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#### Correlations and x-ray scattering in polar smectic-A<sub>1</sub> phases

Jiang Wang and T. C. Lubensky

Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104, U.S.A.

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**Résumé.** — Le modèle proposé par Prost pour les cristaux liquides polaires avec compétition entre deux distances inter-couche dans la phase smectique-A est utilisé dans une étude de l'intensité  $I(\mathbf{q})$  de diffusion des rayons-x dans la phase monocouche (A<sub>1</sub>).  $I(\mathbf{q})$  peut manifester une tache, un anneau, deux anneaux ou deux taches près du vecteur d'onde  $q_0$  de la phase bicouche (A<sub>2</sub>) lorsqu'on approche respectivement les phases A<sub>2</sub>, A, C ou la phase incommensurable. Il peut exister aussi une double tache avec un anneau lorsqu'il y a compétition entre la phase incommensurable et la phase A. Ces formes idéales de  $I(\mathbf{q})$  peuvent être cachées par des fluctuations non critiques si une transition du premier ordre empêche l'approche de la limite de stabilité de la phase A<sub>1</sub>.

Abstract. — The model introduced by Prost to describe polar liquid crystals with competition between two different layer spacings in smectic-A phases is used to calculate the x-ray scattering intensity  $I(\mathbf{q})$  in the monolayer (A<sub>1</sub>) phase.  $I(\mathbf{q})$  can respectively exhibit a single spot, single ring, double ring, or double spot pattern in the vicinity of the bi-layer wavenumber  $q_0$  as the A<sub>2</sub>,  $\tilde{A}$ ,  $\tilde{C}$  or incommensurate phases are approached. There may also be a double-spot-single-ring pattern when there is competition between the incommensurate and  $\tilde{A}$  phases. These idealized patterns may be masked by non-critical fluctuations if first order transitions prevent a close approach to the limit of stability of the A<sub>1</sub> phase.

#### 1. Introduction.

Smectic liquid crystalline mesophases are solid-like in one spatial direction and liquid like in the other two. They are produced when oriented bar-like molecules segregate into stacks of parallel planes as shown in figure 1. When the constituent molecules are not inversion symmetric as is the case when they carry an off centre dipole moment, a variety of smectic phases are possible [1-3] as shown in figure 1 (the normal to the planes is along the z-axis specified by a unit vector  $\hat{\mathbf{e}}_z$ ). In the A<sub>1</sub> (Fig. 1a) or monolayer phase, the repeat distance d normal to the layers is equal to the length of a molecule, *l*, and the dipolar heads are randomly up and down in a given layer; in the  $A_2$  (Fig. 1b) or bilayer phase, d is twice l, and the dipolar heads are preferentially up or down in a given molecular layer; in the  $\tilde{A}$  (Fig. 1c) and  $\tilde{C}$ (Fig. 1d) anti-phases, the direction of dipolar alignment is modulated in the plane of the layers. In addition, there is an  $A_d$  monolayer phase with l < d < 2 l. This phase has a distinct signature, but in fact has the same symmetry as the  $A_2$  phase [4]. Each of these phases and the high temperature nematic phase from which they evolve have characterictic x-ray scattering intensities as shown in figure 2.

Prost [2, 5] proposed a phenomenological model (based on an earlier model for the  $N-A_2$  transition [6])

to describe these phases and the transitions between them. In this model, there are two fields  $\Psi_1$  and  $\Psi_2$ with preference to order with spatial modulations with respective collinear wavenumbers  $\mathbf{k}_1 = k_1 \hat{\mathbf{e}}_z$ 



Fig. 1. — Schematic representation of five smectic-A phases : (a) the monolayer or  $A_1$ , (b) the bilayer or  $A_2$  phase, (c) the  $\tilde{A}$  phase, (d) the  $\tilde{C}$  phase, and (e) the  $A_d$  phase with layer spacing between one and two molecular lengths.



Fig. 2. — Schematic representation of the x-ray scattering intensity in the various liquid crystal phases : (a) the nematic phase with two diffuse spots at  $k_1$  and  $k_2$ , (b) the  $A_1$  phase with a quasi-Bragg peak at  $k_2$  and a diffuse spot at  $k_1$ , (c) the  $A_2$  phase with two quasi-Bragg peaks at  $2q_0$  and  $q_0$ , (d) the  $\tilde{A}$  phase with a Bragg peak at  $q_z = 2q_0$ and two Bragg peaks at  $q_z = q_0$  and non-zero  $q_{\perp}$ , and (e) the  $\tilde{C}$  phase with a Bragg peak at  $q_z = 2q_0$  and two Bragg-peaks at  $(q_z = q_0 + k, q_x = p_0)$  and  $(q_z = q_0 - k, q_x = -p_0)$ , the former being more intense than the latter.

and  $\mathbf{k}_2 = k_2 \, \hat{\mathbf{e}}_z$  corresponding to the peaks in the x-ray intensity in the nematic phase. In the A<sub>1</sub> phase, only  $\Psi_2$  is ordered. In the A<sub>2</sub> phase, both  $\Psi_1$  and  $\Psi_2$  are ordered with the wave number of  $\Psi_1$  locked in at one half that of  $\Psi_2$ . The  $\tilde{A}$  and  $\tilde{C}$  phases represent responses to the frustration imposed by incommensurate  $k_1$  and  $k_2$ . Mean field studies of the phase diagrams of this model have been carried out by Prost and collaborators [2, 7].

In the  $A_1$  phase,  $\Psi_2$  is ordered at wavenumber  $2 q_0 \hat{\mathbf{e}}_z = \mathbf{k}_2$  and produces a periodic potential for the field  $\Psi_1$  that may be incommensurate with its preferred periodicity determined by  $k_1$ . In this paper, we will use the Prost model to study fluctuations in the  $A_1$  phase. We will be particularly interested in the observable signatures in the x-ray intensity  $I(\mathbf{q})$ of the approach to the  $A_2$ ,  $\tilde{A}$  and  $\tilde{C}$  phases. We find that there are five idealized forms depicted in figure 3 that  $I(\mathbf{q})$  can take : (1) a diffuse spot on the z-axis at  $q_0$  signaling an approach to the A<sub>2</sub> phase, (2) a diffuse ring in the xy plane centred along the z-axis at  $q_0$  signaling an approach to the A phase, (3) two diffuse rings in the xy plane with centres equally spaced on the z-axis about  $q_0$  signaling an approach to the  $\tilde{C}$  phase, (4) two diffuse spots equally spaced about  $q_0$  on the z-axis signaling an approach to a phase with coexisting incommensurate wavenumbers, and (5) two diffuse spots and a diffuse ring signaling



Fig. 3. — Idealized limits of the x-ray intensities in the  $A_1$  phase in the vicinity of instabilities into the (a)  $A_2$ , (b)  $\tilde{A}$ , (c)  $\tilde{C}$ , (d) incommensurate phases, (e) show the x-ray intensity when there is competition between  $\tilde{C}$  and incommensurate ordering.

an approach either to the incommensurate or A phase. The double spot pattern characteristic of an approach to an incommensurate phase has not yet been observed experimentally though there is no theoretical reason why it should not exist in systems with sufficient anisotropy along the z-axis and sufficient mismatch between  $k_1$  and  $k_2$ . The forms depicted in figure 3 represent idealized limits that may only be observable near the limit of stability of the  $A_1$ phase.  $\Psi_1$  is a complex order parameter with two independent components. Only one linear combination of independent components orders at the various transitions under consideration.  $I(\mathbf{q})$  probes fluctuations in both components, and only the ordering component that dominates near the limit of stability produces the idealized forms. Inclusion of the non-ordering component leads to the much more complicated contours of constant  $I(\mathbf{q})$  shown in figures 4-8. Since the transitions from the  $A_1$  to the  $\tilde{A}$  and  $\tilde{C}$  are expected to be first order, it may in some cases not be possible to approach close enough to the limit of stability of the  $A_1$  phase to see the respective ideal single and double ring patterns.

#### 2. Development of the model.

To obtain a model for the  $A_1$  phase, we follow Prost [2, 5] and introduce two complex fields  $\Psi_1$  and  $\Psi_2$ with Fourier components in the upper half plane that are responsible for the intensity maxima in  $I(\mathbf{q})$ in the nematic phase at  $\mathbf{k}_1$  and  $\mathbf{k}_2$ . It is convenient but not necessary to identify  $\Psi_2$  with the molecular centre of mass density and  $\Psi_1$  with the dipole moment



Fig. 4. — Contour plots for  $\varepsilon_{-1}^{-}(\mathbf{q})$  and  $I(\mathbf{q})$  illustrating (right) the idealized one spot pattern in  $\varepsilon_{-1}^{-1}$  indicating an approach to the A<sub>2</sub> phase and (left) the resultant pattern in I for  $\overline{r} = 0.6$ ,  $y_1 = 0.5$ ,  $y_2 = 0.3$ ,  $y_3 = 3.0$ ,  $y_4 = 0.5$ .

density of the polar heads. A phenomenological Landau-Ginzburg Hamiltonian with maximum fluctuations in  $\Psi_1$  and  $\Psi_2$  at wavenumbers  $\mathbf{k}_1$  and  $\mathbf{k}_2$  is

$$H = \int d^{d}x \left[ \frac{1}{2} r_{1} | \Psi_{1} |^{2} + \frac{1}{2} D_{1} | (\nabla^{2} + k_{1}^{2}) \Psi_{1} |^{2} + \frac{1}{2} c_{1\perp} | \nabla_{\perp} \Psi_{1} |^{2} \right] + \int d^{d}x \left[ \frac{1}{2} r_{2} | \Psi_{2} |^{2} + \frac{1}{2} D_{2} | (\nabla^{2} + k_{2}^{2}) \Psi_{2} |^{2} + \frac{1}{2} c_{2\perp} | \nabla_{\perp} \Psi_{2} |^{2} \right] - \int d^{d}x w (\Psi_{2}^{*} \Psi_{1}^{2} + \text{c.c.}) + \int d^{d}x (u_{1} | \Psi_{1} |^{4} + u_{2} | \Psi_{2} |^{4} + u_{12} | \Psi_{1} |^{2} | \Psi_{2} |^{2})$$
(2.1)

where  $r_1 \sim 1 - T_{c1}$  and  $r_2 \sim T - T_{c2}$  where T is the temperature and  $T_{c1}$  and  $T_{c2}$  are the mean field transition temperatures for ordering of  $\Psi_1$  and  $\Psi_2$ . In general there could be other terms in H of the form  $\Psi_2^{pp} \Psi_1^q$  for general  $(p, q) \neq (1, 2)$  coupling  $\Psi_1$  and  $\Psi_2$ . For  $k_1 \sim k_2/2$ , the  $\Psi_2^* \Psi_1^2$  term retained in equation (2.1) is the most important one, and we will consider it only. The effect of the other terms on the properties of the A<sub>1</sub> phase can be treated in perturbation theory. They do not qualitatively alter the results presented here. The mean field x-ray intensity predicted by equation (2.1) is

$$I(\mathbf{q}) = \langle | \Psi_{1}(\mathbf{q}) |^{2} \rangle + \langle | \Psi_{2}(\mathbf{q}) |^{2} \rangle =$$
  
= 2[r\_{1} + D\_{1}(q^{2} - k\_{1}^{2})^{2} + c\_{1\perp} q\_{\perp}^{2}]^{-1} + 2[r\_{2} + D\_{2}(q^{2} - k\_{2}^{2})^{2} + c\_{2\perp} q\_{\perp}^{2}]^{-1} (2.2)

where  $\Psi_{1,2}(\mathbf{q})$  is the Fourier transform of  $\Psi_{1,2}(\mathbf{x})$ .  $I(\mathbf{q})$  clearly has the required maxima at  $\mathbf{q} = \mathbf{k}_1$  and  $\mathbf{q} = \mathbf{k}_2$ .

In the A<sub>1</sub> phase,  $\langle \Psi_2 \rangle$  is non-zero and has a spatial modulation at wavenumber  $2 \mathbf{q}_0 = 2 q_0 \hat{\mathbf{e}}_z$ .  $q_0$  can vary with temperature but is of order  $k_2/2$ . Writing

$$\Psi_1 = \psi e^{iq_0 z},$$
  
 $\Psi_2 = \psi_2 e^{2iq_0 z},$  (2.3)

we obtain from equation (2.1) an effective Hamiltonian describing fluctuations of  $\psi$  in the A<sub>1</sub> phase :

$$H = H_0 + \int d^d x u |\psi|^4$$
 (2.4)



Fig. 5. — (a) One ring pattern in  $\varepsilon_{-}^{-1}(\mathbf{q})$  indicating an approach to the  $\tilde{A}$  phase and (b) resultant pattern in I for  $\bar{r} = 0.6$ ,  $y_1 = 0.5$ ,  $y_2 = 0.5$ ,  $y_3 = 0.2$ , and  $y_4 = 1.0$ .

where

$$H_{0} = \int d^{d}x \left[ \frac{1}{2} r_{1} |\psi|^{2} + \frac{1}{2} D |(q_{0}^{2} - k_{1}^{2} + 2 ik_{1} \nabla_{\parallel} + \nabla^{2})\psi|^{2} + \frac{1}{2} c_{\perp} |\nabla_{\perp}\psi|^{2} + \frac{1}{2} (D_{\perp} - D) |\nabla_{\perp}^{2}\psi|^{2} - \frac{1}{2} v(\psi^{2} + \psi^{*2}) \right]$$
(2.5)

where  $v = w \langle \psi_2 \rangle$ . In equations (2.4) and (2.5), we have slightly generalized the original Prost model with the addition of a term  $(D_{\perp} - D) | \nabla_{\perp}^2 \psi |^2$  to *H*. This allows for independent rates of decay of  $I(\mathbf{q})$ for large  $\mathbf{q} = \mathbf{q}_{\perp}$  and  $\mathbf{q} = q_{\parallel} \hat{\mathbf{e}}_z$ . The  $v(\psi^2 + \psi^{*2})$ term in equation (2.5) results from umklapp coupling of fluctuations near  $-\mathbf{q}_0$  to those near  $\mathbf{q}_0$  made possible by the non-vanishing  $\langle \psi_2 \rangle$ . As in the BCS theory of superconductivity, we employ the Nambu [8] notation and introduce

$$\widetilde{\Psi}(\mathbf{q}) = \begin{pmatrix} \widetilde{\Psi}_1(\mathbf{q}) \\ \widetilde{\Psi}_2(\mathbf{q}) \end{pmatrix} = \begin{pmatrix} \psi(\mathbf{q}) \\ \psi^*(-\mathbf{q}) \end{pmatrix}. \quad (2.6)$$



Fig. 6. — (a) Two ring pattern in  $\varepsilon_{-}^{-1}(\mathbf{q})$  indicating an approach to the  $\tilde{C}$  phase and (b) resultant pattern in *I* for  $\bar{r} = 4.5$ ,  $y_1 = 7.0$ ,  $y_2 = 1.8$ ,  $y_3 = 2.6$ , and  $y_4 = 0.17$ .

 $H_0$  is then re-expressed as

$$H_0 = \frac{1}{4} \int \frac{\mathrm{d}^3 q}{(2\pi)^3} \, \tilde{\Psi}^*_{\alpha}(\mathbf{q}) \, \varepsilon_{\alpha\beta}(\mathbf{q}) \, \tilde{\Psi}_{\beta}(\mathbf{q}) \qquad (2.7)$$

where the Einstein convention is understood and

$$\varepsilon_{\alpha\beta} = \begin{bmatrix} r_+(\mathbf{q}) & -v \\ -v & r_-(\mathbf{q}) \end{bmatrix}$$
(2.8)

where

$$r_{\pm}(\mathbf{q}) = r + D[(\mathbf{q} \pm \mathbf{q}_{0})^{2} - k_{1}^{2}]^{2} + c_{\perp} q_{\perp}^{2} + (D_{\perp} - D) q_{\perp}^{4}. \quad (2.9)$$

Mean field correlation functions of  $\Psi_{\alpha}$  follow directly from equation (2.7). We have

$$G_{\alpha\beta} = \langle \tilde{\Psi}^{*}_{\alpha}(\mathbf{q}) \tilde{\Psi}^{*}_{\beta}(\mathbf{q}) \rangle$$
$$= \varepsilon_{\alpha\beta}^{-1}(\mathbf{q}) . \qquad (2.10)$$

 $\varepsilon_{\alpha\beta}$  is a 2 × 2 matrix with eigenvalues

$$\varepsilon_{\pm}(\mathbf{q}) = \frac{1}{2} (r_{+}(\mathbf{q}) + r_{-}(\mathbf{q}) \pm \{ [r_{+}(\mathbf{q}) - r_{-}(\mathbf{q})]^{2} + 4 v^{2} \}^{1/2}$$
(2.11)

and orthonormal eigenvectors

$$e_{\alpha}^{+} = \begin{bmatrix} 1 + v^{2}/(r_{-} - \varepsilon_{+})^{2} \end{bmatrix}^{-1/2} \begin{bmatrix} 1 \\ v/(r_{-} - \varepsilon_{+}) \end{bmatrix},$$
(2.12)
$$e_{\alpha}^{-} = \begin{bmatrix} 1 + v^{2}/(r_{+} - \varepsilon_{-})^{2} \end{bmatrix}^{-1/2} \begin{bmatrix} 1 \\ v/(r_{+} - \varepsilon_{-}) \end{bmatrix}.$$

Thus we can write

$$G_{\alpha\beta} = \frac{1}{\varepsilon_+(\mathbf{q})} e_{\alpha}^+ e_{\beta}^+ + \frac{1}{\varepsilon_-(\mathbf{q})} e_{\alpha}^- e_{\beta}^- . \quad (2.13)$$

The x-ray intensity  $I_1$  due to fluctuations in  $\psi$  is related to  $G_{\alpha\beta}(\mathbf{q})$  via

$$I_{1}(\mathbf{k}) = G_{11}(\mathbf{k} - \mathbf{q}_{0}) + G_{22}(\mathbf{k} + \mathbf{q}_{0}) =$$

$$= \frac{r_{-}(\mathbf{k} - \mathbf{q}_{0})}{\varepsilon_{-}(\mathbf{k} - \mathbf{q}_{0})\varepsilon_{+}(\mathbf{k} - \mathbf{q}_{0})} + \frac{r_{+}(\mathbf{k} + \mathbf{q}_{0})}{\varepsilon_{-}(\mathbf{k} + \mathbf{q}_{0})\varepsilon_{+}(\mathbf{k} + \mathbf{q}_{0})}.$$
(2.14)

Note that  $I_1(\mathbf{k})$  is dominated by  $\varepsilon_{-}^{-1}$  only near the limit of stability of the A<sub>1</sub> phase.

#### 3. Analysis.

We now wish to use the results of the previous section to study instabilities in the  $A_1$  phase and how they are manifested in the x-ray intensity  $I_1(\mathbf{q})$ . The  $A_1$  phase becomes unstable when one of the eigenvalues of  $\varepsilon_{\alpha\beta}$  goes through zero. Since  $\varepsilon_{-} < \varepsilon_{+}$ , we need only be concerned with  $\varepsilon_{-}(\mathbf{q})$ .  $\varepsilon_{-}(\mathbf{q})$  has a minimum value for wavevectors  $\mathbf{q}_{m} = (\mathbf{q}_{m\perp}, q_{m\parallel})$  such that  $\nabla_{\mathbf{q}}\varepsilon_{-}(\mathbf{q}_{m}) = 0$ . If  $\mathbf{q}_{m} = 0$ , the system becomes unstable with respect of the appearance of spatially uniform order in  $\psi(\mathbf{x})$  as *r* decreased. If  $\mathbf{q}_{m} \neq 0$ , then the instability is towards spatially modulated order in  $\psi$  at wavevector  $\mathbf{q}_{m}$ . Only the component of  $\widetilde{\Psi}_{\alpha}(\mathbf{q})$ associated with  $\varepsilon_{-}(\mathbf{q}_{m})$  is critical so that the order parameter

$$\varphi(\mathbf{q}) = \mathbf{e}_{\alpha}^{-}(\mathbf{q}) \, \tilde{\Psi}_{\alpha}(\mathbf{q}) \tag{3.1}$$



Fig. 7. — (a) Two spot pattern in  $\varepsilon_{-}^{-1}(\mathbf{q})$  indicating an approach to in incommensurate phase and (b) resultant pattern in *I* for  $\overline{r} = 0.3$ ,  $y_1 = 0.3$ ,  $y_2 = 1.1$ ,  $y_3 = 0.6$ , and  $y_4 = 0.91$ .

has Ising symmetry rather that the xy symmetry of the full complex field  $\psi$ . This results from the preferred relative phase of the original fields  $\psi$  and  $\psi_2$  impos-

ed by equation (2.1). Long range order in 
$$\varphi$$
 at wave-  
number  $\mathbf{q}_{m}$  leads to  
 $\langle \psi(\mathbf{x}) \rangle = e^{i\mathbf{q}_{m}\cdot\mathbf{x}} e_{1}^{-}(\mathbf{q}_{m}) \langle \varphi(\mathbf{q}_{m}) \rangle +$ 

+ 
$$e^{-i\mathbf{q}_{m}\cdot\mathbf{x}} e_{2}^{-}(\mathbf{q}_{m}) \langle \varphi(\mathbf{q}_{m}) \rangle$$
. (3.2)

It is clear that equation (3.2) can describe the  $A_2$ ,  $\tilde{A}$ , and  $\tilde{C}$  phases discussed in the introduction.  $\mathbf{q}_m = 0$ 



Fig. 8. — (a) Double-spot-single-ring pattern in  $\varepsilon_{-}^{-1}(\mathbf{q})$  indicating an approach either to the incommensurate phase or the  $\tilde{A}$  phase and (b) resultant pattern in I for  $\bar{r} = 0.6$ ,  $y_1 = 1.0$ ,  $y_2 = 1.1$ ,  $y_3 = 0.6$ , and  $y_4 = 0.83$ .

corresponds to the A<sub>2</sub> phase;  $e_1^- = e_2^-$ ,  $\mathbf{q}_m = q_m \hat{\mathbf{e}}_x$ where  $\hat{\mathbf{e}}_x$  is a unit vector in an arbitrary direction perpendicular of  $\hat{\mathbf{e}}_z$  to the  $\tilde{A}$  phase; and  $e_1^- \neq e_2^-$ ,  $\mathbf{q}_m = q_{m\perp} \hat{\mathbf{e}}_x + q_{m\parallel} \hat{\mathbf{e}}_z$  to the  $\tilde{C}$  phase. We will see shortly that the situation  $\mathbf{q}_m = q_{m\perp} \hat{\mathbf{e}}_x + q_{m\parallel} \hat{\mathbf{e}}_z$ ,  $e_1^- = e_2^$ does not exist.

In order to analyse the possible forms of  $\varepsilon_{-}(\mathbf{q})$ , we first introduce unitless variables :

$$y_{1} = \frac{v}{Dq_{0}^{4}}, \quad y_{2} = \frac{k_{1}^{2} - q_{0}^{2}}{q_{0}^{2}}, \quad y_{3} = \frac{c_{\perp}}{Dq_{0}^{2}}$$
$$y_{4} = \frac{D_{\perp}}{D}, \quad \mathbf{p} = \frac{\mathbf{q}}{q_{0}}, \quad \overline{r} = \frac{r}{Dq_{0}^{4}}. \quad (3.3)$$

Then we have

$$\overline{\varepsilon}_{-} = \varepsilon_{-}/Dq_{0}^{4} = \overline{r} + (p_{\parallel}^{2} - y_{2})^{2} + 4p_{\parallel}^{2} + + 2(p_{\parallel}^{2} - y_{2})p_{\perp}^{2} + y_{3}p_{\perp}^{2} + y_{4}p_{\perp}^{4} - [16p_{\parallel}^{2}(p^{2} - y_{2})^{2} + y_{1}^{2}]^{1/2}. \quad (3.4)$$

We now expand  $\overline{\varepsilon}_{-}$  in powers of p :

$$\overline{\varepsilon}_{-} = \varepsilon_{0} + \frac{1}{2} a_{1} p_{\parallel}^{2} + \frac{1}{2} a_{\perp} p_{\perp}^{2} + \frac{1}{4} \dot{b}_{1} p_{\parallel}^{4} + \frac{1}{4} b_{\perp} p_{\perp}^{4} + \frac{1}{2} b_{1\perp} p_{\parallel}^{2} p_{\perp}^{2} \quad (3.5)$$

where

$$\begin{aligned} \varepsilon_{0} &= r - |y_{1}| + y_{2}^{2}, \\ a_{1} &= 4(2 - y_{2} - 4 y_{2}^{2}/|y_{1}|), \\ a_{\perp} &= 2(y_{3} - 2 y_{2}), \\ b_{1} &= 4(1 + 16 y_{2}/|y_{1}| + 32 y_{4}^{4}|y_{1}|^{-3}), \\ b_{\perp} &= 4 y_{4}, \\ b_{1\perp} &= 4(1 + 8 y_{2}|y_{1}|^{-1}). \end{aligned}$$
(3.6)

The fourth order coefficients  $b_1$ ,  $b_{\perp}$ , and  $b_{1\perp}$  are all positive whereas  $a_1$  and  $a_{\perp}$  can be positive or negative. The determination of  $\mathbf{q}_{m} = (\mathbf{q}_{m\perp}, \mathbf{q}_{m\parallel})$  from equation (3.3) is therefore exactly analogous to the mean-field determination of order parameters in the vicinity of a bi- or tetra-critical point [9]. The phase diagram for  $q_{m\parallel}$  and  $q_{m\perp}$  in the  $a_1 - a_{\perp}$  plane is shown in figure 9. Figure 9a is for the tetracritical case with  $b_{1\perp}^2 < b_1 b_{\perp}$ , and figure 9b is the bicritical case with  $b_{1\perp}^2 > b_1 b_{\perp}$ . In both cases, there are four regions in the phase diagram defined by the positive  $a_{\perp}$ and  $a_1$  axes and by the lines  $a_1 = (b_{1\perp}/b_{\perp}) a_{\perp}$  (OC) and  $a_1 = (b_1/b_{1\perp}) a_{\perp}$  (OD) in the third quadrant. In regions I,  $\mathbf{q}_{m} = 0$  leading to the single spot pattern of figure 3a and instability into the A<sub>2</sub> phase; in regions II,  $q_{m\parallel} = 0$  and  $q_{m\perp} > 0$  leading to the single ring pattern of figure 3b and instability into the  $\tilde{A}$ phase; in regions IV,  $q_{m\perp} = 0$  and  $q_{m\parallel} > 0$  leading to the double-spot pattern of figure 3d and instability into the incommensurate phase. Finally regions III are different for the bi- and tetra-critical cases. In the tetracritical case (Fig. 9a), both  $q_{m\parallel}$  and  $q_{m\perp}$ are non-zero leading to the double ring pattern of



Fig. 9. — Phase diagram in the  $a_1 \cdot a_{\perp}$  plane showing the regions where the different patterns shown in figures 3 and 4 occur for small values of  $a_1$  and  $a_{\perp}$ . (a) shows the tetracritical case and (b) the bicritical case. Lines OA and OB are respectively the  $a_{\perp}$  and  $a_1$  axes; OC and OD are the line  $a_1 = (b_{1\perp}/b_{\perp}) a_{\perp}$  and  $a_1 = (b_1/b_{\perp}) a_{\perp}$ ; OE in (b) is the line separating instability into the incommensurate phase from instability into the  $\tilde{C}$  phase. Region I (see text) in (a) is bounded by OA and OB, II by OB and OC, III by OC and OD, and IV by OD and OA, and similarly for (b).

figure 3c and instability into the  $\tilde{C}$  phase. In the bicritical case (Fig. 9b), the patterns of regions II and IV coexist in region III leading to double spotsingle ring pattern of figure 3e. The intensities into the spots and ring are equal along the line OE in figure 9b. Thus above OE, the system becomes unstable toward the  $\tilde{A}$  phase whereas below OE, it becomes unstable toward the incommensurate phase. In the bicritical phase transition analogy, OE is a first order transition line along which two phases coexist.

At the origin in figures 9a and 9b,  $\varepsilon_{-} = \overline{r} + O(q^4)$ . The origin, therefore, corresponds to an n = 1, m = 3 Lifshitz point [10] in three dimensions. Similarly, the positive  $a_1$  and  $a_{\perp}$  axes are respectively lines of n = 1, m = 1 and n = 1, m = 2 Lifshitz points. This implies that the point where the  $A_1$ ,  $A_2$  and  $\tilde{A}$ phases meet is an n = 1, m = 2 Lifshitz point. The lines OA and OB in the tetracritical case are respectively generalized m = 2 and m = 1 Lifshitz lines. Figure 9 represents the phase diagrams in the  $a_1 - a_1$ plane valid near the point where  $a_1$  and  $a_{\perp}$  vanish. In figure 10, we show the global phase diagram obtained from equation (3.4) in the  $y_1 - y_2 - y_3$  space for fixed  $y_4 = 0.17$ . For small  $y_1$ , there is the bicritical point shown in figure 9b. There is also another multicritical point at a larger value of  $y_2$  where single-ring, double-spot, double-ring, and double-spot-single-ring



Fig. 10. — Global phase diagram in the space of the parameters  $y_1$ ,  $y_2$  and  $y_3$  for fixed  $y_4 = 0.17$  showing regions where the various idealized x-ray patterns occur. The single spot region is indicated by I, the single ring by II, the double spot by III, the double ring by IV, and the double spot-single ring by V. Note that for small values of  $y_1$ , the tetracritical point shown in figure 9a does not exist, and the double-ring pattern only appears beyond another multicritical point where regions II, III, IV, and V meet. At larger values of  $y_1$ , the tetracritical point does emerge.

regions meet. At larger values of  $y_1$ , the tetracritical point of figure 9a emerges. This phase diagram is qualitatively the same for other values of  $y_4$ .

As discussed in the previous section,  $I(\mathbf{q} + \mathbf{q}_0)$  measures  $r_{-}(\mathbf{q})/\varepsilon_{-}(\mathbf{q}) \varepsilon_{+}(\mathbf{q})$  rather than  $\varepsilon_{-}^{-1}(\mathbf{q})$  alone. The maximum of  $I(\mathbf{q} + \mathbf{q}_0)$  occurs at  $\mathbf{q} = \mathbf{q}_{\mathbf{I}}$  defined via

$$\nabla_{q} I(\mathbf{q}_{\mathrm{I}} + \mathbf{q}_{0}) = \left[\varepsilon_{-}(\mathbf{q}_{\mathrm{I}}) \varepsilon_{+}(\mathbf{q}_{\mathrm{I}})\right]^{-2} \times \left[\left(\varepsilon_{-}(\mathbf{q}_{\mathrm{I}}) \varepsilon_{+}(\mathbf{q}_{\mathrm{I}})\right) \nabla_{q} r_{-}(\mathbf{q}_{\mathrm{I}}) - r_{-}(\mathbf{q}_{\mathrm{I}}) \varepsilon_{-}(\mathbf{q}_{\mathrm{I}}) \nabla_{q} \varepsilon_{+}(\mathbf{q}_{\mathrm{I}}) - r_{-}(\mathbf{q}_{\mathrm{I}}) \varepsilon_{-}(\mathbf{q}_{\mathrm{I}}) \nabla_{q} \varepsilon_{+}(\mathbf{q}_{\mathrm{I}})\right] = 0.$$
(3.8)

It is clear that  $\mathbf{q}_{I} = \mathbf{q}_{m}$  in the limit that  $\varepsilon_{-}(\mathbf{q}_{m}) = 0$ . With a little algebra, it is possible to show that  $\mathbf{q}_{I} = \mathbf{q}_{m}$  only if  $\varepsilon_{-}(\mathbf{q}_{m}) = 0$  or if  $\mathbf{q}_{m} = 0$  and  $y_{2} = 0$ . Thus,  $I(\mathbf{q})$  will obtain the idealized forms depicted in figure 2 only near the limit of stability of the  $A_{1}$  phase defined by  $\varepsilon_{-}(\mathbf{q}_{m}) = 0$  or for the trivial case when  $\mathbf{q}_{m} = 0$  and  $y_{2} = 0$ . Otherwise, the maximum intensity of  $I(\mathbf{q})$  will not occur at  $\mathbf{q} = \mathbf{q}_{m}$ , and the contours of constant  $I(\mathbf{q})$  can be quite complicated as shown in figures 4-8. Within the mean-field theory presented here, we find

$$q_{\mathbf{I}\parallel} - q_{\mathbf{m}\parallel} \sim \varepsilon_{-}(\mathbf{q}_{\mathbf{m}}) \tag{3.9}$$

near the  $A_2$  and  $\tilde{A}$  phase boundaries and

$$q_{\mathrm{I}\perp} - q_{\mathrm{m}\perp} \sim \varepsilon_{-}^{2}(\mathbf{q}_{\mathrm{m}}) \qquad (3.10)$$

near the  $\tilde{A}$  phase boundary. Equation (3.9) predicts that  $q_{I\parallel} - q_{m\parallel}$  tends to zero more rapidly than is observed experimentally [11] near the  $A_1 - \tilde{A}$  transition. Presumably, however, fluctuations will modify the mean-field result of equation (3.9).

#### 4. Discussion.

In this paper, we have studied the properties of the x-ray scattering intensity  $I(\mathbf{q})$  in the mono-layer  $A_1$  phase in mean field theory using a phenomenological model suggested by Prost [2, 5]. We found that  $I(\mathbf{q})$  assumes characteristic forms as the  $A_2$ ,  $\tilde{A}$ ,  $\tilde{C}$ , and I phases are approached as shown in figures 3 to 8. We will now briefly discuss what is known about phase transitions among the above phases. We will also discuss the relevance to experimental systems and possible limitations of the calculations presented here.

The  $A_1$ - $A_2$  phase transition is observed to be second order [12] and is predicted to be in the Ising universality class [13]. There is a continuous degeneracy of directions for the spatial modulations of the A phase to condense. Thus, just as the nematic to smectic-C transition is first order [14, 15] so the  $A_1$ - $\tilde{A}$  transition is predicted to be first order via arguments due to Brazovskii [16]. The  $A_1$ - $A_2$ - $\tilde{A}$  multi-critical point (occurring for example in mixtures of  $DB_5$  and  $T_8$ ) where the  $A_1$ ,  $A_2$ , and A phases meet corresponds to a point along the  $a_{\perp} = 0$  axis of figure 9. Furthermore, the order parameter of the A1-A2 phase transition has Ising symmetry. Therefore, the  $A_1$ - $A_2$ - $\tilde{A}$  multicritical point is an n = 1, m = 2 Lifshitz point [10] (n refers to the number of components of the order parameter, and m to the number of soft spatial directions with  $q^4$  rather than  $q^2$  in the propagator). The  $A_1$ ,  $A_2$ , and  $\tilde{A}$  phases correspond respectively to the paramagnetic (P), ferromagnetic (F) and modulated (M) phases of magnetic systems exhibiting Lifshitz points. The  $\tilde{A}$ - $A_2$  transition is, therefore, expected to be first order (in agreement with Prost [2]) just as the MF transition is first order in Ising magnetic systems [17]. Though the  $A_1$ - $\tilde{A}$  transition is first order, there should be no trouble in observing its characteristic single ring pattern because as can be seen in figure 4, the difference between  $\varepsilon_{-1}^{-1}(\mathbf{q})$  and  $I(\mathbf{q})$ is not significant. Indeed the single ring pattern has been observed [11]. Finally, we note the possibility [18] of a biaxial monolayer phase  $A'_1$  analogous to the biaxial nematic phase [19] N' in which the two Bragg spots of the  $A_1$  phase in the vicinity of  $q_0$  are replaced by diffuse spots. If this phase exists, then there would be second order  $A_1$ - $A'_1$  and  $A'_1$ - $\tilde{A}$  transitions.

As for the  $\tilde{A}$  phase, there is a continuous degeneracy of directions for the spatial modulations of the  $\tilde{C}$ phase, and the  $A_1$ - $\tilde{C}$  transition should be first order. It may, therefore, be difficult to approach close enough to the limit of stability of the  $A_1$  phase to see the two ring pattern of figure 3c since it is so easily lost in  $I(\mathbf{q})$  (see Fig. 4). We feel, however, that a more detailed experimental study of the  $A_1$ - $\tilde{C}$  transition such as occurs in DB<sub>9</sub> [1] would be of interest.

Within the truncated model considered in this article, the double spot pattern of figure 3d represents an instability into a phase with modulations at two coexisting wavenumbers that could in general have an irrational or incommensurate ratio. Higher order terms not included in H of equation (2.1) of the form  $\Psi_2^p \Psi_1^{*q}$ become important when  $\psi$  orders. These terms favour commensurate lockin with wavenumber ratio p/qand presumably lead to phase diagrams for highly anisotropic systems which are similar to the very complex phase diagrams encountered in the ANNNI model [20, 21] or the Frankel-Kontorova model [20, 22]. To date there has been no experimental observation of the double spot pattern-probably because the anisotropy in liquid crystals is sufficiently weak that the formation of anti-phases with spatial modulation in two or more dimensions is the preferred method of relaxing the frustration imposed by a ratio  $k_2/k_1$ significantly different from two. We see no reason, however, why this pattern should not in principle be obtained by the application, for example, of strong external magnetic fields to enhance anisotropy.

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