

## Thermotropic biaxial nematic liquid crystals: Spontaneous or field stabilized?

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An intermediate nematic phase is proposed for the interpretation of recent experimental results on phase biaxiality in bent-core nematic liquid crystals. The phase is macroscopically uniaxial but has microscopic biaxial, and possibly polar, domains. Under the action of an electric field, the phase acquires macroscopic biaxial ordering resulting from the collective alignment of the domains. A phenomenological theory is developed for the molecular order in this phase and for its transitions to purely uniaxial and to spontaneously biaxial nematic phases. © 2008 American Institute of Physics.  
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### I. INTRODUCTION

Since their theoretical prediction,<sup>1</sup> biaxial nematics have been a constant challenge in liquid crystal (LC) research.<sup>2–15</sup> They differ from the common, uniaxial, nematics in that they exhibit additional orientational order of the molecules along a second macroscopic direction, the “short” axis **m**, perpendicular to the primary nematic director **n**. The expectation that the response of **m** to an applied electric field could be much faster than that of **n** has been sustaining a constant practical interest in low molecular mass biaxial thermotropic nematic LCs (i.e., the biaxial analogs of the conventional nematic LCs used in electro-optic applications). However, it was only recently that strong experimental evidence has been produced for the discovery of such biaxial nematics, first in bent-core systems<sup>16–18</sup> and shortly afterward in laterally substituted tetrapode nematogens.<sup>19</sup>

Subsequent electro-optic switching experiments<sup>20</sup> on the bent-core biaxial nematics demonstrated that the response of **m** to an applied field is indeed much faster than that of **n**. Interestingly, the interpretation of these switching experiments suggests (a) the existence of a high temperature uniaxial nematic phase with practically no biaxial response to an applied electric field and (b) a transition to a low temperature nematic phase which is optically uniaxial and can be brought to a biaxial state by applying an electric field perpendicular to **n**. As the electric fields involved (a few V/μm) are too low to produce a substantial effect directly on the orientations of individual molecules, it is reasonable to attribute the field-induced biaxial state to the preferential alignment of the **m** axes of pre-existing biaxial molecular aggregates (domains or clusters) which, in the absence of an applied field, are uniaxially distributed about **n**. Electric fields of similar strength have been used to switch the **m** director in the x-ray diffraction (XRD) experiments of Ref. 17.

The spinning-sample NMR experiments in Ref. 16 do not involve electric fields but there, the strong external mag-

netic field **H**, when not collinear with the **n** director, would orient the **m** axis (here identified with the direction of smallest diamagnetic susceptibility of the phase) perpendicular to the plane formed by **n** and **H**. Consequently, it is possible that the static sample consists of biaxial domains with their **m** axes uniaxially distributed about a common **n** director (parallel to **H**) and that a macroscopic alignment of the domain **m** axes results from spinning the sample about an axis perpendicular to **H**.

Recent atomistic simulations of nematics made of bent-core molecules<sup>21</sup> indicate the existence of biaxial domains. In general, such domains exhibit dielectric as well as diamagnetic biaxiality and would therefore be readily oriented by external fields. In fact, the domains in Ref. 21 exhibit local ferroelectric (i.e., biaxial and polar) nematic ordering. This endows the domains with a net electric polarization which could also macroscopically orient them in an external field. Dielectric fluctuation studies in the uniaxial nematic phase of bent-core liquid crystals suggest the formation of cybotactic (smectic-like) clusters<sup>22</sup> and, in one instance,<sup>23</sup> randomly oriented nanodomains of anticlinic ferroelectric ordering are proposed for the structure of an optically isotropic phase obtained upon cooling from the nematic. Cybotactic biaxial clusters are clearly identified in XRD studies of calamitic multipole nematics for which the low temperature phases are columnar.<sup>24</sup> Lastly, molecular dynamics simulations of transverse switching in biaxial nematics by an electric field<sup>25</sup> suggest that the switching mechanism involves the reorientations of localized biaxial domains, with intermediate disruption of the long-range biaxial ordering. The above considerations suggest that the existence of uniaxial phases with biaxial clusters and the possibility of field-induced alignment of the clusters might be of key relevance to understanding phase biaxiality in thermotropic nematics. Notably, the existence of locally ordered structures has been invoked in the description of liquid-liquid phase transitions.<sup>26</sup>

An alternative way to view the aligning effect of the external field is in terms of the orientational fluctuations of **m**. The hypothesis that these fluctuations are extensive enough to destroy the spontaneous long-range alignment of

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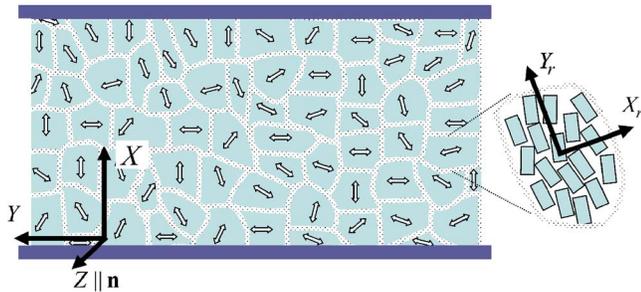


FIG. 1. (Color online) Cross section of a nematic sample between two parallel plates, illustrating the biaxial clusters; the double arrows indicate the  $\mathbf{m}$  axes of the latter. The plates are parallel to the  $YZ$  plane and their rubbing directions, coinciding with the director  $\mathbf{n}$  and the macroscopic  $Z$  axis, are taken normal to the plane of the figure.

the  $\mathbf{m}$  axis has been used<sup>2</sup> as a possible explanation as to why thermotropic biaxial nematics are not commonly observed in experiments. On the other hand, in analogy with what is known from the elastic continuum theory of uniaxial nematics,<sup>27</sup> the application of an external field would quench the low wave-vector orientational fluctuation modes of the  $\mathbf{m}$  axis. Thus, a possible interpretation of the observed field-induced transition to a biaxial state is through the quenching of the low-energy orientational fluctuation modes. However, estimates of cluster sizes and time scales of their reorientational motions indicate that a continuum treatment of the biaxial fluctuations may not be applicable. In any case, the conventional static formulation of the free energy of the nematic phase solely in terms of long-range orientational order parameters refers to a uniformly ordered system and can therefore convey neither the cluster nor the continuum fluctuation picture. In this paper, we introduce a phenomenological description that allows explicitly for nonuniformity of the biaxial orientational order in a thermotropic nematic phase. The formulation is based on the biaxial cluster picture, allowing for a full range of cluster sizes, from single molecule to macroscopic aggregates, thus avoiding the inherent size limitations of a continuum treatment.

The model system and the order parameters on which the phenomenological description is based are introduced in Sec. II. The Landau–deGennes free energy expansion is formulated and the different nematic phases it describes are presented in Sec. III. The effects of an applied electric field are studied in Sec. IV. The results of this work are summarized and their significance and limitations are discussed in Sec. V.

## II. BIAXIAL CLUSTERS AND ORDER PARAMETERS

To identify the relevant order parameters in a phase with local biaxial nematic order, we consider a nematic sample of  $N$  molecules in a volume  $V$  at temperature  $T$  with the director  $\mathbf{n}$  perfectly aligned along the  $Z$  macroscopic axis. Practically, the sample may be pictured (see Fig. 1) as filling the space between parallel plates, with the  $Z$  axis defining the rubbing direction that aligns the director  $\mathbf{n}$  on the plate surfaces. The  $X$  macroscopic axis is chosen to be perpendicular to the plates. For simplicity, we further assume that the molecules are themselves perfectly aligned with their major axis  $z$  par-

allel to the director  $\mathbf{n}$ . This restricts the local biaxial  $\mathbf{m}$  axis and the molecular axes  $x, y$  to be perpendicular to the  $Z$  axis. We also assume that the sample-confining surfaces have no aligning influence on the  $\mathbf{m}$  axis.

We assign to each molecule  $i=1, 2, \dots, N$  in the sample a traceless second rank molecular tensor  $\hat{\mathbf{q}}^i$  which, in the principal frame of molecular axes  $x_i, y_i, z_i \parallel Z$ , may be taken to have the components  $q_{xx}^i = -q_{yy}^i = 1$  and  $q_{zz}^i = 0$ . Long-range biaxial order in the sample is described by the macroscopic second rank tensor  $\langle \hat{\mathbf{q}} \rangle$  representing the ensemble average (denoted by the angular brackets) of the superposition of these molecular tensors, defined by

$$\hat{\mathbf{q}} \equiv \frac{1}{N} \sum_{i=1}^N \hat{\mathbf{q}}^i. \quad (1)$$

In its principal axis frame  $X, Y, Z$ , this tensor has the two nonvanishing components  $\langle q_{XX} \rangle = -\langle q_{YY} \rangle = q$ . The quantity  $q$ , which measures the extent of phase biaxiality, can be expressed as an ensemble average of the molecular orientations

$$q = \frac{1}{N} \left\langle \sum_{i=1}^N \cos 2\alpha_i \right\rangle, \quad (2)$$

with  $\alpha_i$  denoting the angle of the molecular axis  $x_i$  relative to the principal axis  $\mathbf{m}$  of the phase. The direction of the latter axis is defined by the condition  $\langle \sum_{i=1}^N \sin 2\alpha_i \rangle = 0$  and is identified with the  $X$  macroscopic axis. Obviously,  $0 \leq |q| \leq 1$ . The rotationally invariant quantities that can be formed from the components of  $\langle \hat{\mathbf{q}} \rangle$  are the powers of the scalar product  $\langle \hat{\mathbf{q}} \rangle : \langle \hat{\mathbf{q}} \rangle \equiv \langle q_{AB} \rangle \langle q_{AB} \rangle = 2q^2$ , with the indices  $A, B, \dots = X, Y, Z$  denoting Cartesian tensor components and summation over repeated indices implied. Due to the assumed restriction of the molecular  $z$  axis along the macroscopic  $Z$  direction, the higher order invariants  $\langle q_{AB} \rangle \langle q_{BC} \rangle \langle q_{CA} \rangle$ ,  $\langle q_{AB} \rangle \times \langle q_{BC} \rangle \langle q_{CD} \rangle \langle q_{DA} \rangle$ , etc., vanish.

Although a state of the sample described by the value  $q=0$  has no macroscopic biaxial order, it could consist of domains in which the molecules are biaxially ordered. To quantitatively describe this possibility, we consider an instantaneous grouping of the  $N$  molecules of the sample into a number  $R (\leq N)$  of clusters, each labeled by an index  $r$  and containing  $n_r$  molecules in a volume  $v_r$ . The grouping, to be specified in quantitative terms below, is understood to observe the internal connectivity of the cluster volumes and the additivity of the cluster populations and volumes. Thus, the variations of  $R$ ,  $n_r$ , and  $v_r$  in the equilibrium ensemble are subject to the additivity constraints  $\sum_{r=1}^R n_r = N$ ;  $\sum_{r=1}^R v_r = V$ . For each cluster, an ordering tensor  $\hat{\mathbf{q}}^{(r)}$  can be defined in terms of the tensors  $\hat{\mathbf{q}}^i$  associated with the molecules in the cluster

$$\hat{\mathbf{q}}^{(r)} = \frac{1}{n_r} \sum_{i=1}^{n_r} \hat{\mathbf{q}}^i. \quad (3)$$

In its principal axis frame  $X_r, Y_r, Z_r \parallel Z$ , the tensor  $\hat{\mathbf{q}}^{(r)}$  has two nonvanishing components that can be expressed in terms of a single quantity  $q^{(r)} (= q_{X_r X_r}^{(r)} = -q_{Y_r Y_r}^{(r)})$  measuring the biaxiality

of the orientational distribution of the molecules within the cluster. Specifically,

$$q^{(r)} = \frac{1}{n_r} \sum_{i=1}^{n_r} \cos 2\alpha_{i,r}, \quad (4)$$

with  $\alpha_{i,r}$  denoting the angle of the molecular axis  $x_i$  relative to the principal axis  $X_r$  of the cluster. The latter axis is determined by the condition  $\sum_{i=1}^{n_r} \sin 2\alpha_{i,r} = 0$  and is taken to define the direction of the short axis  $\mathbf{m}^{(r)}$  of the cluster. Clearly,  $|q^{(r)}| \leq 1$  and the basic rotationally invariant that can be formed from the tensor of a single cluster is  $\overline{\mathbf{q}}^{(r)} : \overline{\mathbf{q}}^{(r)} = 2(q^{(r)})^2$ .

From the assumed additivity of cluster populations and from the definitions in Eqs. (1) and (3), it follows that the tensor  $\overline{\mathbf{q}}$  can be simply expressed as the ensemble average of a weighed sum over the cluster tensors  $\overline{\mathbf{q}}^{(r)}$ , with cluster weight  $w_r \equiv n_r/N$ , i.e.,

$$\overline{\mathbf{q}} = \left\langle \sum_{r=1}^R w_r \overline{\mathbf{q}}^{(r)} \right\rangle. \quad (5)$$

This relation leads to the following expression of the long-range biaxiality measure  $q$  in terms of the cluster ordering measures  $q^{(r)}$  and the cluster orientations within the macroscopic sample,

$$q = \left\langle \sum_{r=1}^R w_r q^{(r)} \cos 2\phi_r \right\rangle, \quad (6)$$

where  $\phi_r$  denotes the angle of the cluster short axis  $\mathbf{m}^{(r)}$  relative to the macroscopic short axis  $\mathbf{m}$ .

The validity of the expressions in Eqs. (5) and (6) is independent of the particular way in which the sample is partitioned into clusters. It is clear from Eq. (6) that the absence of macroscopic biaxiality in the sample can be due either to the complete absence of local biaxial order ( $q^{(r)}=0$ ) or to the statistically uniform (i.e., uniaxially symmetric about the  $Z$  axis) distribution of the  $\mathbf{m}^{(r)}$  axes of locally biaxial structures ( $q^{(r)} \neq 0$ ). In other words, the defining condition of a macroscopically uniaxial sample,  $q=0$ , is not sufficient to differentiate between the presence and the absence of local biaxial ordering. However, to quantify such differentiation, it is necessary to have a quantitative definition of the partitioning of each accessible microstate of the sample into clusters.

In a continuum approach, the necessity for a quantitative definition of the clusters is in effect bypassed as it is assumed that each elementary volume  $d\mathbf{r}$  of the sample contains a large number of molecules, with local density  $\rho(\mathbf{r})$  and biaxial order tensor  $\overline{\mathbf{q}}(\mathbf{r})$  having principal value  $q(\mathbf{r})$  and local axis  $\mathbf{m}(\mathbf{r})$ . The macroscopic biaxiality tensor of Eq. (5) is then given by  $\overline{\mathbf{q}} = 1/N \int_V d\mathbf{r} \rho(\mathbf{r}) \overline{\mathbf{q}}(\mathbf{r})$ , with principal values  $\pm q, 0$  and principal axis  $\mathbf{m}$ . With  $\phi(\mathbf{r})$  denoting the angle of the local axis  $\mathbf{m}(\mathbf{r})$  relative to  $\mathbf{m}$ , the principal value  $q$  is, according to Eq. (6), expressed as the spatial average  $q = 1/N \int_V d\mathbf{r} \rho(\mathbf{r}) q(\mathbf{r}) \cos(2\phi(\mathbf{r}))$  and the extent of local biaxial order over the entire sample is quantified by the rotationally invariant quantity

$$\overline{q^2} = \frac{1}{2N} \int_V d\mathbf{r} \rho(\mathbf{r}) \overline{\mathbf{q}}(\mathbf{r}) : \overline{\mathbf{q}}(\mathbf{r}). \quad (7)$$

Clearly, a macroscopically biaxial state,  $q \neq 0$ , can only be obtained if  $\overline{q^2} \neq 0$ . In that case, ignoring fluctuations in the density and in the local principal values  $q(\mathbf{r})$  by setting  $\rho(\mathbf{r}) \approx N/V$  and  $q(\mathbf{r}) \approx \sqrt{\overline{q^2}}$  throughout the sample, one has  $q \approx \sqrt{\overline{q^2} \langle \cos 2\phi \rangle}$ , with

$$\langle \cos 2\phi \rangle \equiv \frac{1}{V} \int_V d\mathbf{r} \cos 2\phi(\mathbf{r}). \quad (8)$$

Accordingly, in this approximation,  $\overline{q^2}$  can be used as the order parameter for the local biaxial order and  $\langle \cos 2\phi \rangle$  can be used as the order parameter for the long-range biaxial order. Lastly, the general quadratic form of the invariants that can be obtained from  $\overline{\mathbf{q}}(\mathbf{r})$  is

$$G = \int d\mathbf{r} \int d\mathbf{r}' q_{AB}(\mathbf{r}) G_{AB:A'B'}(\mathbf{r}, \mathbf{r}') q_{A'B'}(\mathbf{r}'), \quad (9)$$

where the fourth rank symmetric tensor  $G_{AB:A'B'}(\mathbf{r}, \mathbf{r}')$  can be constructed from the position variables  $\mathbf{r}, \mathbf{r}'$  and the local principal axes  $\mathbf{m}(\mathbf{r}), \mathbf{m}(\mathbf{r}')$ . In particular, choosing the form  $G_{AB:A'B'}(\mathbf{r}, \mathbf{r}') \sim \delta_{A,A'} \delta_{B,B'} \rho(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')$  gives the invariant  $\overline{q^2} \neq 0$  of Eq. (7), while the generic form  $G_{AB:A'B'}(\mathbf{r}, \mathbf{r}') \sim \rho(\mathbf{r}) \rho(\mathbf{r}') K_{AB:A'B'}^{CC'} \partial_C \partial_{C'} \delta(\mathbf{r} - \mathbf{r}')$ , gives the various gradient terms, which, for constant  $\rho(\mathbf{r})$  and  $q(\mathbf{r})$ , reduce to the biaxial analogs of the gradient terms in the elastic deformation free energy of the uniaxial nematic continuum.<sup>27</sup>

To address the possibility of phase transitions between uniaxial nematic phases differing in the local biaxial order, one has to consider clusters containing a small number of molecules, down to the limit of single-molecule "clusters." In this case, the continuum formulation, being based on clusters containing a large number of molecules, becomes inadequate. On the other hand, the description of the biaxial ordering in a cluster solely in terms of the rotational invariant  $(q^{(r)})^2$ , i.e., without cluster-size discrimination, runs into difficulties when cluster size is reduced. For example, a cluster containing a single molecule has, according to Eq. (4), the same value,  $(q^{(r)})^2 = 1$ , with a cluster containing any number of molecules in perfect biaxial ordering. For a physically sensible description, it is therefore necessary to combine cluster ordering  $q^{(r)}$  with cluster size  $n_r$ . A simple way to achieve this, within the present simplified phenomenological framework, is by defining the following rotationally invariant quantity for each possible partitioning  $\{r\}$  of a microstate of the sample into clusters:

$$\sigma\{r\} = \frac{1}{N-1} \sum_{r=1}^R [n_r (q^{(r)})^2 - 1]. \quad (10)$$

Obviously,  $\sigma\{r\}$  depends on the size of the clusters and their degree of internal biaxial ordering. It strictly vanishes if each cluster contains a single molecule ( $n_r=1; R=N$ ) and takes the highest possible value  $\sigma\{r\}=1$  if the sample consists of a single cluster containing all the  $N$  molecules ( $n_r=N; R=1$ ) with their axes  $x, y$  perfectly aligned along  $X, Y$ , respectively. Clusters consisting of uniaxially distributed molecules

( $q^{(r)}=0$ ;  $n_r > 1$ ) contribute negative values to  $\sigma\{r\}$  while for a sample consisting of  $R$  perfectly ordered clusters (i.e.,  $q^{(r)}=1$  for  $r=1, 2, \dots, R$ ), Eq. (10) gives  $\sigma\{r\}=(N-R)/(N-1)$ .

Denoting by  $\sigma\{\bar{r}\}$  the maximal value that can be obtained from Eq. (10) for any of the different possible ways of partitioning the given microstate of the  $N, V, T$  ensemble into clusters, one may define the cluster order parameter  $\sigma$  as the ensemble average  $\sigma \equiv \langle \sigma\{\bar{r}\} \rangle$ . It follows directly from Eq. (10) that, for the maximization of  $\sigma\{r\}$ , two adjacent clusters with respective tensors  $\hat{\mathbf{q}}^{(r)}$ ,  $\hat{\mathbf{q}}^{(r')}$  and molecular populations  $n_r, n_{r'}$  will merge into a single cluster of  $n_r+n_{r'}$  molecules if  $\frac{1}{2}(\hat{\mathbf{q}}^{(r)}-\hat{\mathbf{q}}^{(r')}) : (\hat{\mathbf{q}}^{(r)}-\hat{\mathbf{q}}^{(r')}) < 1/n_r+1/n_{r'}$ . The reversal of this inequality states the condition for a cluster to be divided into two smaller clusters. Clearly,  $0 \leq \sigma \leq 1$  and, according to its definition and Eq. (10), the order parameter  $\sigma$  will acquire nonvanishing values only if  $\langle \sum_{r=1}^R w_r (q^{(r)})^2 \rangle > 1/n$ , with  $n \equiv N/(R)$  denoting the average cluster size in the ensemble. Therefore, in a thermodynamic state favoring small and not strongly biaxial clusters, the vanishing of  $\sigma$  does not exclude the possibility of long-range biaxiality with order parameter  $|q| < 1/n$ . On the other hand, in states favoring sufficiently large clusters ( $n \gg 1$ ), the order parameter  $\sigma$  tends to the invariant  $\bar{q}^2$  in Eq. (7) and, therefore, the continuum description can be applied in this case.

### III. PHENOMENOLOGICAL FREE ENERGY EXPANSION

With  $\sigma$  and  $q$  taken to be the basic order parameters associated with biaxiality in the clusters and in the macroscopic sample, respectively, a phenomenological Landau–deGennes expansion of the free energy can be formulated in terms of powers of  $\sigma$ ,  $q^2$ , and of contributions from possible interactions with external fields. The electrostatic interaction of the biaxial medium with an applied electric field  $\mathbf{E}$ , taken to have components  $E_x=E$ ,  $E_y=E_z=0$ , is conveyed to lowest order in  $q$  by the rotationally invariant term  $h\mathbf{E} \cdot \langle \hat{\mathbf{q}} \rangle \cdot \mathbf{E} = hE^2q$ , where the scalar factor  $h$  reflects the magnitude of the molecular polarizability anisotropy in the  $x, y$  molecular plane. Accordingly, the leading terms in the expansion of the free energy per molecule, in the presence of an external electric field will be

$$F = a\sigma + \frac{b}{2}\sigma^2 + \frac{g}{3}\sigma^3 + \frac{c}{2}q^2 + \frac{d}{4}q^4 - e\sigma q^2 - hE^2q. \quad (11)$$

Considering  $\sigma$  as the primary order parameter, the coefficient  $a$  is taken to be an increasing function,  $a(T)$ , of the temperature. The other coefficients  $b, c, d, e, h, g$  are assumed to be insensitive to variations of temperature and positive, with the exception of  $b$ , for which both signs are considered. The  $c$  and  $d$  terms are dominated by the entropic drop associated with the long-range biaxial ordering and the  $e$  term conveys the mutual favoring of the local ordering of the individual clusters ( $\sigma$ ) and of their collective ordering ( $q$ ). The interactions among adjacent clusters are assumed in this expansion to be adequately described in terms of  $\sigma$  and  $q$ .

In the absence of an external field ( $E=0$ ), the free energy in Eq. (11) describes three possible nematic phases: (i) A high temperature “proper” nematic phase ( $N_u$ ), in which  $\sigma$

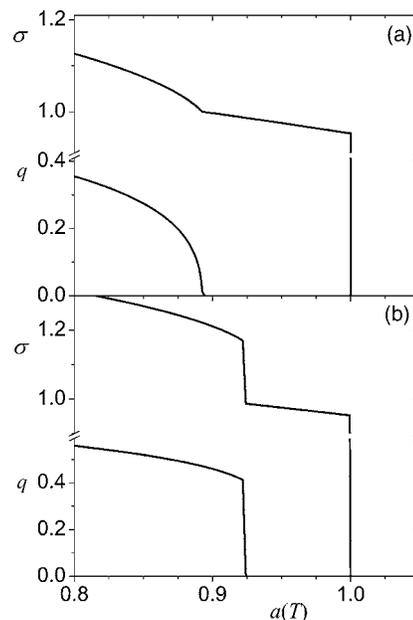


FIG. 2. (a) Plots of the temperature dependence of the calculated order parameters for  $\lambda=1.05$  and  $u=0.5$ ; (b) as in the previous plot but for  $u=0.75$ . The cluster order parameter  $\sigma$  is expressed in units of  $\sigma_c$ , the biaxiality order parameter  $q$  in units of  $\sqrt{c/d}$ . The temperature function  $a(T)$  is scaled by the constant  $a^*=3b^2/16g$ .

$=q=0$ ; (ii) an intermediate, macroscopically uniaxial, nematic phase ( $N_u^{(bc)}$ ) formed by uniaxially distributed biaxial clusters ( $bc$ ), in which  $\sigma > 0$  and  $q=0$ ; (iii) a low temperature, macroscopically biaxial, phase ( $N_b^{(bc)}$ ) formed by aligned biaxial clusters, in which  $\sigma > 0$  and  $q \neq 0$ . Depending on the sign of the coefficient  $b$ , the  $N_u \leftrightarrow N_u^{(bc)}$  phase transition can be of first order (for  $b < 0$ ) or second (for  $b > 0$ ).

The transition to the  $N_b^{(bc)}$  phase is controlled by the values of the parameters  $\lambda=2cg/3|b|e$  and  $u=2e^2/|b|d$ . For  $\lambda > 1$ , the transition to  $N_b^{(bc)}$  occurs from the intermediate  $N_u^{(bc)}$  phase and is of the first or second order, depending on whether  $u$  is, respectively, larger or smaller than  $1+3\lambda/2$ . For  $\lambda < 1$ , the  $N_u^{(bc)}$  phase is removed from the sequence and a direct, first order,  $N_u$  to  $N_b^{(bc)}$  phase transition is obtained. A thorough presentation of the dependence of the phase diagram on the possible values of the expansion coefficients is given in Ref. 28. Here, we focus our attention on the combination  $b < 0$  and  $\lambda$  slightly above 1, which, as shown below, is directly relevant to the observed biaxial electro-optic response of the bent-core nematics and to the associated nematic-nematic phase transitions.<sup>20</sup> In this case, the first order  $N_u \leftrightarrow N_u^{(bc)}$  phase transition is obtained at  $a(T)=a^*$  ( $=3b^2/(16g)$ ) and the cluster order parameter undergoes a jump from  $\sigma=0$  to  $\sigma=\sigma^*(=3|b|/(4g) < 1)$ . The transition from  $N_u^{(bc)}$  to  $N_b^{(bc)}$  is obtained as  $\sigma$  increases beyond a critical value  $\sigma_c(=\lambda\sigma^*=c/2e < 1)$ . Representative order parameter profiles for these phases are depicted in Figs. 2(a) and 2(b).

### IV. FIELD-INDUCED NEMATIC BIAXIALITY

In the presence of an electric field ( $E \neq 0$ ) in the free energy expansion of Eq. (11), the uniaxial phases  $N_u$  and  $N_u^{(bc)}$  acquire field-induced biaxiality. Near  $E=0$ , a measure

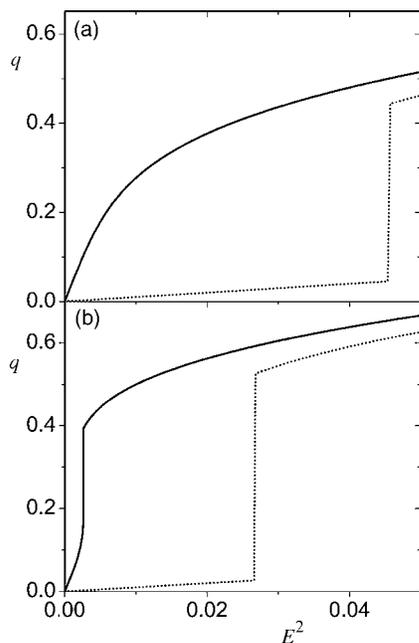


FIG. 3. The dependence of the biaxial order parameter  $q$  on the strength of the applied electric field for the systems in Fig. 2 and for two isotherms  $a(T)=0.95$  (solid line) and  $a(T)=1.05$  (dotted line). The electric field  $E$  is expressed in units of  $(a^*c^2/2eh^2)^{1/4}$ .

of the susceptibility of the system to field-induced biaxial ordering is provided by the “electrobiaxial” coefficient  $k \equiv \partial q / \partial E^2|_{E=0}$ . In the  $N_u$  phase, the value of this coefficient is fixed to  $k_{N_u} = h/c$ , while in the  $N_u^{(bc)}$  phase, it varies with  $\sigma$  (and therefore with temperature) according to  $k_{N_u^{(bc)}} = h/c(1 - \sigma/\sigma_c)^{-1}$ . Thus, the electrobiaxial susceptibility undergoes a jump of  $h/c(\lambda - 1)$  at the  $N_u \rightarrow N_u^{(bc)}$  transition. This can be quite large in systems for which the  $\lambda$  ratio is close to 1. In this case, a weak field could induce considerable biaxial order to a uniaxial nematic phase if the latter is the  $N_u^{(bc)}$ .

The dependence of the biaxiality order parameter  $q$  on the magnitude of the applied electric field is shown in the diagrams of Fig. 3 for values of the temperature function  $a(T)$  above and below the phase transition value  $a^*$ . It is apparent from the plots of  $q(a, E)$  that near  $E=0$  the effect of the electric field is much stronger in the  $N_u^{(bc)}$  phase, where the biaxial ordering is produced by the alignment of the biaxial clusters, compared to the  $N_u$  phase where the field directly influences the orientations of the molecules. As shown in Fig. 3, the applied field can induce second order transitions to the biaxial state of  $N_u^{(bc)}$ . In the case of Fig. 3(b), this transition is followed by a first order biaxial nematic-nematic transition. The transition from a “parabiaxial” state of  $N_u$  to a strongly biaxial state is seen to require much stronger fields, in analogy with what is known for the respective uniaxial paranematic to nematic transition.<sup>29</sup> It is also apparent that at constant applied field near  $E=0$ , the thermotropic transition from  $N_u$  to  $N_u^{(bc)}$  is accompanied by a jump of two orders of magnitude in the biaxiality  $q$ . A phase transition of this type, reflected on the abrupt change in the biaxial response of a uniaxial nematic phase to an applied field of a few  $\text{V}/\mu\text{m}$ , has been experimentally observed<sup>20</sup> in bent-core nematics.

The results regarding the application of an electric field

should be viewed within the practical limitations that the assumed alignment of the director  $\mathbf{n}$  imposes on the possible magnitude of the applied field  $E$ . To actually maintain the uniform orientation of  $\mathbf{n}$  along the rubbing direction ( $Z$  axis) of the plates for a nematic of positive dielectric anisotropy, the field strength cannot exceed the critical value  $E_c$  for the Fredericzs transition that reorients  $\mathbf{n}$  along the  $Y$  axis. Apparently, no such limitation applies for nematics of negative dielectric anisotropy; in this respect, such systems would be advantageous for the study of field-induced biaxial order in the  $N_u^{(bc)}$  phase.

The presently available experimental data are not detailed enough to permit a complete evaluation of the expansion coefficients in Eq. (11). Moreover, the simplified formulation of the theory, particularly the restriction to perfect uniaxial molecular ordering, does not warrant a direct quantitative comparison. Nevertheless, physically consistent estimates can be made by comparing the theoretical predictions with available results of measurements on bent-core nematics.<sup>16,17,20</sup> Thus, assuming that the scaled field strength of  $E=0.05$  at which the jump of the induced  $q$  is observed in Fig. 3(b) corresponds to roughly  $5 \text{ V}/\mu\text{m}$  (which is about half the critical field  $E_c$  for the Fredericzs transition), we estimate the scaling factor of  $E$  to be  $(a^*c^2/2eh^2)^{1/4} \approx 100 \text{ V}/\mu\text{m}$ . With the corresponding value of the induced biaxiality in the  $N_u^{(bc)}$  set at the experimentally measured magnitude  $q \approx 0.1$ , the respective scaling factor estimate is  $\sqrt{c/d} \approx 1/4$ . Combining these estimates with the values used for  $\lambda$  and  $u$  in Fig. 3(b) and the order of magnitude estimate for the  $\sigma$  scaling factor  $\sigma_c \approx 0.1$ , we obtain that  $g \approx 7|b|$ ,  $16c \approx d \approx 3e$ , and  $e \approx |b|$ . A value for  $b$  can be estimated from the scaling factor of  $E$  using  $h \approx 10^{-38} \text{ Fm}^2$  as representative of the transverse molecular polarizability anisotropy for strongly biaxial mesogens. This yields, in terms of Boltzmann’s constant ( $k_B$ ),  $|b|/k_B \approx 10^2 \text{ K}$ .

## V. DISCUSSION AND CONCLUSIONS

To summarize the results, three nematic phases are identified in the absence of an applied field: A purely uniaxial phase, a spontaneously biaxial phase, and an intermediate, macroscopically uniaxial phase consisting of biaxial clusters. The application of an electric field of a few  $\text{V}/\mu\text{m}$  could induce to this intermediate phase biaxial order of comparable magnitude to that of the spontaneous phase and two orders of magnitude larger than the field-induced order of the purely nematic phase. The switching of the intermediate phase between an optically uniaxial and a biaxial state as well as its possible transformation to a nematic phase ( $N_u$ ), in which the application of the electric field does not induce a measurable optical biaxiality, are in agreement with experimental observations on bent-core nematics.<sup>20</sup>

The above properties of the  $N_u^{(bc)}$  phase are not in contradiction with the experimental observations of biaxiality by NMR (Ref. 16) and XRD (Ref. 17) since in both cases an aligning field, magnetic or electric, respectively, is present. Furthermore, the induced nature of biaxiality suggested by the present analysis is in agreement with the interpretation of the texture transitions recently observed<sup>30</sup> in electro-optic

experiments on a bent-core nematic. It is also worth noting that the immergence of macroscopic biaxial nematic ordering from the collective alignment (spontaneous or field induced) of clusters is supported by the experimental observation of biaxial order in nematic tetrapodes.<sup>19</sup> There, the covalent lateral grouping of the nematogen components into quartets promotes the clustering which, in turn, enhances the biaxial tendency relative to that of the nonbonded nematogens.

The free energy expression in Eq. (11) can be readily extended to include the possibility of polar ordering within the biaxial clusters. In close analogy with the formulation of the  $\sigma$  parameter, an additional order parameter is introduced to describe the average magnitude of polar ordering within the clusters in a direction transverse to  $\mathbf{n}$ . The net transverse polarity of the sample is quantified by means of a vector order parameter  $\langle p_A \rangle$  that couples linearly ( $\langle p_A \rangle E_A$ ) to the applied field and quadratically ( $\langle p_A \rangle \langle p_B \rangle \langle q_{AB} \rangle$ ) to the biaxial order parameter. The additional phases described by the extended Landau–deGennes expansion include a macroscopically uniaxial nematic phase of biaxial and polar clusters and a polar-biaxial nematic phase. Details on the possible phase transitions and field-induced effects are given in Ref. 28.

Here, the results presented are based on a simplified formulation of the theory wherein perfect uniaxial nematic order is assumed and, therefore, molecular rotations are restricted in two dimensions. Consequently, any dependence on the degree of uniaxial nematic ordering is suppressed. Removal of this restriction makes the formulation more elaborate and modifies the details of the phase transitions. However, the essential findings regarding field-induced biaxiality and polar ordering are preserved. These findings offer new insights into the nature of phase biaxiality and the related nematic-nematic phase transitions and broaden the current views on what could be considered as a “biaxial nematic” LC for the purposes of electro-optic device applications. In particular, the possibility that some of the known uniaxial nematics could, in fact, consist of uniaxially distributed biaxial clusters, suggests that it might be interesting to study more closely the electro-optics of certain “uniaxial” nematics, especially those with negative dielectric anisotropy. As the possibility of fast, field-induced, switching between uniaxial and biaxial states provides a new concept for the design of biaxial nematic devices, such studies might also be of practical importance.

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