are believed to overcome this problem.

In this letter we show that the de Vries-type SmA–SmC phase transition can be successfully modeled both phenomenologically and using a mean-field molecular approach. The starting point is the classical Chen-Lubensky phenomenological model for the SmA–SmC transition. The smectic free energy is expressed in terms of the wave vector $k$ of the smectic density wave, $k = 2\pi/d$. We choose the $z$-axis along the director $\mathbf{n}$, while the $x$-axis specifies the direction of possible tilt in the smectic plane, $k_x = 0$ in the SmA phase. Neglecting fluctuations, the free energy density is written as:

$$\Delta F = D_{\parallel}(k_x^2 - k_{\parallel}^2)^2 + C_{\perp} k_x^2 + D_{\perp} k_x^4,$$  \hspace{1cm} (1)

The first term favors condensation of the smectic density wave at $k_z = k_{\parallel}$. The last two terms describe the SmA–SmC transition, i.e., the appearance of the nonzero component $k_x$ when the coefficient $C_{\perp}$ changes sign. In the SmC phase the tilt angle $\Theta$ is given by $\tan \Theta = k_x/k_z = -C_{\perp}/2D_{\perp}k_{\parallel}$. In this theory, $k_z = k_{\parallel} \approx \text{const}$, yielding a SmC layer spacing $d_c = 2\pi/k_x \propto \cos \Theta$. This is the conventional SmC layer contraction, which occurs mathematically because the variables $k_z$ and $k_x$ in Eq. (1) are uncoupled.

This result changes dramatically if one adds a simple coupling term $A k_x^2 k_z^2$ to the model free energy. This term is always allowed by symmetry and is of the same order as the quadratic term $C_{\perp} k_z^2$ because $k_z$ is not small. Now the total wave vector of the smectic C structure is

$$k_c^2 = k_{\parallel}^2 - C_{\perp}(1 - A/2D_{\perp})D_{\text{eff}}^{-1},$$  \hspace{1cm} (2)

where $D_{\text{eff}} = D_{\parallel} + D_{\perp} - (1/2)(1 - A/2D_{\perp})^2$. Moreover,
the SmC layer spacing should be constant for $A = 2D_\perp$; strictly speaking the dependence $k_0(T)$ yields a weakly temperature dependent $k_C$. For intermediate values of $A$ between 0 and $2D_\perp$, Eq. 2 describes a slow contraction of smectic layers in the SmC phase, which is observed for many smectic materials. Thus this generalized Chen-Lubensky model can provide a qualitative description of layer contraction in both conventional and de Vries smectics. But the picture is too general to describe specific details of the SmA-SmC transition.

Further phenomenological progress requires the inclusion of the experimental observation that the nematic order parameter $S$ is abnormally small in de Vries materials. The nematic tensor order parameter $Q_{ij} \approx S(n_i n_j - \delta_{ij}/3)$, neglecting the small smectic biaxiality. The free energy can be expanded in powers of $Q$. Retaining linear and quadratic terms in $Q$, the model free energy is now:

$$F = F_0(S) - b_1 S^2 k^2 - e_1 (k \cdot Q \cdot k)$$

$$+ g_1 (k \cdot Q \cdot k + b_2 S^2 k^4 + e_2 (k \cdot Q \cdot k)^2$$

$$+ g_2 k^2 (k \cdot Q \cdot k) + c k^2 (k \cdot Q \cdot k) \cdot k). \quad (3)$$

Substituting the expression for $Q$, we can rewrite the free energy in terms of $k_z = (k \cdot n)$, $k$ and $S$. For $g_2 = c = 0$ minimizing 3 yields $k^2_0 \equiv const$. In this case, no matter what the values of the other model parameters, there is no layer contraction in the SmC phase.

In the case of nonzero $c$ or $g_2$ there exists a partial layer contraction. In particular, minimizing the free energy 4 yields simple expressions for $k$ when $g_1 = g_2 = 0$:

$$k^2_C = k^2_0 \left( 1 - c' (e'_1 S^{-1} - e' c' (2 e'_2 - (c')^2)^{-1} \right) \quad (4)$$

and

$$\sin^2 \Theta = \frac{2 e'_2 + c' - e'_1 S^{-1}(1 + c')} {2 e'_2 - c' e'_1 S^{-1}}, \quad (5)$$

where $k^2_0 = b'_1/2 b'_2$; $e'_1 = 2 e_1/3 b_1$; $e'_2 = 2 e_2/9 b'_1$; $c' = c/9 b_1$; and $b'_2 = b_2 - 4 c/27$. In the SmA phase the wave vector $k_A$ is expressed as:

$$k^2_A = k^2_0 \left( 1 + e'_1 S^{-1} \right) \left( 1 + 2 e'_2 + 2 c' \right)^{-1}. \quad (6)$$

In the model 3, the SmA-SmC transition is governed by the dependence $S(T)$; of necessity $S$ is here far from saturation. The transition occurs when $S$ reaches the critical value $S_{AC} = e'_1 (1 + c')/(2 e'_2 + c')$. In the SmA phase (see Eq. 5) the layer spacing always increases for decreasing temperature; this is also true experimentally for all de Vries materials 3. In the SmC phase the layer contraction is controlled by the parameter $c'$. The spacing is constant for $c' = 0$, which can be regarded as ideal de Vries behavior. On the other hand, $k_z = const$ when $c = c'_2 - 1$. In this case the SmC layer contraction is determined by the factor of $\cos \Theta$; this is ideal conventional smectic behavior.

**FIG. 1:** Experimental data on variation of layer spacing in de Vries-type 3M8422 (above) and conventional DOBAMBC (below) materials fitted by Eqs.(4-6) with $e_2 = 0.248$, $c = 0.09$, $k_0 = 0.169 \AA^{-1}$ for 3MB8422 and $e_1 = 0.439$, $c = 0.49$, $k_0 = 0.238 \AA^{-1}$ for DOBAMBC.

This simple phenomenological model thus describes both limiting cases, de Vries and conventional behavior. Furthermore, intermediate cases observed in experiment correspond to intermediate values of $c'$ between 0 and $c'_2 - 1$. Our simple model cases observed in experiment correspond to intermediate values of $c'$ between 0 and $c'_2 - 1$. Our simple model uses a free energy expansion in terms of the nematic order parameter and components of the smectic wave vector, which in general are not small. Furthermore, the physical origin of the phenomenon is not clear. To validate the model we develop a corresponding molecular field theory, which does not require these approximations.

Molecular models for the SmC phase have been proposed by a number of authors 3, 16, 17, 18, 19, 20. Most of the theories assume the long molecular axis to be very highly oriented. An exception is the recent paper by Govind and Madhusudana 20, which, however, focuses on a particular intermolecular interaction which does not address de Vries materials. We believe that such approaches cannot be used to describe de Vries-type smectics, where the order parameter $S$ is relatively small. Below we present a brief description of our general mean-field theory for the SmA-SmC transition in the system of uniaxial molecules and apply it to de Vries smectics.

We specify the relative position and orientation of two rigid uniaxial molecules '1' and '2' by the internuclear vector $\mathbf{R} = \hat{\mathbf{R}} \hat{\mathbf{r}}$ and the molecular long axis unit vec-
tors $\mathbf{a}_1$ and $\mathbf{a}_2$. For nonpolar molecules, the pair interaction potential must be even in $\mathbf{a}_1$ and $\mathbf{a}_2$. For nonchiral molecules, the potential is also even in $\mathbf{R}$. The pair potential $U(\mathbf{a}_1, \mathbf{R}, \mathbf{a}_2)$ can now be written as:

$$U(\mathbf{a}_1, \mathbf{R}, \mathbf{a}_2) = u_1(\mathbf{R}) \left[ (\mathbf{a}_1 \cdot \hat{\mathbf{r}})^2 + (\mathbf{a}_2 \cdot \hat{\mathbf{r}})^2 \right] + u_2(\mathbf{R})(\mathbf{a}_1 \cdot \mathbf{a}_2)^2 + u_3(\mathbf{R})(\mathbf{a}_1 \cdot \mathbf{a}_2)(\mathbf{a}_1 \cdot \hat{\mathbf{r}})(\mathbf{a}_2 \cdot \hat{\mathbf{r}}) + u_4(\mathbf{R})(\mathbf{a}_1 \cdot \hat{\mathbf{r}})^2(\mathbf{a}_2 \cdot \hat{\mathbf{r}})^2,$$

where all the possible terms quadratic in $\mathbf{a}_{1,2}$ have been taken into account.

To construct a mean-field smectic free energy functional, we neglect departures from perfect smectic translational order and inter-layer interactions. The free energy functional is now:

$$F = \frac{kT}{2} \int d\mathbf{a}_1 d\mathbf{a}_2 f_1(\mathbf{a}_1) f_1(\mathbf{a}_2) U(\mathbf{a}_1, \mathbf{a}_2) + \rho kT \int d\mathbf{a} f_1(\mathbf{a}) \ln(f_1(\mathbf{a})), \quad (8)$$

where $\rho$ is the molecular number density per unit area of the layer, and $f_1(\mathbf{a})$ is the orientational distribution function. Minimizing the free energy yields:

$$f_1(\mathbf{a}) = Z^{-1} \exp \left\{ -\rho U_{MF}(\mathbf{a})/kT \right\}, \quad (9)$$

where the mean field potential $U_{MF}(\mathbf{a})$ is given by:

$$U_{MF}(\mathbf{a}) = \int d\mathbf{a}_2 f_1(\mathbf{a}_2) \int d\mathbf{R} U(\mathbf{a}, \mathbf{R}, \mathbf{a}_2), \quad (10)$$

and $Z = \int d\mathbf{a} \exp \left\{ -\rho U_{MF}(\mathbf{a})/kT \right\}$ is a normalization factor.

Substituting Eq. (7) into Eq. (10) yields an explicit expression for the mean field potential:

$$U_{MF}(\mathbf{a}) = w_1 P_2(\cos \gamma) + w_2 S_k P_2(\cos \gamma) + w_3 P_k \sin^2 \gamma \cos 2\phi + w_4 C \sin 2\gamma \cos \phi. \quad (11)$$

The angles $\gamma$ and $\phi$ are polar and azimuthal angles specifying the orientation of the unit vector $\mathbf{a}$, i.e., $\mathbf{a} = (\sin \gamma \cos \phi, \sin \gamma \sin \phi, \cos \gamma)$. There are three orientational order parameters: $S_k = \langle P_2(\cos \gamma) \rangle$, $P_k = \langle \sin^2 \gamma \cos 2\phi \rangle$, and $C = \langle \sin 2\gamma \cos \phi \rangle$, which determine completely the nematic tensor $\mathbf{Q}$. The interaction constants are given by linear combinations of integrals over the potential $\mathbf{i}$, $w_1 = -\bar{u}_1/3 - (\bar{u}_3 + \bar{u}_4)/9$, $w_2 = 2\bar{u}_2/3 + (\bar{u}_3 + \bar{u}_4)/4$, $w_3 = -\bar{u}_2/2 + \bar{u}_3/4 + \bar{u}_4/8$, $w_4 = \bar{u}_2/2 + \bar{u}_3/8$, with $\bar{u}_k = \int dR R u_k(R)$.

The conventional order parameters of the SmC phase are the nematic order parameter $S$, the nematic tensor biaxiality $P$ and the tilt angle $\Theta$. These can be expressed in terms of the parameters $S_k, P_k$ and $C$:

$$\tan 2\Theta = C(S_k - 0.5 P_k)^{-1}, \quad (12)$$

$$S = S_k/4 + 3P_k/8 + 3C(4\sin 2\Theta)^{-1}, \quad (13)$$

$$P = S_k/2 + 3P_k/4 - C(2\sin 2\Theta)^{-1}. \quad (14)$$

In this theory the order parameter $C$, which is proportional to the tilt angle $\Theta$, is the primary order parameter at the SmA–SmC transition. The biaxiality $P_k$ is a secondary order parameter induced by the SmC tilt. The transition is thus a true order–disorder phase transition. The low temperature phase is now characterized not only by a tilt but by a non-zero order parameter $C$ explicitly defined as a statistical average.

Relations (9, 10) enable the free energy (8) to be minimized self-consistently, which yields the temperature dependences of parameters $S_k, P_k$, and $C$. The conventional order parameters can then be established using Eqs. (12-14). Remarkably, the resulting phase behavior has much in common with that predicted phenomenologically. In both pictures the SmA–SmC transition is directly driven by the growth of $S$ with decreasing temperature. The onset of the SmC phase occurs at a critical value of the nematic order parameter, $S_{AC} = 3w_1/(4w_4 - 3w_2)$. Beyond this value, the tilt responds directly to increases in orientational order: $\sin^2 \Theta(T) \propto \left(\left(S(T) - S_{AC}\right)/S(T)\right)S_{AC}$.

We have selected the average $<\cos \gamma>$ as a simple surrogate of the layer spacing $d$, i.e., we assume that the spacing can be approximated by the average projection of the molecules onto the layer normal. This assumption is supported by recent experimental data which indicate that for several different compounds there exists a good correlation between the temperature vari-
FIG. 3: (a) Effect of the transition on nematic order parameter calculated for \( w_1 = -0.2 \), \( w_2 = -1 \), \( w_3 = -1.35 \) (solid) or \( w_3 = -1.1 \) (dashed), and \( w_4 = -1.1 \). The thin gray line shows the unperturbed values of \( S \). (b) Smectic layer spacing for the two cases above (black); layer spacing calculated if nematic order unperturbed (gray).

...SmC phase and the tilt angle is relatively small. The two cases shown in Figs. 2a and 2b differ only by changing the parameter \( w_3 \) in the model potential. Thus, although the transition temperatures are the same, the properties of the SmC phase are qualitatively different. More generally, we find that there exists an extended region in parameter space for which the theory predicts smectics C with very weak layer contraction.

The molecular model also predicts feedback effects in which the presence of the tilt further increases the nematic orientation. This can lead to an additional change of the layer spacing. The effect is especially pronounced if the transition occurs at low \( S_{AC} \) and has recently been observed [23]. Typical behavior is shown in Fig.3. Although the changes in the nematic order are relatively weak, they trigger a qualitatively different temperature dependence of layer thickness.

In the de Vries scenario of the SmA-SmC transition, the transition is governed by the temperature variation of \( S \). This is realistic only for relatively low nematic order. In order for the picture to be valid, an additional microscopic mechanism is required to stabilize the smectic phases. In fact most de Vries materials possess bulky siloxane or fluorinated groups. These promote microphase separation which, in turn, favors smectic ordering even in the absence of nematic order. This mechanism dominates in lyotropic lamellar phases where layer formation is primarily determined by water-amphiphiles microphase separation. In de Vries materials it appears that both microscopic mechanisms for smectic ordering occur.

In conclusion, we have developed a generalized Chen-Lubensky phenomenological model as well as a molecular model which describe both conventional (layer-contracting) and de Vries smectics C as two limiting cases. The theory also explains various intermediate cases. These correspond to a crossover between structural and order-disorder SmA-SmC transitions, and reflect the observed properties of various real materials. The authors are grateful to P.Collings, C.C.Huang and Yu.Panarin for valuable discussions, and to EPSRC (UK) for funding.

The dependence $S(T)$ is approximated as $S_A(T) \propto (T_A - T)^{\beta_A}$ in SmA phase and $(S_C(T) - S_{AC}) \propto (T_C - T)^{\beta_C}$ in SmC, which is justified by the observed rapid growth of birefringence in the SmC phase of de Vries materials as well as by the molecular theory (see Fig.4).
