

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

M. V. Gorkunov,<sup>1,2</sup> F. Giesselmann,<sup>3</sup> J. P. F. Lagerwall,<sup>3</sup> T. J. Sluckin,<sup>4</sup> and M. A. Osipov<sup>1</sup>

<sup>1</sup>*Department of Mathematics, University of Strathclyde, Glasgow G1 1XH, United Kingdom*

<sup>2</sup>*Institute of Crystallography, Russian Academy of Sciences, 119333 Moscow, Russia*

<sup>3</sup>*Institute of Physical Chemistry, University of Stuttgart, D-70569 Stuttgart, Germany*

<sup>4</sup>*School of Mathematics, University of Southampton, Southampton SO17 1BJ, United Kingdom*

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We develop both phenomenological and molecular-statistical theory of smectic-A–smectic-C phase transition with anomalously weak smectic layer contraction. Using a general mean-field molecular model, we demonstrate that a relatively simple interaction potential suffices to describe the transition both in conventional and de Vries type smectics. The theoretical results are in excellent agreement with experimental data. The approach can be used to describe tilting transitions in other soft matter systems.

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Various soft matter systems exhibit layered orientationally ordered phases including smectic liquid crystals, lamellar phases, biological membranes, and smectic elastomers. In the simplest smectic-A (SmA) liquid crystal phase, the long molecular axis director  $\mathbf{n}$  is normal to the smectic layers [1], while in the smectic-C (SmC) phase, the director is inclined at an angle  $\Theta$  to the layer normal. The origin of the tilt in the SmC phase has long been the subject of some controversy, and several microscopic mechanisms of the transition have been proposed. Revealing the nature of the SmA-SmC transition is very important for understanding and modeling of the broad class of tilt transitions observed in other soft-matter systems. The symmetries of the SmA and SmC phases are identical to those of some lyotropic lamellar phases, tilted phases of Langmuir-Blodgett films (if a single smectic layer is considered) [3], smectic elastomers [4], and mesogenic polymers. In particular, the SmA-SmC transition corresponds to the  $L_\alpha$ - $L_\beta$  transition in phospholipid cell membranes which play a role in the formation of some biological structures. For example, the molecular tilt below the  $L_\alpha$ - $L_\beta$  transition, together with chirality, is responsible for the formation of self-assembled lipid tubule [5].

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 as the nature of the ordering in the two phases is essentially the same [6]. In this case the layer spacing  $d$  decreases with tilt as  $\cos \Theta$ . Recently, however, materials have been discovered with diverse molecular structures [7–10], 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 [11], 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 requires an abnormally low orientational order which is indeed confirmed by the experiment [2,12–14].

However, different materials exhibit various degrees of layer contraction in the SmC phase, and this observation should also be explained theoretically. The underlying physi-

cal mechanism is both of fundamental physical interest and of key practical importance. Chiral tilted smectic ferro- and antiferroelectric materials are extremely promising for the new generation of fast electro-optic displays as well as various nondisplay applications. Layer contraction causes the emergence of chevron structures and “zigzag” defects, which present serious obstacles for the commercialization of such devices. However, novel de Vries type materials are believed to overcome this problem [2].

In this Rapid Communication we show that the de Vries type SmA-SmC phase transition can be successfully modeled both phenomenologically and by using a mean-field molecular approach. The starting point is the classical Chen-Lubensky phenomenological model [15] for the SmA-SmC transition. The smectic free energy is expressed in terms of the wave vector  $\mathbf{k}$  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

$$\Delta F = D_{\parallel}(k_z^2 - k_{\parallel}^2)^2 + C_{\perp}k_x^2 + D_{\perp}k_x^4. \quad (1)$$

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  $\tan \Theta = k_x/k_z = \sqrt{-C_{\perp}/2D_{\perp}k_{\parallel}^{-1}}$ . In this theory,  $k_z = k_{\parallel} \approx \text{const}$ , yielding a SmC layer spacing  $d_C = 2\pi/k_C \propto \cos \Theta$ . 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  $Ak_x^2k_z^2$  to the model free energy (1). This term is always allowed by symmetry and is of the same order as the quadratic term  $C_{\perp}k_x^2$  because  $k_z$  is not small. Now the total wave vector of the smectic-C structure is  $k_C^2 = k_{\parallel}^2 - C_{\perp}(1 - A/2D_{\perp})D_{\text{eff}}^{-1}$ , 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  $k_{\parallel}(T)$  yields a weakly temperature dependent  $k_C$ . For intermediate values of  $A$  between 0 and  $2D_{\perp}$ , the model describes a slow contraction of smectic layers in the SmC phase. 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 mechanisms 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 equals  $Q_{ij} \approx S(n_i n_j - \delta_{ij}/3)$ , neglecting the small smectic biaxiality. The free energy can be expanded in powers of  $\mathbf{Q}$ . Retaining linear and quadratic terms in  $\mathbf{Q}$ , the model free energy is now

$$F = F_0(S) - b_1 S^2 k^2 - e_1 (\mathbf{k} \cdot \mathbf{Q} \cdot \mathbf{k}) + g_1 (\mathbf{k} \cdot \mathbf{Q} \cdot \mathbf{Q} \cdot \mathbf{k}) + b_2 S^2 k^4 + e_2 (\mathbf{k} \cdot \mathbf{Q} \cdot \mathbf{k})^2 + g_2 k^2 (\mathbf{k} \cdot \mathbf{Q} \cdot \mathbf{k}) + c k^2 (\mathbf{k} \cdot \mathbf{Q} \cdot \mathbf{Q} \cdot \mathbf{k}). \quad (2)$$

Substituting the expression for  $\mathbf{Q}$ , we can rewrite the free energy in terms of  $k_z = (\mathbf{k} \cdot \mathbf{n})$ ,  $k$ , and  $S$ . For  $g_2 = c = 0$  minimizing Eq. (2) yields the constant wave vector in the SmC phase,  $k_C^2 \equiv \text{const}$ . In this case, no matter what the values of the other model parameters are, no layer contraction accompanies the tilting.

In the case of nonzero  $c$  or  $g_2$  there exists a partial layer contraction. In particular, minimizing the free energy (2) yields simple expressions for  $k$  and  $\Theta$  when  $g_1 = g_2 = 0$ :

$$k_C^2 = k_0^2 \{1 - c' (e_1' S^{-1} - c') [2e_2' - (c')^2]^{-1}\}, \quad (3)$$

$$\sin^2 \Theta = \frac{2}{3} \frac{2e_2' + c' - e_1' S^{-1} (1 + c')}{2e_2' - c' e_1' S^{-1}}, \quad (4)$$

where  $k_0^2 = b_1'/2b_2'$ ;  $e_1' = 2e_1/3b_1$ ;  $e_2' = 2e_2/9b_2'$ ;  $c' = c/9b_1$ ; and  $b_2' = b_2 - 4c/27$ . In the SmA phase the wave vector  $k_A$  is expressed as

$$k_A^2 = k_0^2 (1 + e_1' S^{-1}) (1 + 2e_2' + 2c')^{-1}. \quad (5)$$

In the model (2) 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  $S_{AC} = e_1' (1 + c') / (2e_2' + c')$ . 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 [2]. 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,  $k_z = \text{const}$  when  $c = e_2' - 1$ . In this case the SmC layer contraction is determined by the factor of  $\cos \Theta$ ; this is ideal conventional smectic behavior.

This 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  $e_2' - 1$ . Our simple model expressions allow excellent fitting of experimental data for different materials of both de Vries and conventional type as illustrated by Fig. 1 [16].

The phenomenological model (2) uses a free energy expansion in terms of the order parameter and components of the smectic wave vector, which in general are not small. Furthermore, the microscopic origin of the phenomenon is

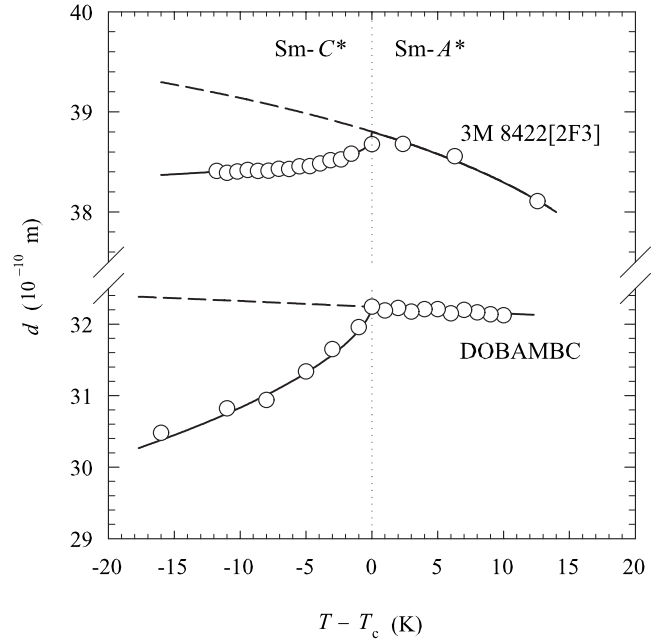


FIG. 1. Experimental data on variation of layer spacing in de Vries type 3M8422 (above) and conventional DOBAMBC (below) materials fitted by Eqs. (4)–(6) with  $e_2 = 0.18$  and  $e_1 = 0.248$ ,  $c = 0.09$ ,  $k_0 = 0.169 \text{ \AA}^{-1}$  for 3M8422, and  $e_1 = 0.439$ ,  $c = 0.49$ ,  $k_0 = 0.238 \text{ \AA}^{-1}$  for DOBAMBC.

not clear. To overcome these limitations we develop a general molecular field theory which is free of these approximations.

Molecular models for the SmC phase have been proposed by a number of authors [6,17–21]. Most of the theories assume the long molecular axis to be very highly oriented. An exception is the recent paper by Govind and Madhusudana [21], 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 approach to the theory for the SmA-SmC transition and apply it to de Vries smectics.

We specify the relative position and orientation of two rigid uniaxial molecules “1” and “2” by the intermolecular vector  $\mathbf{R} = R\hat{\mathbf{r}}$  and the molecular long axis unit vectors  $\mathbf{a}_1$  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

$$U(\mathbf{a}_1, \mathbf{R}, \mathbf{a}_2) = u_1(R) [(\mathbf{a}_1 \cdot \hat{\mathbf{r}})^2 + (\mathbf{a}_2 \cdot \hat{\mathbf{r}})^2] + u_2(R) (\mathbf{a}_1 \cdot \mathbf{a}_2)^2 + u_3(R) (\mathbf{a}_1 \cdot \mathbf{a}_2) (\mathbf{a}_1 \cdot \hat{\mathbf{r}}) (\mathbf{a}_2 \cdot \hat{\mathbf{r}}) + u_4(R) (\mathbf{a}_1 \cdot \hat{\mathbf{r}})^2 (\mathbf{a}_2 \cdot \hat{\mathbf{r}})^2, \quad (6)$$

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 or-

der and interlayer interactions. The free energy functional is now

$$F = \frac{\rho^2}{2} \int d\mathbf{a}_1 d\mathbf{a}_2 f_1(\mathbf{a}) f_1(\mathbf{a}_2) U(\mathbf{a}_1, \mathbf{r}, \mathbf{a}_2) + \rho kT \int d\mathbf{a} f_1(\mathbf{a}) \ln[f_1(\mathbf{a})], \quad (7)$$

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 (7) yields

$$f_1(\mathbf{a}) = Z^{-1} \exp[-\rho U_{MF}(\mathbf{a})/kT], \quad (8)$$

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

$$U_{MF}(\mathbf{a}) = \int d\mathbf{a}_2 f_1(\mathbf{a}_2) \int d\mathbf{R} U(\mathbf{a}, \mathbf{R}, \mathbf{a}_2). \quad (9)$$

Substituting Eq. (6) into Eq. (9) yields an explicit expression for the mean-field potential:

$$U_{MF}(\mathbf{a}) = w_1 P_2(\cos \gamma) + w_2 S_k P_2(\cos \gamma) + w_3 P_k \sin^2 \gamma \cos 2\phi + w_4 C \sin 2\gamma \cos \phi. \quad (10)$$

The angles  $\gamma$  and  $\phi$  specify the orientation of the unit vector  $\mathbf{a}$  in the  $\mathbf{k}$  frame, i.e.,  $\mathbf{a} = (\sin \gamma \cos \phi, \sin \gamma \sin \phi, \cos \gamma)$ . The theory employs a complete set of three orientational order parameters which are explicitly expressed as averages of the corresponding microscopic quantities:  $S_k = \langle P_2(\cos \gamma) \rangle$ ,  $P_k = \langle \sin^2 \gamma \cos 2\phi \rangle$ , and  $C = \langle \sin 2\gamma \cos \phi \rangle$ . The interaction constants are given by linear combinations of integrals over the potential (6):  $w_1 = -\bar{u}_1/3 - (\bar{u}_3 + \bar{u}_4)/9$ ,  $w_2 = 2\bar{u}_2/3 + (\bar{u}_3 + \bar{u}_4)/9$ ,  $w_3 = \bar{u}_2/2 + \bar{u}_3/4 + \bar{u}_4/8$ ,  $w_4 = \bar{u}_2/2 + \bar{u}_3/8$ , with  $\bar{u}_\alpha = \int d\mathbf{R} R R u_\alpha(R)$ .

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  $C$ :

$$\tan 2\Theta = C(S_k - 0.5P_k)^{-1}, \quad (11)$$

$$S = S_k/4 + 3P_k/8 + 3C(4 \sin 2\Theta)^{-1}, \quad (12)$$

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

In this theory the tilt angle  $\Theta$  is proportional to the tilt order parameter  $C$ , which is the primary order parameter at the SmA-SmC transition, and which is explicitly expressed as a statistical average. The biaxiality  $P_k$  is a secondary order parameter induced by the SmC tilt. The transition is thus a true order-disorder phase transition.

Relations (8) and (10) enable the free energy (7) 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. (11)–(13). 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

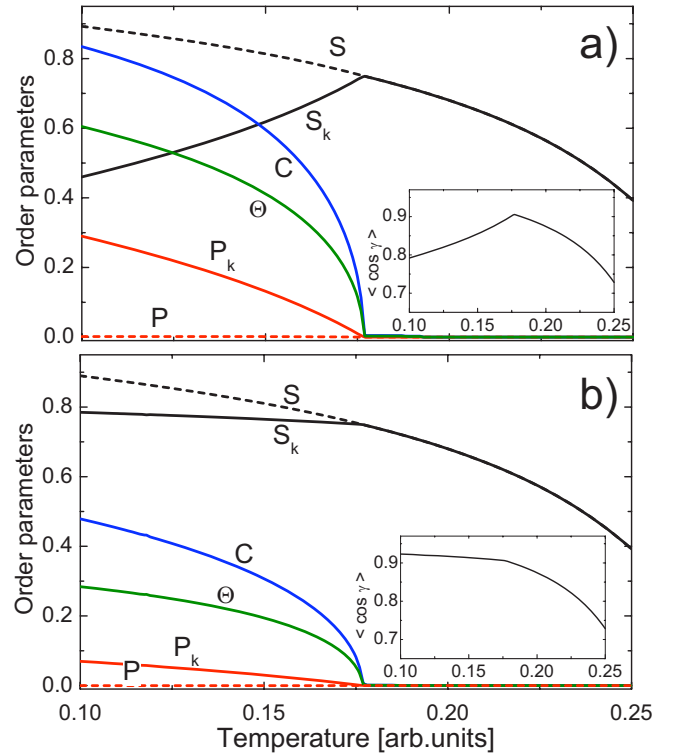


FIG. 2. (Color online) Temperature dependence of order parameters for “conventional” (a) and de Vries type (b) transitions. Insets show layer thickness changes. The model parameters are  $w_1 = -0.05$ ,  $w_2 = -1$ ,  $w_3 = -0.9$  (a) or  $w_3 = -0.75$  (b),  $w_4 = -0.8$ .

parameter,  $S_{AC} = 3w_1/(4w_4 - 3w_2)$ . Beyond this value, the tilt responds directly to increases in orientational order:  $\sin^2 \Theta(T) \propto \{[S(T) - S_{AC}]/S(T)\}$ .

We have selected the average  $\langle \cos \gamma \rangle$  as a simple surrogate of the layer spacing [22], 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 [23] which indicate that for several different compounds there exists a good correlation between the temperature variation of the smectic period  $d$  and the order parameter  $S_k$ . At the same time,  $\langle \cos \gamma \rangle \approx 1 - 0.5 \langle \sin^2 \gamma \rangle$  and  $S_k = 1 - 1.5 \langle \sin^2 \gamma \rangle$ , which yields  $\langle \cos \gamma \rangle \approx (2 + S_k)/3$ .

Numerical minimization of the free energy indicates that the range of possible behaviors appears to be surprisingly broad. A typical conventional SmC case is shown in Fig. 2(a). The tilt angle is relatively large while the biaxiality is small. In the SmC phase itself the layer spacing decreases approximately proportionally to  $\cos \Theta$ .

An example of a de Vries type behavior is shown in Fig. 2(b). Here the layer spacing is nearly constant in the SmC phase and the tilt angle is relatively small. The two cases shown in Figs. 2(a) and 2(b) 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

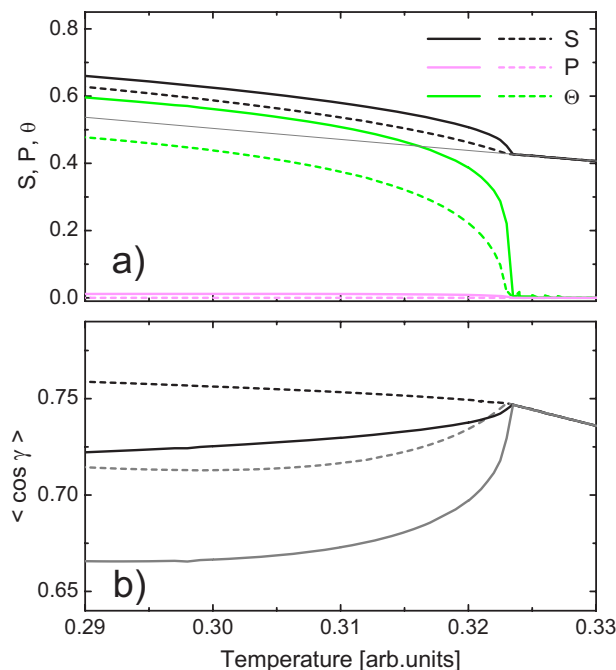


FIG. 3. (Color online) (a) Effect of the transition on nematic order parameter calculated for  $w_1 = -0.2$ ,  $w_2 = -1$ ,  $w_3 = -1.35$  (solid) or  $w_3 = -1.1$  (dashed), and  $w_4 = -1.1$ . The thin gray line shows the unperturbed values of  $S$ . (b) Smectic layer spacing for the two cases above (black); layer spacing calculated if nematic order unperturbed (gray).

for which the theory predicts smectics  $C$  with very weak layer contraction.

The molecular model also predicts that the presence of the tilt further increases the nematic ordering. 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 [24]. 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. The abnormally low layer contraction in the tilted phase is related to a compensation of the contraction due to the factor of  $\cos \Theta$  by the layer expansion due to the growth of  $S(T)$  which is rather strong in de Vries materials.

In the present model the transition is governed by the temperature variation of  $S$ . This is realistic only for relatively low nematic order, and requires an additional microscopic mechanism to stabilize the smectic phases. In fact most de Vries materials possess bulky siloxane or fluorinated groups. These promote microphase separation [2,25] which, in turn, favors smectic ordering even in the absence of nematic order. This mechanism dominates in lyotropic lamellar phases. In de Vries materials both mechanisms for smectic ordering occur.

In conclusion, we have developed phenomenological and molecular models, which describe both conventional (layer-contracting) and de Vries smectics  $C$  as well as various intermediate cases, and reflect the observed properties of real materials. In contrast to the previous models of the SmA-SmC transition, we use a complete set of order parameters which are expressed as statistical averages of microscopic quantities. The tilt angle is proportional to the corresponding tilt order parameter. In this general form the model can be applied to various tilt transitions observed in other soft matter systems.

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