

## Surface Interactions and Applied-Field Effects in Cholesteric Helicoidal and Blue Phases

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The electric-field dependence of the correlation region induced by a surface potential in cholesteric liquid-crystal phases is considered theoretically. Based upon arguments given for the helicoidal and cubic blue phases I and II, it is argued that recent experimental results on blue phase III rule out a cubic or icosahedral structure for this state but are consistent with one composed of cylindrical elements, in each of which the order is characterized by a curling or double-twist configuration. In the bulk, these flexible cylinders interlace and form a three-dimensional mesh. Near a boundary, however, they lie preferentially in the bounding plane as a consequence of the surface potential.

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The effect of surface interactions on bulk liquid-crystalline ordering has been of interest for many years. Even in the simplest disordered nematic systems, a surface potential induces local ordering and can even lead to strong orientational ordering over distances substantially greater than the coherence length [1,2]. Here we consider the combined effect of a surface interaction and an applied electric field on the ordering of *cholesteric* liquid-crystal phases. The implications of these results, particularly for blue phase III (BP III, also known as the cholesteric fog phase [3]), are also discussed.

We begin with a system characterized by a pitch sufficiently long that there exists *no* intermediate BP between the disordered and cholesteric helicoidal phases [4]. In the absence of an external field, the latter is described *exactly* by the tensor order parameter [4,5]

$$\mu_{ij} = -\frac{1}{\sqrt{6}}\mu_0(\zeta) \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix} + \frac{1}{2\sqrt{2}}\mu_2(\zeta) \left\{ \begin{bmatrix} 1 & i & 0 \\ i & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix} e^{i\kappa\zeta} + \text{c.c.} \right\}. \quad (1)$$

Here  $\zeta$  is a normalized [4,5] coordinate in the direction of the wave vector of (reduced) magnitude  $\kappa$ ,  $\mu_0$  and  $\mu_2$  are amplitudes to be determined by free-energy minimization, and c.c. denotes complex conjugate. For the usual bulk helicoidal phase,  $\mu_0$  and  $\mu_2$  are constants; here we introduce a coordinate dependence as we shall consider ordering in the presence of a bounding plane,  $\zeta=0$ .

In an external field, Eq. (1) is no longer exact; however, for a "weak field" [which, as we shall discuss later, can in fact be as much as (50–60)% of the threshold field required [6] for a cholesteric-nematic field-induced phase transition], it is an excellent approximation [7]. Of course,  $\mu_0$  and  $\mu_2$  are now functions of the applied field amplitude as well as  $\zeta$ .

We consider a system wherein (a) the liquid crystal is confined to the half-space  $\zeta > 0$ , (b) the dielectric anisotropy is *positive*, and (c) a weak electric field  $\mathbf{E}$  is applied normal to  $\hat{\zeta}$ .

In this case, the bulk free energy per unit area of the helicoidal cholesteric phase described by Eq. (1), in suitably normalized units [4,5], becomes

$$f_b = \int d\zeta \left\{ \frac{1}{4} [(t - \kappa^2)\mu_2^2 + t\mu_0^2 + (\mu_2')^2 + (1 + \frac{2}{3}\rho)(\mu_0')^2] - \mu_0 e^2 - \sqrt{3}\mu_2 e^2 \cos\kappa\zeta + (\mu_0^3 - 3\mu_0\mu_2^2) + (\mu_0^2 + \mu_2^2)^2 \right\}. \quad (2)$$

Here  $t$  is a reduced temperature parameter,  $e$  is proportional to  $E$ ,  $\rho$  is a ratio of elastic constants, and a prime denotes differentiation with respect to  $\zeta$ .

For  $e=0$ , the system described by Eq. (2) exhibits a bulk ordered helicoidal phase (i.e., one in which  $\mu_0$  and  $\mu_2$  are  $\zeta$  independent) for [5]  $t \leq t_c(\kappa)$ . As we are interested in surface-induced ordering, we assume  $t > t_c$ . Then  $\mu_0, \mu_2 \rightarrow 0$  as  $\zeta \rightarrow \infty$ .

We now supplement  $f_b$  with a surface term which models the torques pinning the cholesteric order parameter in a given direction at the surface. Specifically [2,8],

$$f_s = -(\mu_0 + \sqrt{3}\mu_2)v\delta(\zeta), \quad (3)$$

where  $v$  is the magnitude of the surface pinning torque in our reduced units.

Minimizing  $f = f_b + f_s$  with respect to  $\mu_0$  and  $\mu_2$  gives

$$\begin{aligned} -(1 + \frac{2}{3}\rho)\mu_0'' + t\mu_0 - 2e^2 + 6\mu_0^2 - 6\mu_2^2 + 8(\mu_0^2 + \mu_2^2)\mu_0 &= 4v\delta(\zeta), \\ -\mu_2'' + (t - \kappa^2)\mu_2 - 2\sqrt{3}e^2 \cos\kappa\zeta - 12\mu_0\mu_2 + 8(\mu_0^2 + \mu_2^2)\mu_2 &= 4\sqrt{3}v\delta(\zeta). \end{aligned} \quad (4)$$

Consider now the so-called [2] “weak state,” in which the magnitude of the order at the boundary is small. We set  $\mu_0 = \bar{\mu}_0 + \sigma e^2$  and approximate Eqs. (4) by

$$-(1 + \frac{2}{3}\rho)\bar{\mu}_0'' + (t + 12\sigma e^2)\bar{\mu}_0 + (t\sigma - 2)e^2 = 4\nu\delta(\zeta), \quad (5a)$$

$$-\mu_2'' + (t - \kappa^2)\mu_2 - 2\sqrt{3}e^2 \cos\kappa\zeta - 12\mu_0\mu_2 = 4\sqrt{3}\nu\delta(\zeta). \quad (5b)$$

The solution of Eq. (5a) is  $\sigma = 2/t$  and

$$\mu_0 = \frac{2e^2}{t} + \frac{2\nu}{[(t + 24e^2/t)(1 + 2\rho/3)]^{1/2}} \times \exp\left[-\left(\frac{t + 24e^2/t}{1 + 2\rho/3}\right)^{1/2}\zeta\right]. \quad (6a)$$

Substituting Eq. (6a) into Eq. (5b), the solution for  $\mu_2$ , to  $O(\nu)$ , is

$$\mu_2 = \frac{2\sqrt{3}\nu}{(t - \kappa^2 - 24e^2/t)^{1/2}} \exp[-(t - \kappa^2 - 24e^2/t)^{1/2}\zeta] + \frac{2\sqrt{3}e^2 \cos\kappa\zeta}{t - 24e^2/t}. \quad (6b)$$

Comparing Eqs. (6a) and (6b), we see that the two amplitudes in the cholesteric order parameter are effected differently by the field. The  $\kappa$ -independent amplitude,  $\mu_0$ , behaves essentially like the analogous quantity in a nematic system—to lowest order, it is shifted by the applied field and has a nonzero bulk value. Also, there is a *decrease* in its correlation length, which becomes (in reduced units)  $[(1 + \frac{2}{3}\rho)/(t + 24e^2/t)]^{1/2}$ .

For  $\mu_2$ , on the other hand, there is an *increase* in the correlation length, together with an increase in the surface amplitude. (The latter is a consequence of our choice of  $f_s$ , which is appropriate when the bulk phase is disordered [2]. For an ordered bulk phase, it is the magnitude of the order parameter which is  $e$  independent at  $\zeta=0$ .) There is also a term proportional to  $\cos(\kappa\zeta)$ , which describes a distortion of the helix. The latter would *not* appear for the case of negative dielectric anisotropy, where the field is applied parallel to  $\hat{\zeta}$ .

From Eq. (6b), it follows that the Bragg reflection with scattering wave vector  $\kappa$  (which comes from the periodic part of  $\mu_{ij}$ ), has a Lorentzian line shape and that its peak intensity  $I$  is proportional to

$$I \sim \frac{\nu^2}{(t - \kappa^2 - 24e^2/t)^2}. \quad (7)$$

Thus

$$\Delta I \equiv I(e) - I(0) \sim e^2. \quad (8a)$$

That is, the intensity of the Bragg reflection *increases* with the *square* of the field amplitude. Similarly, since the Lorentzian linewidth is proportional to the inverse of

the correlation length, we have

$$\delta\lambda(e) = \delta\lambda(0)[1 - 24e^2/t(t - \kappa^2)]^{1/2}. \quad (8b)$$

As noted above, Eqs. (7) and (8) are also valid for *negative* dielectric anisotropy materials where the field is applied along  $\hat{\zeta}$  (one need only replace the numerical factor of 24 by 48).

For the “strong state,” where the order-parameter amplitude at  $\zeta=0$  is not longer small [2] (but, again, there is no bulk ordering), the result is the same; in a weak field, the Bragg-peak-intensity increase is proportional to the square of the field amplitude. The line shape, however, is no longer Lorentzian.

Two key factors lead to the quadratic field dependence of the Bragg intensity for the helicoidal structure. One is the existence of a spatially uniform  $\mu_0$  component in the order parameter characterizing the zero-field bulk helicoidal phase as only  $\mu_0$  couples directly to the field. The Bragg-intensity change then occurs via the cubic term in the bulk free energy,  $\mu_0\mu_2^2$ , which is the lowest-order coupling between the spatially uniform and periodic components of the order parameter describing the helicoidal phase.

To emphasize the importance of a zero-field  $\mu_0$  component for obtaining a quadratic field dependence of the Bragg intensity, consider a similar calculation [9] carried out for *bulk* BP I and BP II. Because of their cubic  $e=0$  structures, there is *no*  $\mu_0$  component in their order parameters. The latter is instead *induced* by the field (via a distortion of the cubic unit cell). This induced  $\mu_0$  is *itself* proportional to  $e^2$  and the low-field Bragg-peak intensity is proportional [9] to  $e^4$ .

Consider, however, an ordered BP I or BP II region existing only in the vicinity of a bounding surface. This is possible [10] and BP I and BP II regions have been nucleated at boundaries [11,12]. Now, although neither BP I nor BP II has a  $\mu_0$  component in its bulk order parameter, such a component could appear (even at  $e=0$ ) as a *spatial transient* near the surface which decays to zero in the bulk. Just as in the helicoidal case, this  $\mu_0$  component would then asymptotically approach a bulk value proportional to  $e^2$  in an applied field. However, the essential difference between bulk helicoidal and BP structures—the former is uniaxial while the latter are cubic—means that the term  $\mu_0\mu_2^2$ , which is symmetry forbidden in the latter, can itself appear in the free-energy density only as a consequence of the surface. We therefore expect this term’s coefficient to be proportional to the strength  $\nu$  of the surface pinning. Then the change in the  $\mu_2$  correlation length arising from this coupling goes as  $\nu e^2$ , while that arising from the higher-order coupling term,  $\mu_0^2\mu_2^2$ , is proportional to  $e^4$  and *independent* of  $\nu$ . Thus one expects a dominant  $e^4$  dependence for the Bragg-line-peak-intensity enhancement of BP I or BP II surface-induced ordering when the surface potential is weak, just as occurs in the bulk. This is indeed what is

observed [11,12].

We now turn to BP III. While a range of theoretical ideas and models have been put forward to characterize this phase's structure, none have been confirmed experimentally [3]. Recently, it has been observed [13], for the case of *negative*-dielectric-anisotropy material, that an electric field (applied along the normal to the bounding surfaces of the sample) results in significant intensity enhancement and linewidth narrowing of the very broad reflection characteristically observed for this phase [14]. This does not occur in positive-dielectric-anisotropy material [15].

We stress that even for the relatively strong applied fields used in Ref. [13], the "weak-field" approach [i.e., Eq. (1)] remains valid. Direct calculation [16] for a positive-anisotropy helicoidal phase shows that the amplitude of the second harmonic is less than 6% of the primary one, even for fields as high as 4 V/ $\mu\text{m}$ . (The same result is valid for negative-dielectric-anisotropy materials if the spiral is prevented from rotating in the field.)

These experimental results are, of course, for a different problem from that analyzed here (i.e., they are obtained with an ordered phase—BP III—in the bulk rather than a disordered one.) Nevertheless, the observed field-induced enhancement and simultaneous narrowing of an initially weak and broad Bragg reflection are exactly the phenomena characteristic of surface-induced ordering [17]. Moreover, as regards structure, it appears that bulk BP III has more in common with the disordered phase than with the other ordered cholesteric ones. That is, while bulk BP III is apparently strongly ordered locally (much as in BP I or BP II), it does not have long-range order [3].

Kitzerow, Crooker, and Heppke [18] have carried out a detailed quantitative study of the field dependence of the Bragg-peak intensity and linewidth in BP III for negative-anisotropy material. Their results were as follows: (a) The line shape was Lorentzian to within the experimental precision. (b) The peak intensity was fitted by

$$I = \frac{I_0}{1 - (V/V_0)^n}, \quad (9a)$$

with  $I_0$ ,  $V_0$ , and  $n$  adjustable parameters and  $V$  the voltage across the specimen. (Of course,  $V \sim e$ .) A best least-squares fit was obtained for  $n \approx 2$ . (c) The linewidth was similarly fitted by

$$\delta\lambda = \delta\lambda_0 [1 - (V/V_0')^{n'}]^{1/2}, \quad (9b)$$

with now  $\delta\lambda_0$ ,  $V_0'$ , and  $n'$  as adjustable parameters. A best least-squares fit was found with  $n' \approx 2$  and  $V_0' \approx V_0$ .

These results are consistent with the following:

(1) The broad zero-field reflection line observed in the case of BP III is a *surface* effect. This is also consistent with the observations that, unlike BP I and BP II Bragg peaks, that of BP III is *not* narrowed by annealing [14]

and that the observed reflection is sensitive to tilting of the specimen [18].

(2) The coupling between the liquid-crystal molecules and the bounding surface is weak.

(3) Since  $V_0 \approx V_0'$ , the magnitude of the order parameter at the surface is essentially field independent. This differs from the result found [see Eq. (6b)] for the helicoidal phase where [see Eqs. (7) and (8b)] the value of  $V_0$  was *twice* that of  $V_0'$ . However, there is a significant difference between the two cases: For the zero-field helicoidal phase  $\mu_2$  is *induced* at  $\zeta=0$  by the surface pinning [2]; for BP III, it exists spontaneously. Thus  $\mu_2(\zeta=0)$  in BP III, as in *all* ordered liquid-crystal phases, is essentially field independent. This is particularly so when the material has negative dielectric anisotropy and the field is applied normal to the surface while the eigenvector of the largest eigenvalue (the director axis in the uniaxial limit) lies in this plane. It follows that  $I$  is no longer proportional to  $(t - \kappa^2 - 24e^2/t)^{-2}$  as in Eq. (7), but rather to  $(t - \kappa^2 - 24e^2/t)^{-1}$ . As Eq. (8b) is unchanged, we have  $V_0 = V_0'$ . Thus  $V_0 \approx V_0'$  is indeed reasonable for the case of a bulk-ordered BP III sample with a surface-aligned layer. This alignment (which underlies for the Bragg peak) decays exponentially with distance from the surface.

(4) Since  $n \approx n' \approx 2$ , the region near the bounding surface (whose width is field dependent) gives a  $\mu_0\mu_2^2$  contribution to the free energy. Further, since the experimental results are consistent with weak surface coupling, the coefficient of this contribution must be *v independent* for the same reasons given earlier when discussing BP I and BP II. This rules out those models for bulk BP III which lead to a surface region having, to a first approximation, cubic or icosahedral symmetry.

A model which appears to be consistent with the experimental results [18] regards BP III as a three-dimensional mesh of randomly oriented, interwoven cylindrical elements, in each of which the largest eigenvector of the order parameter (which defines the director in the uniaxial limit) is in a curling or double-twist configuration. Hornreich, Kugler, and Shtrikman [19] have shown rigorously that *one* such cylinder is indeed a minimum of the bulk free-energy function; however, no analysis of a possible nonperiodic state formed by a mesh of such elastic cylinders has as yet been carried out. Suppose, however, that the BP III surface layer is composed of such cylinders and that, due to pinning, these cylinders preferentially lie with their axes in the surface plane. This orientation is favored when the potential prefers homogeneous director orientation, as assumed for the nematic [1,2] and (by us, here) helicoidal cholesteric phases.

Given a surface layer in which curled cylinders lie preferentially in the bounding plane, there exists a repeat distance equal to the average spacing, taken normal to the planes, between cylinder axes in adjoining layers. This underlies the observed zero-field Bragg scattering line which, due to the limited thickness of the surface layer, is

necessarily both weak and broad.

When a field is applied normal to the surface, the preferential ordering of cylindrical units parallel to the bounding plane is *strengthened* for the case of negative-anisotropy material [7(b)]. In other words, the surface correlation length *increases* with field intensity and there is a corresponding intensity growth and line narrowing of the Bragg reflection. Since the tubes, individually, are uniaxial, they do have a  $\mu_0$  component in their order parameter [19]. Further, the surface layer ordering induced by the pinning is also at least uniaxial (the surface normal is always a unique direction—whether, in addition, there is in-plane ordering depends upon the pinning potential) and there is a  $\mu_0\mu_z^2$  contribution to the free-energy density from this region. This, as we have shown for the helicoidal phase, leads to an  $e^2$  dependence of the correlation length. Moreover, since this  $\mu_0\mu_z^2$  term exists due to the *orientation* of the cylindrical units and *not* to their distortion, its coefficient is essentially  $v$  independent, as required.

We conclude, therefore, that the data [18] are consistent with a bulk BP III structure formed of interlaced, randomly orientated elastic tubes, in each of which there is a curling or double-twist configuration of the order parameter (i.e., a “cooked spaghetti” phase). Near a surface, the pinning potential stiffens and orients these tubes so that they lie preferentially in the bounding plane (“uncooked spaghetti”). The resulting Bragg scattering would have the experimentally observed properties; that from cubic or icosahedral structures would not.

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