

## Mean-field study of uniaxial smectic liquid crystals with polarized layers

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A mean-field calculation based on a simple model is reported. The numerical results indicate that only a relatively small polar interaction is required to induce a transformation from a nonpolar uniaxial smectic phase (smectic A) to a uniaxial smectic phase with polar layers within a reasonable temperature range. The polar order may accompany the smectic phase in all or in part of its range of existence. Arora, Taylor, and Ferguson (ATF) observed that some compounds show two phases with the smectic-A morphology and suggested that the lower-temperature phase has polar order. Our results can reproduce the main features as far as the transition temperatures are concerned. The small transition entropies reported by ATF are in agreement with our results; however, there are not enough data to permit any correlation with the model parameters.

### INTRODUCTION

In the molecular theories of the smectic A phase that have appeared so far,<sup>1,2</sup> the role of the polarity of the molecules is not taken into account. This is reflected by the use of the second-order Legendre polynomial in the angular part of the intermolecular interaction potential. As a consequence, the mean potential energy for a given molecule that results from the interaction with the rest of the molecules in the sample is even under the transformation  $\theta \rightarrow \pi - \theta$ , where  $\theta$  is the angle between the preferred direction and the long axis of the molecule. If, however, the molecules are anisometric, this transformation may lead to a different energy and under certain conditions a smectic phase with polar order may become the most stable. There is, in fact, some experimental evidence that a transition to polar order occurs. Arora *et al.*<sup>3</sup> observed that some members of the homologous series of 4-*n*-alkoxybenzylidene-4'-aminopropiophenones show two phases with the morphology of the smectic A phase, and suggested that the lower-temperature phase has polar order within the layers.

In the present paper, using the mean-field approximation, we will investigate the conditions under which the polar order may establish itself. In particular, using a simple model potential, we will estimate the relative strength of the polar part of the interaction, as compared to the nonpolar part, that is required for the polar order to appear within a reasonable mesomorphic range. The model to be used here is an extension of the one used by Krieger and James<sup>4</sup> in connection with the crystalline phase.

### FORMULATION OF THE PROBLEM

In the mean-field approximation one assumes that each molecule moves in the average potential field produced by the other molecules in the sample and is otherwise independent. This potential is the same for all the molecules and the boundary effects are thus neglected. In what follows we will assume that the smectic layers are planes and that the preferred direction is normal to the layers. We will also assume, for simplicity, that the layers are unstructured and that the molecules are, in effect, cylindrically symmetric about their long axes. We choose a Cartesian coordinate system with the  $z$  axis parallel to the preferred direction and denote by  $\theta_i$  and  $\phi_i$  the polar and azimuthal angles of the long axis of the  $i$ th molecule. Under these assumptions, and neglecting the excluded volume effects, one can show<sup>5</sup> that for a general additive intermolecular interaction the mean field is given by

$$V_1(z_1, \theta_1) = \frac{1}{2d} \int d(\cos\theta_2) dz_2 f(z_2, \theta_2) \langle V_{12} \rangle_p, \quad (1)$$

where  $d$  is the spacing of the smectic layers,  $f$  is the one-particle distribution function, and  $\langle V_{12}(z_{12}) \rangle_p$  is the intermolecular potential averaged (with equal weights) over  $\phi_1$  and  $\phi_2$  and over the plane  $z_{12} = \text{const}$  ( $z_{12} = z_1 - z_2$ ).

This average has the form<sup>5</sup>

$$\langle V_{12} \rangle_p = \sum_{i_1 i_2} v_{i_1 i_2}(z_{12}) P_{i_1}(\cos\theta_1) P_{i_2}(\cos\theta_2). \quad (2)$$

Given the mean field one can calculate the one-particle distribution function

$$f(z, \theta) = (1/Q') \exp[-(1/kT)V_1(z, \theta)],$$

where  $1/Q'$  is the normalization factor,

$$Q' = \frac{1}{2V} \int_{-1}^1 d \cos \theta \int_V dV \exp[-(1/kT)V_1(z, \theta)].$$

$V$  is the volume of the sample. In other words, Eq. (1) implicitly determines  $V_1$ . The free energy per molecule is given by

$$F/kT = -(1/2kT)\langle V_1(z, \theta) \rangle - \ln Q'. \quad (3)$$

Here we will assume that the one-particle potential is an even and periodic function of  $z$ , with period equal to the spacing of the smectic layers,  $d$ , and propose a very simple form for the average  $\langle V_{12} \rangle_p$ , namely,

$$V_{12} = \begin{cases} -A[\gamma + \beta P_1(\cos \theta_1)P_1(\cos \theta_2) + P_2(\cos \theta_1) \\ \quad \times P_2(\cos \theta_2)] \cos^2(\pi z_{12}/d), & |z_{12}| \leq \frac{1}{2}d \\ 0, & |z_{12}| > \frac{1}{2}d. \end{cases}$$

Equation (1) yields

$$V(z_1, \theta_1) = -\frac{1}{2}A(g(\theta_1) + f(\theta_1) \cos 2\pi z_1/d). \quad (4)$$

Here we use the definitions

$$\begin{aligned} g(\theta) &= \gamma + \beta \eta_1 P_1(\cos \theta) + \eta_2 P_2(\cos \theta), \\ f(\theta) &= \gamma \tau + \beta \sigma_1 P_1(\cos \theta) + \sigma_2 P_2(\cos \theta), \\ \tau &= \langle \cos(2\pi z_2/d) \rangle, \end{aligned}$$

and

$$\eta_i = \langle P_i(\cos \theta_2) \rangle, \quad \sigma_i = \langle P_i(\cos \theta_2) \cos(2\pi z_2/d) \rangle,$$

Self-consistency requires

$$i = 1, 2.$$

$$\begin{aligned} \tau &= Q^{-1} \int_{-1}^1 I_1(Jf) e^{Jg} d(\cos \theta), \\ \eta_i &= Q^{-1} \int_{-1}^1 P_i(\cos \theta) I_0(Jf) e^{Jg} d(\cos \theta), \\ \sigma_i &= Q^{-1} \int_{-1}^1 P_i(\cos \theta) I_1(Jf) e^{Jg} d(\cos \theta), \end{aligned} \quad (5)$$

where  $Q = \int I_0(Jf) e^{Jg} d \cos \theta$  and  $I_m(x) = (1/\pi) \times \int_0^\pi e^{x \cos u} \cos mu du$  are the modified Bessel functions, and

$$J = A/2kT.$$

The quantities  $\eta_1$ ,  $\eta_2$ ,  $\sigma_1$ ,  $\sigma_2$ , and  $\tau$  are the order parameters.  $\eta_2$ ,  $\sigma_2$ , and  $\tau$  are familiar from the existing molecular theories of the nematic<sup>6</sup> and the smectic  $A$  phases.<sup>1,2</sup> The other two refer to the polar order. In particular,  $\eta_1$  is a measure of the long-range polar order, while  $\sigma_1$  is a measure of the coupling between polar and translational order. The relative strength of the polar and nonpolar contributions is measured by  $\beta$ .

The self-consistency equations, Eq. (5), may admit more than one solution for a given temperature, each solution corresponding to a different phase. One then has to evaluate the free energy corresponding to each solution. The most stable phase is the one with the minimum free energy.

The details on the numerical methods used for the solution of the self-consistency equations are given in the Appendix.

## NUMERICAL RESULTS

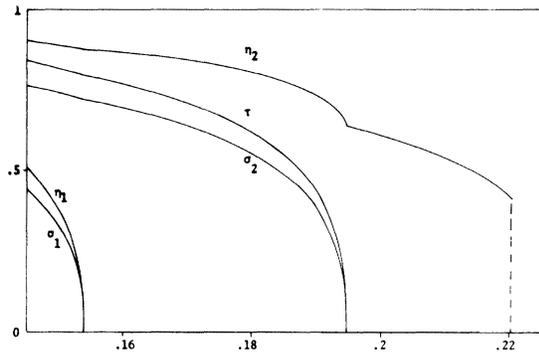
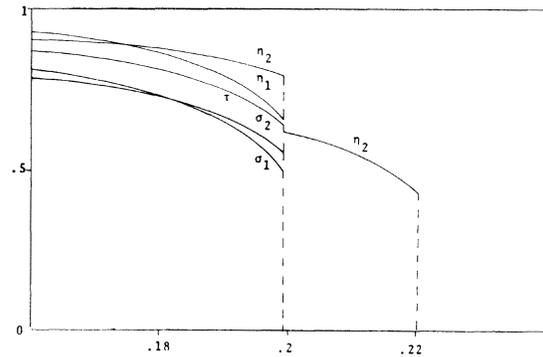
We start by considering the case  $\beta=0$  first. Following the procedure prescribed in the Appendix, we solve the self-consistency equations numerically; then using Eq. (3) we determine the most stable state. The results can be summarized as follows:

(i) For  $0.75 > \gamma \geq -0.01$  we have two phases, the smectic and the isotropic, that transform to each other via a first-order transition. For  $\gamma > 0.75$ , the model predicts a stable phase with translational order in one direction (i.e., above a certain temperature one has  $\sigma_2 = \eta_2 = 0$ ,  $\tau \neq 0$ ). This unphysical result means that the model is not valid for large values of  $\gamma$ .

(ii) For  $\gamma < -0.01$  we have three phases, smectic, nematic, and isotropic. The smectic-nematic transition is first order if  $\gamma > -0.2$  and second order if  $\gamma < -0.2$ . The nematic-isotropic transition is first order. The nematic range increases with decreasing  $\gamma$ .

In other words, the model potential for  $\beta=0$  gives a broad description of the system, smectic nematic isotropic.<sup>2</sup>

We next consider the case  $\beta \neq 0$ . We assume that the interaction is dominated by the nonpolar contribution and thus we limit our analysis to small values of  $\beta$  (the maximum value of  $\beta$  considered here is 0.2). Again, following the procedure prescribed in the Appendix, we solve the self-consistency equations, evaluate the free energy corresponding to each solution, and establish the most stable phase. The results are illustrated in Figs. 1–5. The fact that there exists a range where the most stable phase corresponds to  $\eta_1 \neq 0$  means that stable arrangements with polarized layers can exist, according to our model. The polar-order parameters may vanish together with the smectic order parameter (Figs. 3 and 5) or separately (Figs. 1, 2, and 4). In the first case we have a transition from the “polar” smectic phase to the nematic phase (Fig. 3) or to the isotropic phase (Fig. 5). This transition is of first order for the cases investigated here. In the second case we have a transition from the polar to the nonpolar smectic phase. This transition can be of either first (Fig.

FIG. 1. Order parameters vs  $1/J$  for  $\beta = 0.1$ ,  $\gamma = -0.2$ .FIG. 3. Order parameters vs  $1/J$  for  $\beta = 0.2$ ,  $\gamma = -0.2$ .

2) or second order (Figs. 1 and 4).

Figure 6 is a plot of the transition entropy of the polar to nonpolar transformation versus  $\gamma$  for different values of  $\beta$ . We note that the transition entropies are small and they show the tendency to decrease with increasing  $\gamma$  (i.e., with decreasing nematic range).

#### DISCUSSION

We have presented a simple molecular theory to study the polar order in connection with the unstructured uniaxial smectic phase. We have studied the ferromagnetic analog only, i.e., we have limited our analysis to positive values of  $\beta$ . The antiferromagnetic analog was not considered here, since at least within the same layer it is not possible to distinguish between the antiferromagnetic order and the disordered state in the absence of a lattice.

In the proposed model potential, Eq. (4), the polar and nonpolar contributions have the same spatial dependence. This assumption might not be justified, but it simplifies the situation consider-

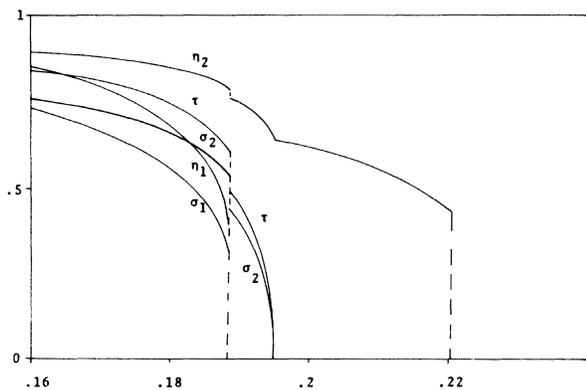
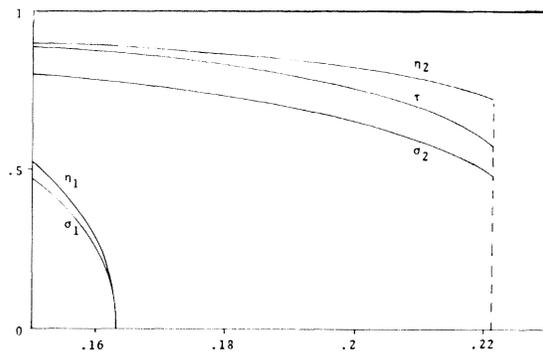
ably. We have also assumed that the nonpolar contribution is dominant and have limited our study to values of  $\beta \leq 0.2$ .

Our results indicate that a relatively small polar contribution is required for a smectic phase with polarized layers to become stable within a reasonable mesomorphic range.

The polar order may accompany the smectic arrangement in all or in part of its range of existence. In both cases it enhances orientational and translational order.

(i) In the first case the thermal stability of the smectic phase is increased. For example, for  $\beta = 0$  the melting of the smectic phase occurs at  $J^{-1} = 0.2212$  for  $\gamma = 0$  and at  $J^{-1} = 0.1945$  for  $\gamma = -0.2$ , while the corresponding values for  $\beta = 0.2$  are  $J^{-1} = 0.2232$  (for  $\gamma = 0$ ) and  $J^{-1} = 0.1993$  (for  $\gamma = -0.2$ ). In particular, for  $\gamma = -0.2$  and  $\beta = 0$ , the smectic phase disappears via a second-order transition, while for  $\gamma = -0.2$  and  $\beta = 0.2$  this transition becomes first order (Fig. 3).

(ii) In the second case, the enhancement of the orientational and translational order by the polar

FIG. 2. Order parameters vs  $1/J$  for  $\beta = 0.16$ ,  $\gamma = -0.2$ .FIG. 4. Order parameters vs  $1/J$  for  $\beta = 0.1$ ,  $\gamma = 0$ .

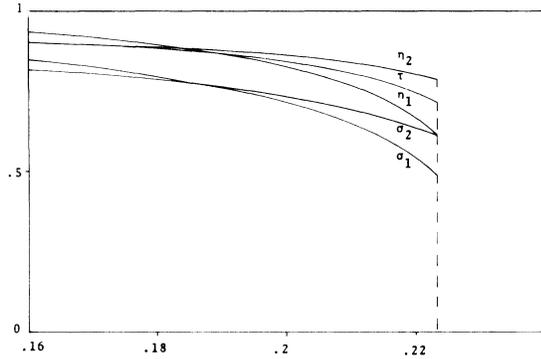


FIG. 5. Order parameters vs  $1/J$  for  $\beta = 0.2$ ,  $\gamma = 0$ .

contribution is reflected by the discontinuities in the corresponding order parameters ( $\tau$ ,  $\eta_2$ ,  $\sigma_2$ ) (Fig. 2) or by the discontinuous change in their slope (Figs. 1 and 4, though hardly perceptible in Fig. 4) that accompany the appearance of the polar order.

As mentioned earlier, Arora *et al.*<sup>3</sup> have observed that some members of the homologous series of 4-*n*-alkoxybenzylidene-4-aminopropiophenones show two phases with the morphology of the smectic A phase, in that they are uniaxial, show the stepped drops and the focal conic texture. Arora *et al.* did not report any apparent change in the mechanical or optical properties across the transition, and they suggested that the lower-temperature phase has polar order within the layers. The transition occurs approximately 65 °C below the clearing point. According to our model this requires a small polar contribution. It may correspond, for example, to  $\gamma = 0$  and  $\beta = 0.12$ . The theory then gives a second-order transition. Arora *et al.* measured the transition entropies for two

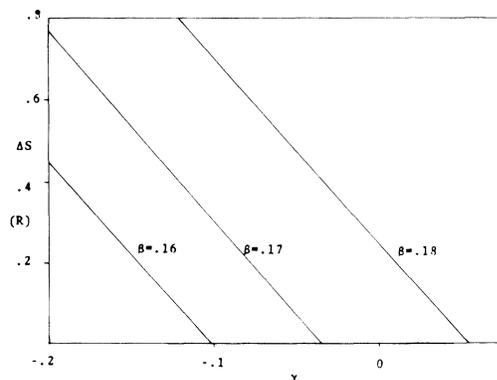


FIG. 6. Transition entropy vs  $\gamma$  for the polar to non-polar transition.

members, namely, the butoxy ( $\Delta S = 0.198R$ ) and the octyloxy ( $\Delta S = 0.056R$ ). The values are in fact small and therefore compatible with the theoretical expectation. However, the data are insufficient to establish a correlation with the model parameters  $\beta$  and  $\gamma$ .

Finally, we note that in the present work, for simplicity, we have assumed that the direction of polarity is the same throughout the sample (since we have assumed that the one-particle potential has a period equal to the smectic layers). However, other arrangements might be possible. Most likely is a double-layer formation so that the direction of polarity alternates from one layer to the next. The period of this arrangement is twice the layer thickness and this arrangement might be easier to investigate experimentally.

#### APPENDIX

The modified Bessel functions  $I_0(x)$  and  $I_1(x)$  can be approximated by the following expressions<sup>7</sup>:

$$I_n(x) = x^n \sum_{k=0}^6 e_{kn} \left( \frac{x}{3.75} \right)^{2k} + \epsilon_n(x),$$

where

$$n = 0, 1, \quad -3.75 \leq x \leq 3.75,$$

$$\max |\epsilon_0(x)| \leq 10^{-7}, \quad \max |\epsilon_1(x)| \leq 10^{-8},$$

and

$$I_n(x) = e^{x^2} x^{-1/2} \sum_{k=0}^8 g_{kn} \left( \frac{x}{3.75} \right)^{-k} + \epsilon_n(x),$$

where

$$n = 0, 1, \quad 3.75 \leq x < \infty,$$

$$\max |\epsilon_0(x)| \leq 11 \times 10^{-9}, \quad \max |\epsilon_1(x)| \leq 11 \times 10^{-9}.$$

The coefficients  $e_{kn}$  and  $g_{kn}$  are given in Ref. 7.

The integrations over  $\cos\theta$  are then performed numerically in steps of 0.01, using the parabolic approximation. To solve the self-consistency equations we use the following iteration process: For a given value of  $J$  we choose a set of initial values for the order parameters ( $\tau^0$ ,  $\eta_1^0$ ,  $\sigma_1^0$ ,  $\eta_2^0$ ,  $\sigma_2^0$ ) and calculate  $\tau$ . Call this value  $\tau^1$ . Using the set ( $\tau^1$ ,  $\eta_1^0$ ,  $\sigma_1^0$ ,  $\eta_2^0$ ,  $\sigma_2^0$ ) we calculate  $\eta_1$ . We call this value  $\eta_1^1$ . The using the set ( $\tau^1$ ,  $\eta_1^1$ ,  $\sigma_1^0$ ,  $\eta_2^0$ ,  $\sigma_2^0$ ) we calculate  $\sigma_1$  and so forth, until the values obtained are stable to the desired decimal place. In view of the error introduced by the approximations used for  $I_0$  and  $I_1$ , as well as the integration, it seemed reasonable not to proceed beyond the sixth decimal place. The calculations were done using a Burroughs B5700 computer.

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- <sup>7</sup>See, for example, Y. L. Luke, *Integrals of Bessel Functions* (McGraw-Hill, New York, 1962), p. 38.