

This article was downloaded by: [Tomsk State University of Control Systems and Radio]

On: 19 February 2013, At: 13:40

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954

Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

### Mean Field Theory for the Biaxial Nematic Phase and The NN'AC Critical Point

T. C. Lubensky<sup>a</sup>

<sup>a</sup> Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania, 19104

Version of record first published: 13 Dec 2006.

To cite this article: T. C. Lubensky (1987): Mean Field Theory for the Biaxial Nematic Phase and The NN'AC Critical Point, *Molecular Crystals and Liquid Crystals*, 146:1, 55-69

To link to this article: <http://dx.doi.org/10.1080/00268948708071802>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages

whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Mean Field Theory for the Biaxial Nematic Phase and The $NN'AC$ Critical Point

T. C. LUBENSKY

*Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104*

*(Received January 5, 1987)*

The Chen-Lubensky model for the  $NAC$  critical point is modified to include a bond-angle order parameter describing the biaxial nematic ( $N'$ ) phase. When reasonable assumptions are made about fluctuation effects at the  $NAC$  point, an  $N'$  phase always occurs leading to an  $NN'AC$  tetracritical point as predicted by Grinstein and Toner. The x-ray scattering intensity is found to consist of two off-axis diffuse spots near the  $NN'AC$  point and to evolve continuously toward a ring with a  $\cos\theta$  modulation as the point where the  $N$ ,  $N'$ , and  $C$  phases meet is approached. Powder averages of the x-ray intensity in the  $N'$  phase will be difficult to distinguish from the intensity predicted by the Chen-Lubensky model throughout most of the  $N'$  phase.

*Keywords: multicritical points, biaxial nematic,  $NAC$  critical point*

## I. INTRODUCTION

The  $NAC$  point where nematic, smectic-A and smectic-C phases meet has been the subject of increasingly precise experimental study in recent years.<sup>1–6</sup> There is good agreement among experiments performed in different laboratories and among different experimental probes. The  $NC$  line is a first order line with a latent heat going to zero as the  $NAC$  point is approached. The  $NA$  and  $AC$  lines are second order within experimental accuracy near the  $NAC$  point, though the  $AC$  transition is reported to become more tricritical<sup>6,7</sup> near this point.

There are a number of theories for the  $NAC$  multicritical point.<sup>6,8–11</sup> Of these, those of Refs. 6 and 8–10 are mean field theories. Only

the dislocation melting theory of Grinstein and Toner<sup>12</sup> (GT) is a true three dimensional critical theory. All of the mean field theories predict that only the  $N$ ,  $A$  and  $C$  phases meet at the  $NAC$  point. In the Chen-Lubensky theory<sup>8</sup> (CL), the  $NAC$  point is an  $n = 2$ ,  $m = 2$  Lifshitz point<sup>13</sup> in which the  $NC$  transition is first order because of fluctuations. In the other mean field theories, which introduce order parameters related to bond angle order, the  $NAC$  point is either a kind of bicritical point<sup>9</sup> or a critical end point.<sup>6,10</sup> The GT theory predicts that a biaxial nematic ( $N'$ ) phase intervenes between the  $N$  and  $C$  phases so that the  $NAC$  point becomes an  $NN'AC$  tetracritical point. Though the GT model is on the most rigorous theoretical footing of all of the theories, there is as yet no experimental evidence for the  $N'$  phase; and the CL model appears to be in better agreement with experimental than any of the others.

The purpose of this paper is to investigate the effect of including fluctuations and the possibility of bond angle order in the nematic phase in the CL model. Fluctuations will be treated using one loop perturbation theory. The principal result of this analysis is that fluctuations reduce the transition temperature  $T_{NAC}$  of the  $NAC$  Lifshitz point to zero in three<sup>15</sup> dimensions so that a biaxial nematic phase will intervene between the  $N$  and  $C$  phases, in agreement with the GT theory. This result depends strongly on spatial dimensionality  $d$ . At one loop order the lower critical dimension of the  $n = 2$ ,  $m = 2$   $NAC$  Lifshitz point is three leading to  $T_{NAC} = 0$  at  $d = 3$ . Above  $d = 3$ ,  $T_{NAC}$  is not zero, and either the Lifshitz topology (Figure 1a) or the tetracritical topology (Figure 1b) is possible, and analyses based on  $\epsilon$ -expansions predict<sup>11</sup> both behaviors. The GT theory, however, correctly treats three dimensional fluctuations and rules out the Lifshitz topology as long as the  $NA$  and  $AC$  transitions are second order with negative specific heat exponents. This point will be discussed further in the discussion section.

A second result of this paper is that the powder averaged x-ray scattering intensity throughout most of the  $N'$  phase will be very difficult to distinguish from that of the  $N$  phase. It is thus imaginable that the  $N'$  phase exists in a small region of the phase diagram but that it is invisible to x-ray scattering and presents such small thermal anomalies that it cannot easily be detected with calorimetry.

## II. FLUCTUATIONS AND THE CL MODEL

The order parameter for the CL model as explained in detail in Ref. 8 is the mass density  $m(\vec{x})$  with Fourier components in the neigh-

FIGURE 1 (a) Typical phase diagram near the *NAC* multicritical point. The *NA* and *AC* lines (unbroken in the diagram) are second order, and the *NC* line (broken) is first order. *T* is the temperature, and *x* the concentration of one molecular species in a mixture. (b) A possible phase diagram predicted by Grinstein and Toner,<sup>12</sup> showing the biaxial *N'* phase and the *NN'AC* tetracritical point. The crosses represent tricritical points, and the open circle a triple point where the *N*, *N'*, and *C* phases coexist. The tricritical and triple points are not predicted by the GT theory. Since the *NC* line is first order, however, there must be a tricritical point on either the *NN'* line or on the *N'C* line. It is, therefore, possible that either the *NN'* or the *N'C* line meets the *NC* line at a critical end point.

borhood of the ordering wavevectors for the smectic-A and smectic-C phases. The Landau-Ginzburg-Wilson Hamiltonian is

$$H_{CL} = H_0 + u \int d^3x m^4(\vec{x}) + \frac{1}{2} w \int d^3x m^2(\vec{\nabla}_\perp m)^2, \quad (2.1)$$

where

$$H_0 = \frac{1}{2} \int \frac{d^3q}{(2\pi)^3} [r + D_\parallel(q_\parallel^2 - q_0^2)^2 + c_\perp q_\perp^2 + D_\perp q_\perp^4 + D_{\parallel\perp} q_\perp^2 (q_\parallel^2 - q_0^2)] |m(\vec{q})|^2, \quad (2.2)$$

where  $m(\vec{q})$  is the Fourier transform of  $m(\vec{x})$  and  $q_\parallel$  and  $q_\perp$  are respectively the components of the wavevector parallel and perpendicular to the direction of molecular alignment specified by the Frank director,  $\vec{n}$ .  $u > 0$ ,  $w > 0$ ,  $D_\parallel > 0$ ,  $D \geq 0$ ,  $c_\perp$ , and  $D_{\parallel\perp}$  are phenomenological parameters, and  $\vec{q}_0 = q_0 \vec{n}$  is the wavevector of the smectic-A order.

$$r = a(1 - T_{NA}^0/T) \quad (2.3)$$

goes to zero at the mean field NA transition temperature  $T_{NA}^0$ .

The x-ray scattering intensity is proportional to  $G(\vec{q}, r) = \langle |m(\vec{q})|^2 \rangle$  where  $\langle \rangle$  represent a thermal average with respect to  $H_{CL}$ . In mean field theory in the nematic phase,

$$G(\vec{q}, r) = [r + D_\parallel(q_\parallel^2 - q_0^2)^2 + c_\perp q_\perp^2 + D_\perp q_\perp^4 + D_{\parallel\perp} q_\perp^2 (q_\parallel^2 - q_0^2)]^{-1} \\ \equiv [r(\vec{q})]^{-1}. \quad (2.4)$$

Thus for  $c_\perp > 0$ ,  $G(\vec{q}, r)$  has diffuse spots centered at  $\vec{q} = \pm q_0 \vec{n}$  for  $r > 0$ . When  $c_\perp > 0$ , the diffuse spots open into rings in the plane perpendicular to  $\vec{n}$  centered at  $\pm q_0 \vec{n}$  with radius  $q_{\perp 0} = |c_\perp|/2D_\perp$ . The Lifshitz NAC point occurs at  $c_\perp = 0$ , and the mean field NC transition occurs at

$$T_{NC}^0 = T_{NA}^0 (1 - c_\perp^2/4D_\perp a)^{-1} \sim T_{NA}^0 (1 + c_\perp^2/D_\perp a), \quad (2.5)$$

leading to the phase diagram shown in Figure 2a.

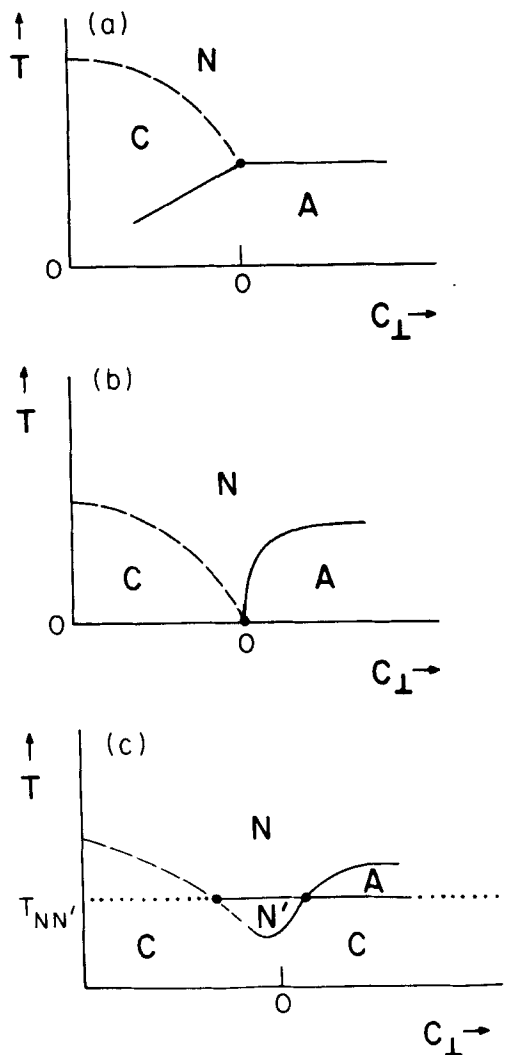


FIGURE 2 (a) Mean field phase diagram for the CL model. The NC line is first order because of fluctuations.

(b) The one-loop phase diagram for the CL model showing the depression of  $T_{NAC}$  to zero.

(c) Phase diagram for the CL model with one-loop fluctuations and a bond-angle order parameter.  $T_{NN'}$  is independent of  $c_{\perp}$  in the model. Thus, near  $c_{\perp} = 0$ ,  $T_{NN'}$  is always greater than  $T_{NA}$  or  $T_{NC}$ , and a biaxial nematic phase results. Since  $T_{NA}$  fall very rapidly to zero near  $c_{\perp} = 0$  when bond angle order is not included, the  $N'$  phase may exist in only a very small region of the phase diagram. This diagram shows a tricritical point on the  $N'C$  line and the  $NN'$  line hitting the  $N'C$  and  $NC$  line at a critical endpoint. The topology of Figure 2(b) is also possible in the model.

In one loop, self-consistent perturbation theory, there is a correction to  $G^{-1}(\vec{q})$  coming from the diagram shown in Figure 3, yielding

$$t \equiv G^{-1}(\vec{q} = q^0 \vec{n}, t) = r + 12u \int \frac{d^3 q}{(2\pi)^3} G(\vec{q}, t). \quad (2.6)$$

The  $NA$  transition temperature  $T_{NA}$  is determined by  $t = 0$  in the above with  $c_{\perp} > 0$ , or

$$a \left( 1 - \frac{T_{NA}^0}{T_{NA}} \right) = -12u \int \frac{d^3 q}{(2\pi)^3} \frac{1}{D_{\parallel}(q_{\parallel}^2 - q_0^2)^2 + c_{\perp} q_{\perp}^2 + D_{\perp} q_{\perp}^4}, \quad (2.7)$$

where for simplicity we have set  $D_{\parallel\perp} = 0$ . The Lifshitz critical temperature  $T_{NAC}$  is determined by this equation with  $c_{\perp} = 0$ . Setting  $q_{\parallel} = (q_0 + k_{\parallel})$  and  $\vec{q}_{\perp} = q_{\perp}(\sin\phi, \cos\phi, 0)$  and using  $d^3 q = dk_{\parallel} \frac{1}{2} dq_{\perp}^2 d\phi$ , it is easy to see that the integral on the right hand side of Eq. (2.7) is logarithmically divergent as  $c_{\perp} \rightarrow 0$ . This leads to

$$T_{NA} = \frac{T_{NA}^0}{1 + 3u(\pi a)^{-1}(2D_{\parallel}D_{\perp}q_0^2)^{-1/2}\ln[2\Lambda D_{\perp}^{1/2}/c_{\perp}]} \quad (2.8)$$

where  $\Lambda$  is a cutoff on the value of  $\vec{k} = \vec{q} - q_0$ . Note that  $T_{NA}$  tends very sharply to zero (as one over a logarithm) as  $c_{\perp} \rightarrow 0$  implying  $T_{NAC} = 0$ . For  $c_{\perp} < 0$ , the  $NC$  transition is first order leading to the phase diagram shown in Figure 2b.

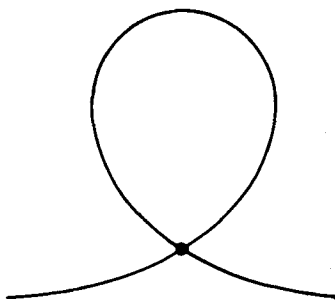


FIGURE 3 One loop contribution to  $G^{-1}(\vec{q}, t)$ .



Fluctuations at the one loop level depress  $T_{NAC}$  to zero, and any ordering that might occur for  $T > T_{NAC}$  will eliminate the Lifshitz point. The next section will show that a biaxial  $N'$  phase will always occur before  $T_{NAC} = 0$  is reached. It should be stressed at this point that the above results were derived using one loop self-consistent perturbation theory. There is no rigorous proof that  $T_{NAC}$  will remain zero in an exact theory when all loop contributions are retained. A Kosterlitz-Thouless type transition<sup>16</sup> is, for example, imaginable. The GT theory, however, rules out the existence of an  $n = 2, m = 2$  type NAC Lifshitz point in three dimensions.

### III. BIAxIAL ORDER

The molecules in nematic and smectic liquid crystals can conveniently be modeled as rigid rods with center of mass at positions  $\vec{x}^\alpha$  and unit vectors  $\vec{v}^\alpha$  along their long axes as shown in Figure 4. The deGennes order parameter  $Q_{ij}$ , for the nematic phase, can be constructed from  $\vec{v}^\alpha$ :

$$\rho Q_{ij}(\vec{x}) = \left\langle \sum_{\alpha} \left( v_i^\alpha v_j^\alpha - \frac{1}{3} \delta_{ij} \right) \delta(\vec{x} - \vec{x}^\alpha) \right\rangle, \quad (3.1)$$

where the sum is over all molecules  $\alpha$  and where  $\rho$  is the uniform mass density (not to be confused with  $m$  which is the mass density

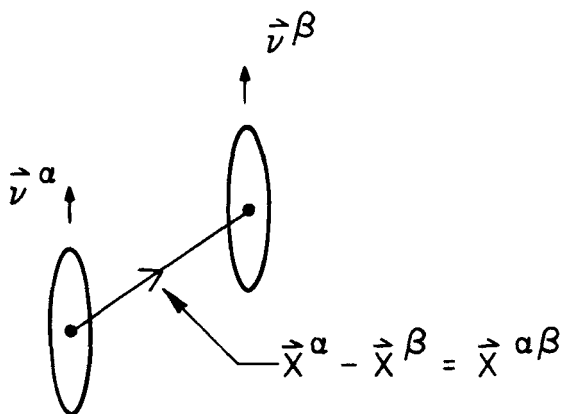


FIGURE 4 Schematic representation of two molecules  $\alpha$  and  $\beta$  in a nematic showing their local orientation vectors  $\vec{v}^\alpha$  and  $\vec{v}^\beta$  and the vector  $\vec{x}^{\alpha\beta}$  connecting their centers of mass.

with wave vector in the vicinity of  $\vec{q}_0$ ). Another symmetric traceless tensor order parameter  $P_{ij}$  can be constructed from the unit vectors

$$\vec{e}^{\alpha\beta} = \frac{\vec{x}^\alpha - \vec{x}^\beta}{|\vec{x}^\alpha - \vec{x}^\beta|} \quad (3.2)$$

connecting the centers of mass of molecules  $\alpha$  and  $\beta$ :

$$\rho P_{ij}(\vec{x}) = \left\langle \sum_{\alpha \neq \beta} \left( e_i^{\alpha\beta} e_j^{\alpha\beta} - \frac{1}{3} \delta_{ij} \right) f(\vec{x}^\alpha - \vec{x}^\beta) \delta \left[ \vec{x} - \frac{1}{2}(\vec{x}^\alpha - \vec{x}^\beta) \right] \right\rangle, \quad (3.3)$$

where  $f(\vec{x})$  is the pair correlation function that tends to zero at large  $\vec{x}$ .  $P_{ij}$  measures the degree to which there is alignment of the position vectors between neighboring molecules, i.e. it measures bond angle order.

If both  $Q_{ij}$  and  $P_{ij}$  are uniaxial matrices, they will have respective amplitudes  $S$  and  $P$  and principal axis vectors  $\vec{n}$  and  $\vec{e}$  so that

$$\begin{aligned} Q_{ij} &= S \left( n_i n_j - \frac{1}{3} \delta_{ij} \right), \\ P_{ij} &= P \left( e_i e_j - \frac{1}{3} \delta_{ij} \right), \end{aligned} \quad (3.4)$$

where

$$\begin{aligned} S &= \frac{3}{2} n_i Q_{ij} n_j = \frac{1}{2} \langle \langle 3 \cos^2 \theta^\alpha - 1 \rangle \rangle_m, \\ P &= \frac{3}{2} e_i P_{ij} e_j = \frac{1}{2} \langle \langle 3 \cos^2 \theta^{\alpha\beta} - 1 \rangle \rangle_p, \end{aligned} \quad (3.5)$$

where  $\theta^\alpha$  is the angle between  $\vec{v}^\alpha$  and  $\vec{n}$  and  $\theta^{\alpha\beta}$  the angle between  $\vec{e}$  and  $\vec{e}^{\alpha\beta}$ .  $\langle \rangle_m$  and  $\langle \rangle_p$  signify, respectively, averages over all molecules and pairs of molecules. In the nematic phase the principal axes of  $Q_{ij}$  and  $P_{ij}$  are parallel, i.e.  $\vec{e} = \vec{n}$ . In most nematics  $S$  is positive.  $P$ , however, can easily be either positive or negative depending on whether  $\vec{e}^{\alpha\beta}$  is more likely to be parallel or perpendicular to  $\vec{e}$  as shown in Figures 5a and 5b.

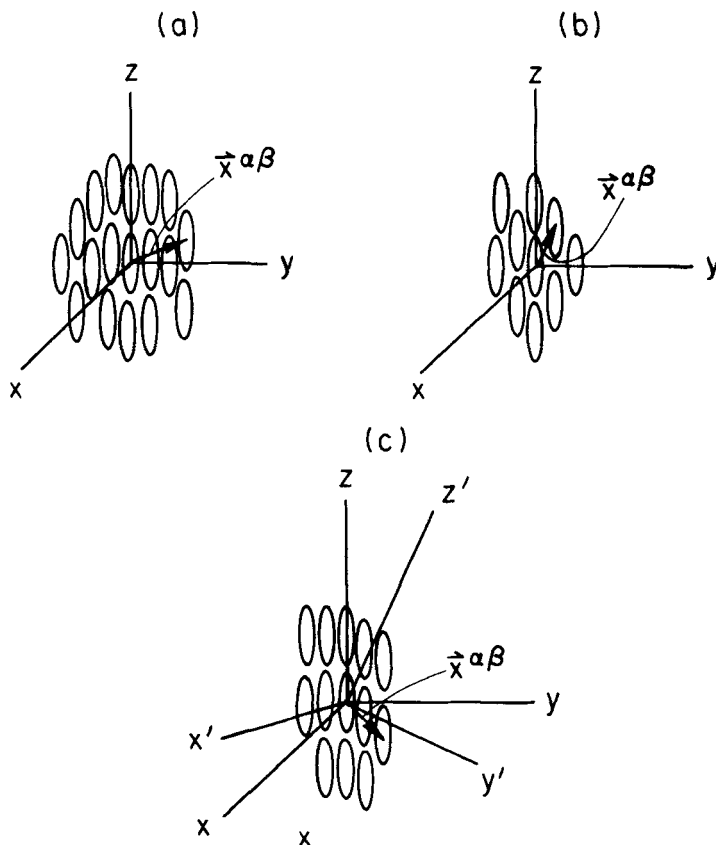


FIGURE 5 (a) Schematic representation of molecules in a nematic with  $P < 0$ .  $\vec{n}$  is along the z-axis and parallel to  $\vec{e}$ . The vector connecting the centers of mass of nearest neighbor molecules is more likely to have a large component in the plane perpendicular to  $\vec{n}$  than a large component parallel to  $\vec{n}$ .

(b) Molecules in a nematic with  $P > 0$ . Here the vector connecting nearest neighbor molecules has a large component along  $\vec{n}$ .

(c) Molecules in a biaxial nematic with  $\vec{n}$  and  $\vec{e}$  not parallel. There is a local structure similar to that in the C phase with the vector between nearest neighbors at an angle to  $\vec{n}$ .

When  $\vec{n}$  and  $\vec{e}$  are no longer parallel as shown in Figure 5c, the nematic phase becomes biaxial. A natural order parameter for the biaxial phase is

$$\vec{\eta} = \sin\theta \vec{e}_\perp = [1 - (\vec{n} \cdot \vec{e})^2]^{-1/2} \vec{e}_\perp, \quad (3.6)$$

where  $\vec{e}_\perp$  is a two dimensional unit vector perpendicular to  $\vec{n}$ . A

free energy for the  $N$  to  $N'$  transition can be obtained from the invariants that can be constructed from  $Q_{ij}$  and  $P_{ij}$ . For example

$$Q_{ij}P_{ji} = SP \left( \cos^2\theta - \frac{1}{3} \right) = SP \left( \frac{3}{2} - \eta^2 \right). \quad (3.7)$$

Here and in what follows, summation over repeated indices is understood. The LGW Hamiltonian for the  $N$ – $N'$  transition is thus

$$H_\eta = \int d^3x \left[ \frac{1}{2} r_\eta \eta^2 + u_\eta \eta^4 + \frac{1}{2} c_{ijkl} \nabla_i \eta_j \nabla_k \eta_l \right], \quad (3.8)$$

where

$$r_\eta = a_\eta (1 - T_{NN'}^0/T), \quad (3.9)$$

where  $T_{NN'}$  is the mean field  $NN'$  transition temperature and  $c_{ijkl}$  has three independent components whose precise form is irrelevant to the present discussion. In the absence of smectic ordering there will be a mean field  $NN'$  phase transition at  $T_{NN'}$ . In general, once  $\eta$  is non-zero, both  $Q_{ij}$  and  $P_{ij}$  become biaxial with three distinct principal axes requiring a modification of Eq. (3.4). The addition of biaxial contributions to  $Q_{ij}$  and  $P_{ij}$  will not alter the results presented here and will not be considered.

$P_{ij}$  couples to the smectic order parameter via gradient terms. For example

$$P_{ij} \nabla_i m \nabla_j m \rightarrow P \left[ (\vec{q} \cdot \vec{e})^2 - \frac{1}{3} q^2 \right] |m(\vec{q})|^2 \quad (3.10)$$

where

$$(\vec{q} \cdot \vec{e})^2 = (q_\parallel (1 - \eta^2)^{1/2} + \vec{q}_\perp \cdot \vec{\eta})^2 \approx q_\parallel^2 + 2q_\parallel \vec{q}_\perp \cdot \vec{\eta}. \quad (3.11)$$

Thus, coupling to  $P_{ij}$  will change the magnitudes of the parameters in  $H_0$  and introduce couplings between  $\vec{\eta}$  and  $m$ . To lowest order in  $\vec{\eta}$ ,

$$H_{m\eta} = -v \int \frac{d^3q}{(2\pi)^3} q_\parallel (\vec{q}_\perp \cdot \vec{\eta}) |m(\vec{q})|^2. \quad (3.12)$$

In general, higher order terms in  $\vec{\eta}$  must be included, especially if the neighborhood of the  $N'C$  transition is to be properly discussed.

The linear coupling in Eq. (3.12) is, however, adequate for most of the present discussion. The complete Hamiltonian for the  $NN'AC$  transition region is

$$H = H_\eta + H_{CL} + H_{m\eta}. \quad (3.13)$$

It is clear that  $T_{NN'} > T_{NAC} = 0$  so that there will always be a biaxial phase that appears in the vicinity of  $c_\perp = 0$  as depicted in Figure 2c. As will be shown shortly, the biaxial order of the  $N'$  phase removes the divergence that lead to  $T_{NAC} = 0$  so that there will be an  $N'-C$  transition at finite temperature. Note that  $c_\perp$  may be either positive or negative in the  $N'$  phase, and the x-ray scattering intensity can obtain quite different forms:

$$G_{N'}(\vec{q}, r) = [r + D_\parallel(q_\parallel^2 - q_0^2) + c_\perp q_\perp^2 + D_\perp q_\perp^4 + D_{\parallel\perp} q_\perp^2 (q_\parallel^2 - q_0^2) - vq_\parallel \vec{\eta} \cdot \vec{q}_\perp]^{-1} \quad (3.14)$$

When  $c_\perp > 0$ , the maximum of  $G_{N'}(\vec{q}, r)$  occurs at two points tilted off the  $\vec{n}$ -axis at  $\vec{q}_c = \pm q_0[\vec{n} + (v/2c_\perp)\vec{\eta}]$ . The angle  $\gamma = \tan^{-1}(v\eta/2c_\perp) \sim (v/2c_\perp)\eta$  that  $\vec{q}_c$  makes with  $\vec{n}$  is not in general equal to the angle  $\theta$  between  $\vec{n}$  and  $\vec{e}$ . The diffuse spot at  $\vec{q}_c$  is ellipsoidal in shape with widths along its three principal axes determined by correlation lengths  $\xi_1$ ,  $\xi_2$ , and  $\xi_3$ . The axes 1 and 2 with lengths  $\xi_1$  and  $\xi_2$  are mutually orthogonal and lie in the plane defined by  $\vec{n}$  and  $\vec{\eta}$  but are not necessarily parallel to either  $\vec{n}$  or  $\vec{\eta}$ . The third axis is perpendicular to the  $\vec{n}$ - $\vec{\eta}$  plane. To reiterate, when  $c_\perp > 0$ , the biaxial phase is obtained from the nematic phase merely by moving the diffuse scattering spot at  $\vec{q} = \vec{q}_0$  off the axis parallel to  $\vec{n}$  as shown in Figure 6(c).

When  $c_\perp > 0$ , the onset of biaxial order leads to a  $\cos\phi$  modulation in the diffuse scattering ring of the nematic phase as shown in Figure 6(d). The maximum intensity will occur at

$$\vec{q}_{\perp c} = q_{\perp 0} \frac{\vec{\eta}}{|\vec{\eta}|} + \frac{vq_0}{4|c_\perp|} \vec{\eta} + O(\eta_2). \quad (3.15)$$

As temperature is lowered, the harmonic content of the ring modulation increases (i.e.  $\cos n\phi$  terms for  $n = 2, 3, \dots$  become important) until eventually at the  $C$  phase, there is a quasi-Bragg spot off

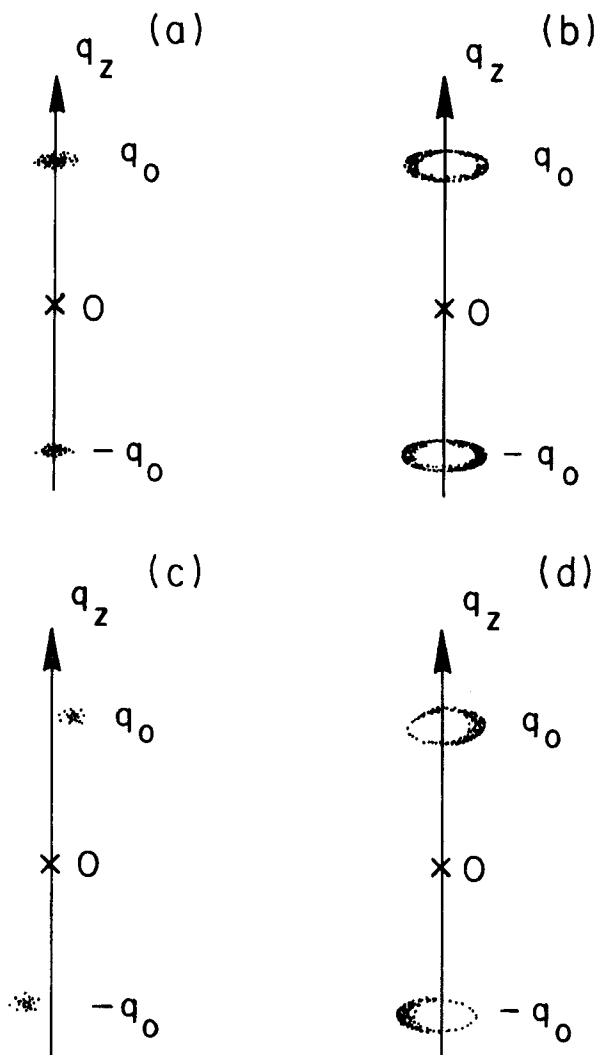


FIGURE 6 Schematic representation of the x-ray scattering intensity in (a) the  $N$  phase with  $c_{\perp} > 0$ , (b) the  $N$  phase with  $c_{\perp} < 0$ , (c) the  $N'$  phase with  $c_{\perp} < 0$ , and (d) the  $N'$  phase with  $c_{\perp} < 0$ . The  $z$ -axis is parallel to  $\vec{n}$ .

axis. When  $c_{\perp} = 0$ , a diffuse spot moves off axis as for  $c_{\perp} > 0$ , but more rapidly with increasing  $\vec{\eta}$ :

$$q_{\perp c} = \left( \frac{aq_0}{4D_{\perp}} |\vec{\eta}| \right)^{1/3} \frac{\vec{\eta}}{|\vec{\eta}|}. \quad (3.16)$$

It is now straightforward to see why  $T_{N'C}$  is non-zero. The equation determining  $T_{N'C}$  to one loop order has exactly the same form as Eq. (2.6) with  $G(\vec{q}, t)$  replaced by  $G_{N'}(\vec{q}, t)$ .  $G_{N'}(\vec{q}, t)$  has a maximum at a single value of  $\vec{q} = \vec{q}_c = (q_{\perp c}, q_0)$  for a given sign of  $q_{\parallel}$ . Thus  $G_{N'}^{-1}(\vec{q}, t) = t + 1/2 M_{ij} k_i k_j$  where  $\vec{k} = \vec{q} - \vec{q}_c$  and  $M_{ij} = \partial^2 G_{N'} / \partial q_i \partial q_j |_{\vec{q} = \vec{q}_c}$  has three positive eigenvalues. In Eq. (2.7) a similar expansion for  $G$  leads to  $M_{ij}$  with two zero eigenvalues when  $c_{\perp} = 0$ . Thus the integral in Eq. (2.6) is convergent if  $G$  is replaced by  $G_{N'}$ . A possible phase diagram is shown in Figure 2c. The present analysis cannot determine when first order transitions occur. It does, however, predict an  $NN'AC$  tetracritical point in agreement with GT.

If the  $N'$  phase exists, it will presumably be difficult to obtain single crystal alignment. X-ray scattering will see a powder average of  $G_{N'}(\vec{q}, r)$ . When only linear terms in  $\eta$  are included as in Eq. (3.14) the powder average integral over can be done analytically:

$$\begin{aligned} \overline{G} &= \int \frac{d\phi}{2\pi} G_{N'}(\vec{q}, r) \\ &= [r^2(\vec{q}) - v^2 q_{\parallel}^2 q_{\perp}^2 \eta^2]^{-1/2} \end{aligned} \quad (3.17)$$

where  $r(\vec{q})$  is defined in Eq. (2.4). This scattering form is similar to that proposed by Andereck and Patton.<sup>17</sup> When  $c_{\perp} < 0$ , Eq. (3.16) will be difficult to distinguish from the intensity of the CL model [Eq. (2.4)]. When  $c_{\perp} > 0$ , this is exactly the form obtained by Chu and MacMillan<sup>9,18</sup> for the scattering intensity in the  $N$ -phase above the  $C$ -phase.

#### IV. DISCUSSION

The  $NAC$  multicritical point like the  $NA$  transition remains incompletely understood. Present theory does not easily admit the possibility that the  $NAC$  point is a true Lifshitz critical point at which second order  $xy$ -like  $NA$  and  $AC$  lines meet a first order  $NC$  line. The dislocation melting treatment of GT categorically rules out this possibility if the specific heat exponents  $\alpha$  of the  $NA$  and  $AC$  line are negative as theories based on symmetries and universality class arguments would have them be. The fluctuation corrected treatment of the CL model with bond angle order presented here strongly supports the GT theory. X-ray experiments<sup>1</sup> strongly support the Lifshitz-like character of the  $NAC$  point with  $c_{\perp}$  going to zero along a line that passes through the  $NAC$  point. Though the experimental sin-

gularities in the heat capacity along the *NA* line are consistent with  $\alpha$  slightly negative,<sup>5</sup> those along the *AC* line consistently yield a positive  $\alpha$ . This suggests other scenarios for the *NAC* point that have not as yet received careful theoretical attention. The first is that the *NAC* point is in fact a critical endpoint with a tricritical point along the *AC* line near the *NAC* point. This is the scenario predicted by the mean field theories of Ref. 6 and 10. These theories do not, however, address the nature of the x-ray scattering intensity in the nematic phase. In their present form, they do not predict a  $c_{\perp} = 0$  line. Theoretical study of a model in which there is both a critical endpoint and a  $c_{\perp} = 0$  line is clearly called for. Though the critical endpoint scenario is not theoretically forbidden, it is not strongly supported by experiment in that a tricritical point on the *AC* line near the *NAC* point has not definitely been identified. Another possibility is that the *AC* tricritical point and the *NAC* point actually coincide. It is not completely clear whether this is an acceptable theoretical scenario since the *AC* transition would presumably be second order with  $\alpha < 0$  all of the way up to the tricritical point leading to the prediction of a tetracritical point with arguments similar to those of GT. A one loop calculation similar to that presented here would also appear to rule out this possibility. In addition, one would have to explain why the *NAC* Lifshitz point and the *AC* tricritical point always coincide. If they coincide only because of accidental values of potential, the apparent universality of the *NAC* behavior would be difficult to explain. If there is some symmetry reason why the two point coincide, it has yet to be found.

In conclusion, theory still prefers the appearance of a biaxial *N'* phase in the vicinity where the *N*, *A*, and *C* phases meet. Though there is no experimental evidence that the *N'* phase exists, there is also no strong experimental support for the alternate scenario accepted by theory that the *NAC* point is a critical endpoint in the vicinity of an *AC* tricritical point. It is possible that the final cause of the discrepancy between theory and experiment is our incomplete understanding of the *NA* transition. If it should turn out that the specific heat exponent for the *NA* transition really is positive, then the GT theory would predict a bicritical rather than a tetracritical point where the *N*, *A* and *C* phases meet.

### Acknowledgments

The author is grateful for informative discussions with C. Garland, R. J. Birgeneau, M. A. Anisimov and C. C. Huang. This work was supported in part by the National Science Foundation under Grant No. DMR 85-19216.



## References

1. L. J. Martinez-Miranda, A. R. Kortan and R. J. Birgeneau, *Phys. Rev. Lett.*, **56**, 2264 (1986).
2. L. Soloman and J. D. Litster, *Phys. Rev. Lett.*, **56**, 2268 (1986).
3. D. Brisbin, D. L. Johnson, H. Fellner, Nd M. E. Meubert, *Phys. Rev. Lett.*, **50**, 178 (1983); S. Shashidhar, B. K. Ratna and S. Krishna Prasad, *Phys. Rev. Lett.*, **53**, 2141 (1984).
4. D. Johnson, D. Allender, R. DeHoff, C. Maxe, E. Oppenheim and R. Reynolds, *Phys. Rev.*, **B16**, 470 (1977); G. Sigaud, F. Hardouin and M. F. Achard, *Solid State Commun.*, **23**, 35 (1977); R. De Hoff, R. Biggers, D. Brisbin and D. L. Johnson, *Phys. Rev.*, **A25**, 472 (1982).
5. M. A. Anisimov, V. P. Voronov, A. O. Kulkov and F. Kholomurodov, *J. Physique (Paris)*, **46**, 2137 (1985); C. W. Garland and M. Huster (MIT preprint).
6. C. C. Huang and S. C. Lien, *Phys. Rev. Lett.*, **47**, 1917 (1981).
7. C. C. Huang and J. M. Viner, *Phys. Rev.*, **A25**, 3385 (1982); R. J. Birgeneau, C. W. Garland, A. R. Kortan, J. D. Litster, M. Meichle, B. M. Ocko, C. Rosenblatt, L. Yu and J. Goodby, *Phys. Rev.*, **A27**, 1251 (1983).
8. J. Chen and T. C. Lubensky, *Phys. Rev.*, **A14**, 1202 (1976).
9. K. C. Chu and W. L. McMillan, *Phys. Rev.*, **A15**, 1181 (1977).
10. L. Benguigui, *J. Phys. Colloq.*, **40**, C3-222 (1979).
11. P. Bak and R. Bruinsma, *Phys. Rev. Lett.*, (Comments) **54**, 1731 (1985); G. Grinstein and J. Toner, *Phys. Rev. Lett.*, (Comments) **54**, 1732 (1985).
12. G. Grinstein and J. Toner, *Phys. Rev. Lett.*, **51**, 2386 (1983).
13. R. M. Hornreich, M. Luban and S. Shtrikman, *Phys. Rev. Lett.*, **35**, 1678 (1975); D. Mukamel and M. Luban, *Phys. Rev.*, **B18**, 3631 (1978).
14. S. A. Brazovskii, *Sov. Phys. JETP* **41**, 85 (1975); J. Swift, *Phys. Rev.*, **A14**, 2274 (1976).
15. J. Sak and G. S. Grest, *Phys. Rev.*, **B17**, 3602 (1978).
16. J. M. Kosterlitz and D. J. Thouless, *J. Phys.*, **C6**, 1181 (1973); J. M. Kosterlitz, *ibid.*, 1046 (1974).
17. B. S. Anderreck and B. R. Patton, (Ohio State preprint).
18. It should be noted, however, that the Chu-Macmillan treatment of the tilt order parameter is inconsistent. They argue that it is only defined once the smectic layering is established, and, therefore, do not consider the possibility of a biaxial nematic phase with tilt but no layering. Nevertheless, in the nematic phase, they calculate the x-ray scattering intensity as though there were long range biaxial order. A consistent treatment of the tilt order parameter in the Chu-Macmillan model would in fact lead to a biaxial nematic phase with the scattering intensity of Eq. (3.17). The scattering intensity of the nematic phase would be that of Eq. (2.4) with  $D_{\perp} = 0$  and  $D_{\parallel} = 0$ .