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Luckhurst–Romano model of thermotropic biaxial nematic phase

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Recent experiments show that the long looked for thermotropic biaxial nematic phase is finally stabilized in a low mass liquid crystalline system. Inspired by this experimental observation we concentrate on some theoretical issues concerned with this phase. In particular we show that the simplest Lebwohl–Lasher biaxial model, as introduced by Luckhurst and Romano, is consistent with the minimal coupling Landau–de Gennes phenomenological approach. The model shows a rich spectrum of possibilities, in particular a direct isotropic–biaxial nematic phase transition. A possible bridge between molecular and phenomenological approaches, in particular an interpretation of the alignment tensor, is discussed.

1. Introduction

The simplest of the orientationally ordered liquid crystalline phases are uniaxial and biaxial nematics [1–3]. In both phases no long range positional order is present, as in the isotropic liquid (I), but molecules lie, on average, parallel to each other. This preferred direction, the *director*, is often denoted by a unit vector \hat{n} . The directions \hat{n} and $-\hat{n}$ are equivalent as no long range ferroelectric order is found in nematics.

In many cases there exists a rotational symmetry about \hat{n} . The corresponding liquid crystalline phase is then called a uniaxial nematic (N_U). Two uniaxial nematic phases can be distinguished: one of them, denoted N_{U+} , is formed from prolate-like molecules. Molecules that are, on average, oblate in shape usually stabilize the N_{U-} phase. Both, N_{U+} and N_{U-} are of $\mathcal{D}_{\infty h}$ point-group symmetry.

But nematogenic molecules do not possess cylindrical symmetry, sometimes have appreciable dipole moments and very often are characterized by a considerable degree of flexibility. When this deviation from the uniaxial symmetry becomes relevant, new phases, with non-uniaxial one-particle distribution, may form. The corresponding nematic phase is then called biaxial and denoted N_B .

For biaxial nematics a second director \hat{m} , orthogonal to \hat{n} must be introduced. This means that in the N_B phase an orthonormal, right-handed tripod $\{\hat{l} = \hat{m} \times \hat{n}, \hat{m}, \hat{n}\}$ of the directors characterizes the

symmetry of the phase. To date no long range polar order has been detected in the biaxial nematic phase. Consequently, one expects that \hat{l} and $-\hat{l}$, \hat{m} and $-\hat{m}$ and \hat{n} and $-\hat{n}$ directions are equivalent, which means that the N_B phase is a structure of \mathcal{D}_{2h} point-group symmetry.

Experimentally the biaxial nematic phase was discovered by Yu and Saupe [4] in a lyotropic system in 1980 and later in polymeric systems [5]. Generally, first and second order phase transitions are observed experimentally between the isotropic phase and different nematic phases and between the nematic phases. Since 1986 there have been many attempts to find the N_B phase in low molar mass thermotropic materials (for a comprehensive review see [6, 7]), but only recent experiments on ‘boomerang-shaped’ oxadiazole mesogenic compounds [8–11] and on liquid crystalline organo-siloxane tetrapodes [12] seem finally to provide evidence of thermodynamically stable thermotropic biaxial nematic behaviour. This discovery raises an interesting question as to what mechanism is likely to be responsible for the enhanced stability of the biaxial ordering in these systems. That this mechanism may differ from what we know for lyotropic systems is suggested, for example, by a strong central dipole moment associated with the oxadiazole group of the boomerang molecules. One possible scenario might be that the second director in these systems is actually a polar vector. However, in what follows we are not going to discuss this possibility.

The (non-polar) biaxial nematic phase was predicted theoretically by Freiser in 1970 [13, 14], long before the

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first experimental evidence became available. Since that time, the possible effects of deviations from cylindrical symmetry on nematic order have been studied theoretically, both at phenomenological and molecular levels. More specifically, the Landau–de Gennes approach [2, 3, 15, 16] allowed for a systematic account of \mathcal{D}_{2h} symmetry and classification of possible topologies of phase diagrams with the N_B phase. Molecular field (MF) [13, 14, 17–24] as well as simulation studies [25–31], have shown that molecules possessing D_{2h} symmetry and interacting by appropriately chosen pair potentials, like biaxial extensions of a single site Gay–Berne potential [29–31], figure 1, can produce the biaxial nematic phase. Similar conclusions have emerged from the studies of ensembles of hard biaxial molecules [32–43].

In the majority of cases studied, the transitions involving isotropic phase, and biaxial and uniaxial nematic phases are found to belong to the class schematically shown in figures 2 and 3. Only recently a different scenario with a direct transition between isotropic and biaxial nematic phases, figure 4, not being reduced to a single Landau point, has also been discussed [24, 44]. One of the interesting features of the calculated phase diagram is the presence of a tricritical point, separating uniaxial and biaxial phases.

In this paper we demonstrate that many properties of the models of biaxial nematics discussed in the literature can, in fact, be understood by referring to the generic, Lebwohl–Lasher type of model as introduced by Luckhurst and Romano (LR) [25] and recently re-examined by Longa *et al.* [44]. In particular we show

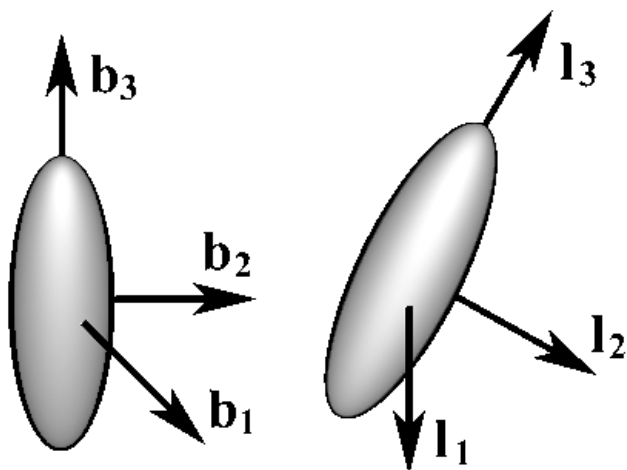


Figure 1. Tripods of vectors parameterizing molecular orientations. The parametrization is sufficient to describe mutual interactions between two rigid molecules and to characterize single site potentials.

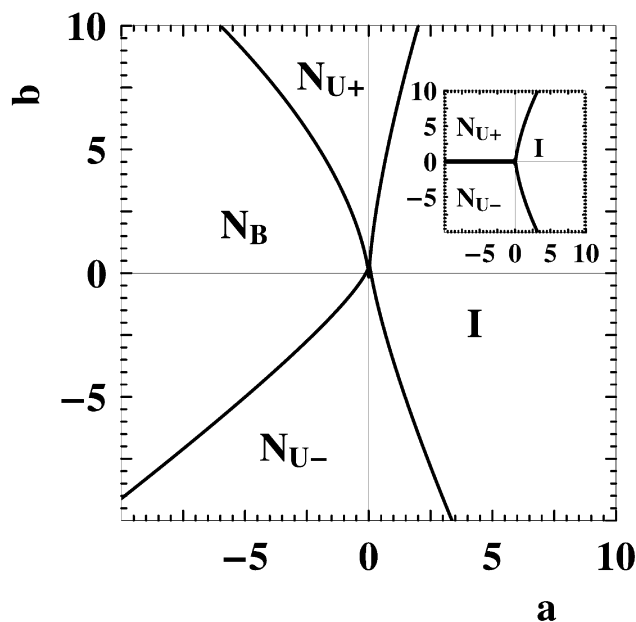


Figure 2. Generic phase diagrams with an isolated Landau point as predicted by the expansion (4). Exemplary calculations are carried out for $(c, d, f) = (0, 3, 12)$ and for $(c, d, f) = (0, 0, 6)$ (inset).

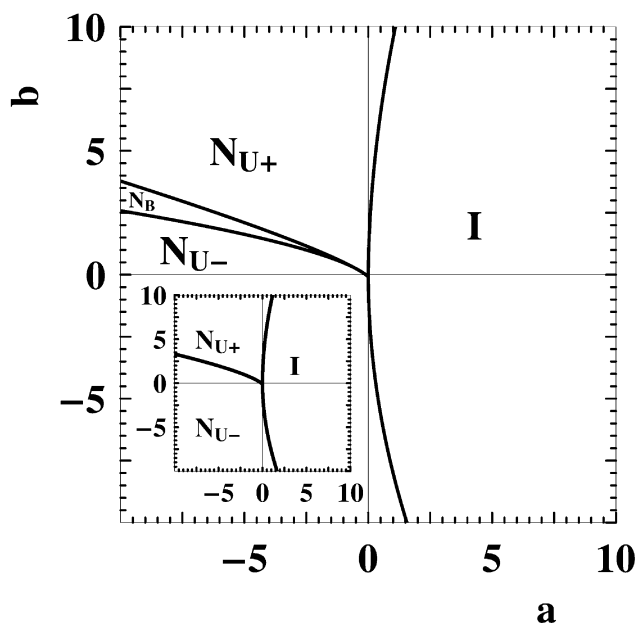


Figure 3. Generic phase diagrams as predicted by the expansion (4). They show phase transitions between uniaxial nematic phases with and without (inset) an intermediate biaxial nematic phase. Exemplary calculations are carried out for $(c, d, f) = (3, 3, 7)$ and for $(c, d, f) = (3, 3, 6)$ (inset).

that a slight generalization of the LR model is able to reproduce the topology of phase diagrams as predicted by the minimal coupling Landau–deGennes phenomenological approach. The model also clearly shows the

sectors in the potential parameter space where the biaxial nematic is most likely to become stable. When the coupling constants of the LR model are interpreted as coefficients of expansion of the direct pair correlation function [44], the stability criterion of the N_B phase with respect to the I phase can be addressed in a thermodynamically exact way, giving a bridge between density functional theory and computer simulation. Finally, the model can be used to illustrate how the phenomenological alignment tensor can be calculated from molecular theories.

2. Phenomenological theory of the biaxial nematic phase

The biaxial nematic phase can be described in the language of Landau–Ginzburg phenomenological theory of phase transitions, where orientational properties of liquid crystals are quantified in terms of a symmetric and traceless alignment tensor $Q_{\alpha\beta}$: $Q_{\alpha\beta} = Q_{\beta\alpha}$, $\text{Tr } \mathbf{Q} = 0$. The anisotropic part of the dielectric (diamagnetic) susceptibility is an example of experimentally realized \mathbf{Q} . In a standard parametrization \mathbf{Q} can be written as

$$\mathbf{Q} = S \left(\hat{\mathbf{n}} \otimes \hat{\mathbf{n}} - \frac{1}{3} \mathbf{1} \right) + P \left(\hat{\mathbf{m}} \otimes \hat{\mathbf{m}} - \frac{1}{3} \mathbf{1} \right) \tag{1}$$

$$= \frac{(2S-P)}{\sqrt{6}} \left[\frac{1}{\sqrt{6}} \left(3\hat{\mathbf{n}} \otimes \hat{\mathbf{n}} - \mathbf{1} \right) \right] - \frac{P}{\sqrt{2}} \left[\frac{1}{\sqrt{2}} \left(\hat{\mathbf{l}} \otimes \hat{\mathbf{l}} - \hat{\mathbf{m}} \otimes \hat{\mathbf{m}} \right) \right] \tag{2}$$

where $\{\hat{\mathbf{l}} = \hat{\mathbf{m}} \times \hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{n}}\}$ are orthonormal eigenvectors of \mathbf{Q} (see Introduction) corresponding to the eigenvalues $-\frac{1}{3}S - \frac{1}{3}P$, $\frac{2}{3}S - \frac{1}{3}P$, $-\frac{1}{3}S + \frac{2}{3}P$, respectively. The eigenvector of \mathbf{Q} corresponding to the maximal modulus of a non-degenerate eigenvalue, defines the director of the system.

The isotropic state corresponds to the case when all three eigenvalues of \mathbf{Q} vanish, which yields $\mathbf{Q} = \mathbf{0}$. For the $\mathcal{D}_{\infty h}$ -symmetric uniaxial states two out of the three eigenvalues of \mathbf{Q} are equal, i.e. $S \neq 0, P = 0$ or $S = 0, P \neq 0$ or $S = P$. These conditions could be written in a coordinate-independent form as one condition: $w^2 = 1$, where

$$w = \frac{\sqrt{6} \text{Tr } \mathbf{Q}^3}{(\text{Tr } \mathbf{Q}^2)^{\frac{3}{2}}}, \quad w^2 \leq 1. \tag{3}$$

In the general case, \mathbf{Q} has three different real eigenvalues that account locally for the \mathcal{D}_{2h} -symmetric biaxial state of $w^2 < 1$. Maximal phase biaxiality is reached for $w = 0$. Also note that for uniaxial \mathbf{Q} -tensors a transformation $\hat{\mathbf{u}} \rightarrow [(Q_{\alpha\beta} - c\delta_{\alpha\beta})u_\alpha u_\beta]$, where c is an arbitrary constant making the bilinear form [...] positive-definite, transforms a unit sphere $|\hat{\mathbf{u}}| = 1$ into

an axially symmetric, prolate ($w = 1$) or oblate ($w = -1$) closed surface. Hence, $w = 1$ and $w = -1$ cases correspond to N_{U+} and N_{U-} , respectively.

Although the representation (1) is commonly used in the phenomenological description of biaxial nematics, actually, from a symmetry point of view, a more appropriate parametrization is that given by equation (2) (see Appendix). The tensors in square brackets of (2) are the irreducible (with respect to the \mathcal{D}_{2h} symmetry) parts of \mathbf{Q} . In the Appendix they are denoted $\mathbf{T}_0^{(2)}$ and $\mathbf{T}_2^{(2)}$, respectively, with $\mathbf{T}_0^{(2)}$ representing purely uniaxial contribution of maximal uniaxiality ($w = 1$) and $\mathbf{T}_2^{(2)}$ being purely biaxial of maximal biaxiality ($w = 0$). Importantly, the tensors $\mathbf{T}_0^{(2)}$ and $\mathbf{T}_2^{(2)}$ are orthogonal (in the sense of taking Tr), which means that for appropriately chosen parameters in the Landau expansion the biaxial nematic can be stabilized with the vanishing $\mathbf{T}_0^{(2)}$ part. This, in turn, implies that both the $I-N_B$ and the $N_{U-}N_B$ phase transitions can be either first or second order. In other words we may expect tricritical points between $I-N_B$ and $N_{U-}N_B$ and Landau points, depending on details of the free energy expansion.

More specifically, thermodynamic properties of the system can be found from a non-equilibrium free energy, which is constructed as an $SO(3)$ -symmetric expansion in powers of \mathbf{Q} . The only restriction on the expansion is that it must be stable against an unlimited growth of the order parameter. In the absence of electric and magnetic fields, the minimal coupling expansion describing the biaxial phase reads (see, e.g., [2, 3])

$$F = F_o + a \text{Tr } \mathbf{Q}^2 - b \text{Tr } \mathbf{Q}^3 + c (\text{Tr } \mathbf{Q}^2)^2 + d \text{Tr}(\mathbf{Q}^2) \text{Tr}(\mathbf{Q}^3) + e \text{Tr}(\mathbf{Q}^2)^3 + (f - 6e) \text{Tr}(\mathbf{Q}^3)^2 \tag{4}$$

$$= aq^2 - \frac{(b-dq^2)wq^3}{\sqrt{6}} + cq^4 + \left[e + \left(\frac{f}{6} - e \right) w^2 \right] q^6. \tag{5}$$

The notation in equation (4) is as follows: F_o is the (unknown and usually disregarded) free energy of the reference isotropic phase, $a = a_o(T - T^*)$ where T is the temperature, T^* is the spinodal for a first order phase transition from the isotropic phase to the nematic phase or transition temperature otherwise, $a_o > 0$, and $e > 0, f > 0$ for stability of the expansion. Out of six parameters only four are relevant. We take $e = 1$ and investigate dependence of the phase diagram in the (a, b) -plane on the sign of $f - 6e$. Owing to the inequality $-1 \leq w \leq 1$ and utilizing the parametrization: $\text{Tr } \mathbf{Q}^2 = q^2$, $\text{Tr } \mathbf{Q}^3 = \frac{q^3 w}{\sqrt{6}}$ the expansion (4) can be written down in an equivalent form (5), which allows a simple minimization of F over w and $q \geq 0$.

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Generally, a stable biaxial nematic phase is found for $f-6e>0$. The phase diagrams could be divided into many distinct classes, some of them being shown in figures 2–4.[†]

- (a) Diagrams with a line of first order $I \leftrightarrow N_{U+}$ phase transitions ($b>0$) and a line of first order $I \leftrightarrow N_{U-}$ phase transitions ($b<0$). The lines terminate at the Landau point $a=b=0$. Line $b=0$ (inset in figure 2) corresponds to a degenerated biaxial phase of maximal biaxiality ($w=0$).
- (b) Diagrams as in (a) but with an additional first order phase transition between the two uniaxial nematic phases. If both phases are characterized by the same sign of the w parameter (3) the transition between them terminates at a critical point. An example of the $N_{U+} \leftrightarrow N_{U-}$ line of first order phase transitions is shown as an inset in figure 3. The line is positioned between the $I \leftrightarrow N_{U-}$ and $I \leftrightarrow N_{U+}$ lines. All three lines meet at the $I \leftrightarrow N_{U+} \leftrightarrow N_{U-}$ triple point.
- (c) Diagrams as in (a,b) but with the line separating N_{U+} and N_{U-} split into two lines: $N_{U+} \leftrightarrow N_B$ and $N_{U-} \leftrightarrow N_B$. Generally this topology is found for $c \geq 0$. Phase transition between the uniaxial and the biaxial nematic phases can be either first or second order and the line $N_{U\pm} \leftrightarrow N_B$ can have a tricritical point. Also the line $I \leftrightarrow N_B$ can have a tricritical point. At the Landau point four phases meet: $I \leftrightarrow N_{U+} \leftrightarrow N_B \leftrightarrow N_{U-}$ (figures 2 and 3).
- (d) Diagrams as in (c) but with the Landau point split into two triple points, figure 4: $I \leftrightarrow N_{U+} \leftrightarrow N_B$ and $I \leftrightarrow N_{U-} \leftrightarrow N_B$. The two points are connected by a direct $I \leftrightarrow N_B$ line of first order phase transitions. This topology is observed for $c < 0$.

Now we show that the above mentioned phenomenological phase diagrams can be recovered from a model which is a slight generalization of that proposed by Luckhurst and Romano [25]. Although we restrict ourselves to mean-field analysis it will become clear from the presentation that many predictions are in fact mean-field-independent. In particular, a connection between molecular order parameters and \mathbf{Q} , which we shall discuss, is of such general nature.

[†] Note that to a given phase diagram its mirror image diagram with respect to the $b=0$ line could be generated by a reversal of sign of the parameters in the Landau expansion that multiply terms with odd powers of $\text{Tr } \mathbf{Q}^3$. Additionally $N_{U\pm}$ should be replaced by $N_{U\mp}$ in the mirror image diagrams.

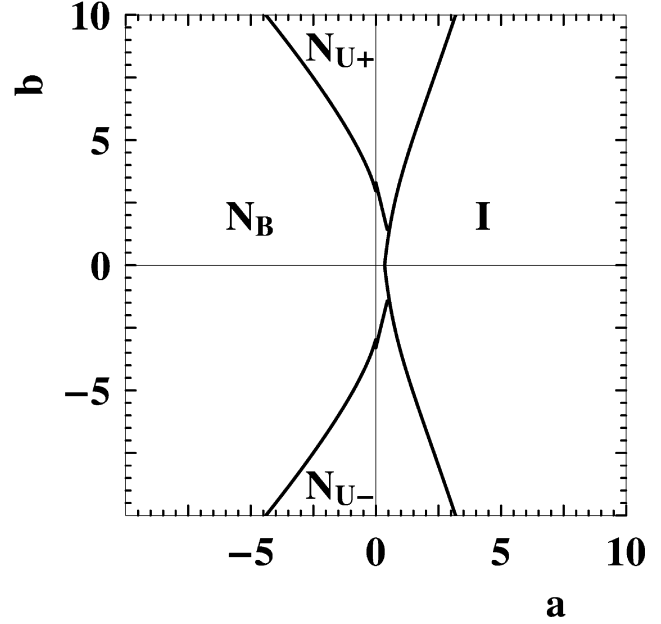


Figure 4. Generic phase diagram with a line of phase transitions between isotropic and biaxial nematic phases as predicted by the expansion (4). Exemplary calculations are carried out for $(c, d, f) = (-1, 0, 12)$.

3. Luckhurst-Romano model of biaxial ordering

Following Luckhurst and Romano [25] we consider a regular lattice of biaxial, D_{2h} -symmetric particles interacting through a pairwise additive interaction

$$\begin{aligned}
 V &= -|v_{00}| \left\{ s_0 \Delta_{0,0}^{(2)}(\tilde{\mathbf{Q}}) + v_0 \left[\Delta_{2,0}^{(2)}(\tilde{\mathbf{Q}}) + \Delta_{0,2}^{(2)}(\tilde{\mathbf{Q}}) \right] + v_2 \Delta_{2,2}^{(2)}(\tilde{\mathbf{Q}}) \right\} \quad (6) \\
 &= -|v_{00}| \{ s_0 \mathbf{L}_0 \cdot \mathbf{B}_0 + v_0 [\mathbf{L}_2 \cdot \mathbf{B}_0 + \mathbf{L}_0 \cdot \mathbf{B}_2] + v_2 \mathbf{L}_2 \cdot \mathbf{B}_2 \} \quad (7) \\
 &= -|v_{00}| \left[(v_2 - \sqrt{3}v_0) (\mathbf{b}_1 \cdot \mathbf{I}_1)^2 + (v_2 + \sqrt{3}v_0) (\mathbf{b}_2 \cdot \mathbf{I}_2)^2 + \right. \\
 &\quad \left. \left(\frac{3}{2}s_0 - \frac{v_2}{2} \right) (\mathbf{b}_3 \cdot \mathbf{I}_3)^2 - \frac{s_0 + v_2}{2} \right] \quad (8)
 \end{aligned}$$

where $s_0 = \text{sign}(v_{00})$. A direct connection between equation (6) and the case studied by LR [25], also referred to as a dispersion model [44], is established if we set:

$$s_0 = 1, \quad v_0 = \pm \sqrt{2}\lambda, \quad v_2 = 2\lambda^2. \quad (9)$$

In this special, but important, case describing point dispersive interactions the parameters v_{00} and λ can be directly expressed in terms of the diagonal elements of the molecular polarizability tensor, α , in which case they read [28]

$$\lambda = \left(\frac{3}{2} \right)^{\frac{1}{2}} \frac{\alpha_{xx} - \alpha_{yy}}{2\alpha_{zz} - (\alpha_{xx} - \alpha_{yy})} \quad (10)$$

$$v_{00} = [2\alpha_{zz} - (\alpha_{xx} - \alpha_{yy})]^2. \quad (11)$$

Going beyond point dispersive forces makes the parameters $\{s_0, v_0, v_2\}$ no longer related via the geometric mean rule (9).

The pair interaction (6) is written down in three equivalent forms, each having an advantage depending on the specific calculations being carried out. More specifically, the representation (6) gives the potential in terms of the symmetry-adapted functions $\Delta_{m,n}^{(L)}(\tilde{\Omega})$ [34, 45], which are orthogonal, D_{2h} -symmetrized linear combinations of Wigner rotation functions $\mathcal{D}_{m,n}^{(L)}(\tilde{\Omega})$. Here $\tilde{\Omega}$ denotes the set of Euler angles defining the intermolecular rotation transforming molecule-fixed orthonormal coordinate system $\{\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3\}$ into $\{\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3\}$, figure 1, and the expansion is complete up to $L=2$ terms. The representation in terms of $\Delta_{m,n}^{(L)}$ is particularly useful for density functional and bifurcation theories as it allows one to use the orthogonality properties of Δ s [34, 44], which enormously simplify the calculations.

In formula (7) the symmetry-adapted functions $\Delta_{m,n}^{(L)}(\tilde{\Omega})$ are given in an equivalent Cartesian form as a linear combination of full contractions of irreducible Cartesian tensors over Cartesian indices. The form of the interaction potential, equation (7), proves very convenient for discussion of a connection between density functional approach and Landau expansion. The relevant tensors $\Delta_{m,n}^{(2)}(\tilde{\Omega})$, \mathbf{L}_m and \mathbf{B}_m are given in the Appendix.

The most appealing form of the potential is that given in terms of scalar products between orthonormal triplets of vectors, equation (8) (see also figure 1). It clearly displays the symmetry of the interaction and the meaning of the coupling constants. Also it shows the permutation symmetry of the interaction, which yields a non-trivial duality transformation between prolate and oblate states at various temperatures [44]. Exploring the duality considerably reduces the relevant parameter space of the model, which shrinks to the shaded region of figure 5. It is sufficient to study phase diagrams for the parameters taken from that area. They correspond to states of predominantly prolate symmetry while the image states (white region of figure 5) are of predominantly oblate symmetry. The self-dual line separating the regions is thus the line of the Landau points. As the duality represents a geometrical property of the model the line of the Landau points is independent of the way in which the phase diagram is calculated. It terminates at the point of coordinates (0, 1), represented by a dot in figure 5, where all coefficients in equation (8) are equal. The line of points $(0, v_2:v_2 > 1)$ corresponds to a direct I-B bifurcation, which also seems to be the exact property of the model. Details are published elsewhere [44].

Now we concentrate our discussion on further properties of the model, in particular we find its

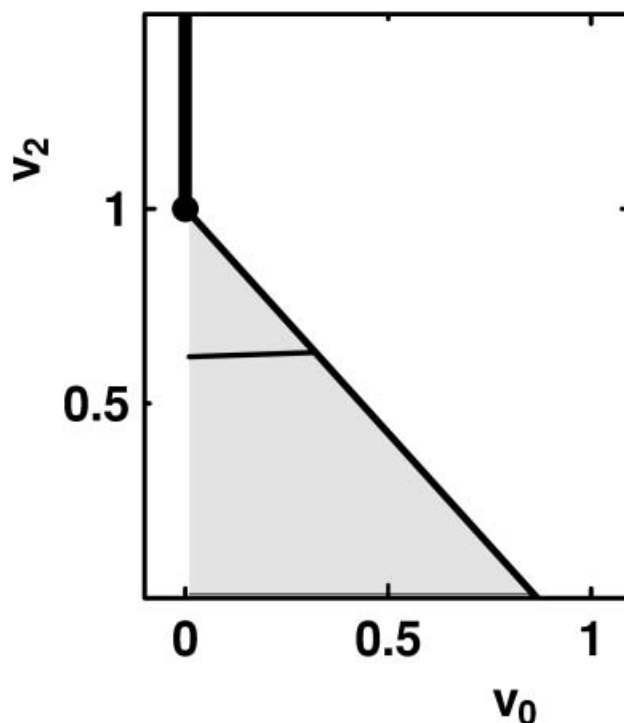


Figure 5. Relevant parameter space (grey area) for the model (6). Prolate states (grey area) are separated by the line $v_2 = s_0 - \frac{2v_0}{\sqrt{3}}$ of Landau points from oblate states (white area). The thick $\sqrt{3}$ vertical line represents points where a direct isotropic biaxial nematic phase transition is predicted. The thin line within the grey area represents parameters where a tricritical point between uniaxial and biaxial phases is found within mean-field calculations (adapted from [44]).

mesoscopic \mathbf{Q} -tensor. It transpires that the form of equations we shall study will be insensitive to the perturbation (density functional) scheme used in calculations. However, for the sake of clarity, we carry out exemplary calculations using a simple mean-field model. More specifically, we consider a system formed by a lattice of N identical particles interacting with the potential V . The total potential energy, U , is given by the sum of pairwise contributions, where the summation runs over nearest neighbours on the lattice. We approximate the configurational part, \mathcal{F} , of the free energy of the system by its mean-field value. It amounts in replacing \mathbf{X}_α by $\overline{\mathbf{X}}_\alpha + \delta\mathbf{X}_\alpha$ ($\mathbf{X} = \mathbf{B}, \mathbf{L}$), and disregarding fluctuation terms $\delta\mathbf{L}_\alpha\delta\mathbf{B}_\beta$, where $\delta\mathbf{X}_\alpha = \mathbf{X}_\alpha - \overline{\mathbf{X}}_\alpha$ and where $\overline{\mathbf{X}}_\alpha$ is the thermodynamic average of \mathbf{X}_α . After simple algebra the final expression for \mathcal{F} reads:

$$f = \frac{\mathcal{F}}{Nk_B|v_{00}|d} = \frac{1}{2} \left[s_0 \left(\overline{\Delta_{0,0}^{(2)}}^2 + \overline{\Delta_{2,0}^{(2)}}^2 \right) + v_2 \left(\overline{\Delta_{2,2}^{(2)}}^2 + \overline{\Delta_{0,2}^{(2)}}^2 \right) + 2v_0 \left(\overline{\Delta_{0,0}^{(2)}\Delta_{0,2}^{(2)}} + \overline{\Delta_{2,2}^{(2)}\Delta_{2,0}^{(2)}} \right) \right] - t \ln(Z) \quad (12)$$

where

$$Z = \int dx d \cos(\beta) d\gamma \exp \left\{ \frac{1}{t} \left[\left(s_0 \overline{\Delta_{0,0}^{(2)}} + v_0 \overline{\Delta_{0,2}^{(2)}} \right) \Delta_{0,0}^{(2)}(\boldsymbol{\Omega}) + \left(v_0 \overline{\Delta_{0,0}^{(2)}} + v_2 \overline{\Delta_{0,2}^{(2)}} \right) \Delta_{0,2}^{(2)}(\boldsymbol{\Omega}) + \left(s_0 \overline{\Delta_{2,0}^{(2)}} + v_0 \overline{\Delta_{2,2}^{(2)}} \right) \Delta_{2,0}^{(2)}(\boldsymbol{\Omega}) + \left(v_0 \overline{\Delta_{2,0}^{(2)}} + v_2 \overline{\Delta_{2,2}^{(2)}} \right) \Delta_{2,2}^{(2)}(\boldsymbol{\Omega}) \right] \right\} \quad (13)$$

and where $t = k_B T / |v_{00}|d$ is the dimensionless temperature. $\boldsymbol{\Omega}$ represents the Euler angles $\{\alpha, \beta, \gamma\}$. For models with particles not restricted to a lattice the parameters v_{00} , v_0 and v_2 are obtained from an averaging over translational degrees of freedom and the lattice coordination number, d , becomes the average density of the system. Minimization of equation (12) with respect to the average values of the order parameters $\overline{\Delta_{m,n}^{(2)}}$ gives the ordinary mean-field self-consistent equations, which could be analysed, e.g. with the help of bifurcation theory [34, 46–48]. Following this method [46–48] we Taylor expand equation (12) about the isotropic phase ($\Delta_{m,n}^{(2)} \approx 0$) and convert it to the Landau expansion (4). This allows one not only to find the bifurcation point from the isotropic phase to an ordered phase, but also gives a molecular interpretation of the alignment tensor \mathbf{Q} .

We start with the expansion of the equation (12) up to a quadratic order in $\Delta_{m,n}^{(2)}$. It reads

$$f_2 = \frac{1}{2t} \left[\left(t v_2 - \frac{v_0^2}{5} - \frac{v_2^2}{5} \right) \left(\overline{\Delta_{2,2}^2} + \overline{\Delta_{0,2}^2} \right) + \left(2 t v_0 - \frac{2 s_0 v_0}{5} - \frac{2 v_0 v_2}{5} \right) \times \left(\overline{\Delta_{2,2}^2 \Delta_{2,0}^2} + \overline{\Delta_{0,0}^2 \Delta_{0,2}^2} \right) + \left(t s_0 - \frac{1}{5} - \frac{v_0^2}{5} \right) \left(\overline{\Delta_{2,0}^2} + \overline{\Delta_{0,0}^2} \right) \right]. \quad (14)$$

The phase transition is driven by the order parameter combination corresponding to the largest temperature, t_* , at which the expansion (14) becomes unstable. Performing diagonalization of (14), t_* can be determined explicitly in terms of the expansion coefficients. This gives (compare with [34, 44])

$$t_* = \frac{1}{10} \left\{ s_0 + v_2 + \left[(s_0 - v_2)^2 + 4 v_0^2 \right]^{\frac{1}{2}} \right\} = \frac{1}{10} (s_0 + v_2 + \phi) \geq 0 \quad (15)$$

and

$$f_2 = \frac{5}{2} \left[\delta t_* (y_0^2 + y_1^2) + \left(\frac{t_*}{t_{**}} \right) \delta t_{**} (y_2^2 + y_3^2) \right] \quad (16)$$

where $t_{**} = t_* - \phi/5$, $\delta t_a = t - t_a$, $\tau = s_0 - v_2 + \phi \geq 0$, $2\phi \geq \tau$, and where

$$y_0 = \frac{\tau \overline{\Delta_{0,0}^2} + 2 v_0 \overline{\Delta_{0,2}^2}}{\sqrt{2} \sqrt{\tau} \sqrt{\phi}}, \quad y_1 = \frac{(2\phi - \tau) \overline{\Delta_{2,2}^2} + 2 v_0 \overline{\Delta_{2,0}^2}}{\sqrt{2} \sqrt{\phi} \sqrt{2\phi - \tau}} \quad (17)$$

$$y_2 = \frac{-(2\phi - \tau) \overline{\Delta_{0,0}^2} + 2 v_0 \overline{\Delta_{0,2}^2}}{\sqrt{2} \sqrt{\phi} \sqrt{2\phi - \tau}}, \quad y_3 = \frac{-\tau \overline{\Delta_{2,2}^2} + 2 v_0 \overline{\Delta_{2,0}^2}}{\sqrt{2} \sqrt{\tau} \sqrt{\phi}}.$$

We note that for $\phi > 0$ the phase transition from I to an ordered phase is driven by the first term in equation (16), proportional to $(y_0^2 + y_1^2)$, while the second term involves the secondary order parameter $(y_2^2 + y_3^2)$ with the bifurcation temperature $t_{**} < t_*$. Taking into account that $\overline{\Delta_{m,n}^{(2)}}$ is the component of $\overline{\mathbf{X}_n}$ in the director basis $\mathbf{T}_m^{(2)}(\hat{\mathbf{l}}, \hat{\mathbf{m}}, \hat{\mathbf{n}})$ (see the Appendix): $\overline{\Delta_{m,n}^{(2)}} = \mathbf{T}_m^{(2)}(\hat{\mathbf{l}}, \hat{\mathbf{m}}, \hat{\mathbf{n}}) \cdot \overline{\mathbf{X}_n}$ and observing relations (A8, A9) we identify the \mathbf{Q} -tensor (up to normalization) with a linear combination of $\mathbf{T}_0^{(2)}$ and $\mathbf{T}_2^{(2)}$ weighted by y_0 and y_2 terms, respectively. It reads

$$\mathbf{Q} = y_0 \mathbf{T}_0^{(2)}(\hat{\mathbf{l}}, \hat{\mathbf{m}}, \hat{\mathbf{n}}) + y_1 \mathbf{T}_2^{(2)}(\mathbf{l}, \mathbf{m}, \mathbf{n}). \quad (18)$$

Note that all limiting cases known in the literature can easily be recovered from (17). For example the Mayer–Saupe model gives $y_0 = \overline{\Delta_{0,0}^2}$, $y_1 = y_2 = y_3 = 0$.

The components $\{y_2, y_3\}$ introduce the secondary alignment tensor (secondary order parameter), which we denote \mathbf{R} :

$$\mathbf{R} = y_2 \mathbf{T}_0^{(2)}(\hat{\mathbf{l}}, \hat{\mathbf{m}}, \hat{\mathbf{n}}) + y_3 \mathbf{T}_2^{(2)}(\mathbf{l}, \mathbf{m}, \mathbf{n}). \quad (19)$$

As the bifurcation temperature associated with \mathbf{R} is lower than that of \mathbf{Q} , the former tensor can be eliminated in a systematic way from the Landau expansion by performing a partial minimization of the free energy [46–48] with respect to \mathbf{R} for fixed \mathbf{Q} . The procedure allows one to express \mathbf{R} in terms of \mathbf{Q} with the leading term being proportional to \mathbf{Q}^2 : $\mathbf{R} \sim \mathbf{Q}^2(1 + \dots)$. Substituting \mathbf{R} back in to the expansion finally gives the Landau expansion about $\mathbf{Q} = 0$, expressed in terms of $f(\text{Tr}(\mathbf{Q}^2), \text{Tr}(\mathbf{Q}^3))$, which matches precisely the phenomenological formula (4). The first two terms read

$$f_2 = \frac{5}{2} \delta t_* \text{Tr}(\mathbf{Q}^2) - \frac{25 t_* \sqrt{\tau} (2\tau - 3\phi)}{7\sqrt{3}\phi^{\frac{3}{2}}} \text{Tr}(\mathbf{Q}^3) + \dots \quad (20)$$

Please note that the coefficient of the cubic invariant (20) predicts the Landau points to fulfil the equation $2\tau = 3\phi$, which is precisely the self-dual line $v_2 = 1 - \frac{2v_0}{\sqrt{3}}$ shown in figure 5 [44].

In order to illustrate a connection between the molecular parameters $\{y_0, y_1, y_2, y_3\}$ (17) and the tensors \mathbf{Q} and \mathbf{R} , we performed explicit mean-field

calculations of $\{y_0, y_1, y_2, y_3\}$ for the self-dual dispersion case. That is, the model parameters chosen were consistent with (9), where $\lambda = \frac{1}{\sqrt{6}}$ [28, 44]. At this particular value the cubic term in the expansion (20) vanishes, which yields a direct $I-N_B$ transition across the Landau point. Results of numerical calculations are shown in figures 6 and 7. The calculated phase uniaxiality w , figure 7, of the tensors clearly shows that \mathbf{Q} remains (to within numerical error) maximally biaxial down to $t=0$. It is also clear as to why \mathbf{R} is the secondary order parameter. Interestingly, despite the negative values of y_2 and y_3 , the \mathbf{R} -tensor is of prolate symmetry.

4. Summary

In principle, a more general bifurcation analysis could be carried out if, instead of expanding the pair potential in symmetry-adapted basis functions, we would expand the free energy functional expressed in terms of the direct correlation functions [34, 44]. Interestingly, the formulas (15–17) would still remain valid given that molecules are D_{2h} -symmetric. The formula (20) would be an approximate one, with contributions coming from the triplet direct correlations being disregarded.

The method provides a simple interpretation of the alignment tensor in terms of molecular parameters and shows how to distinguish between primary and second-

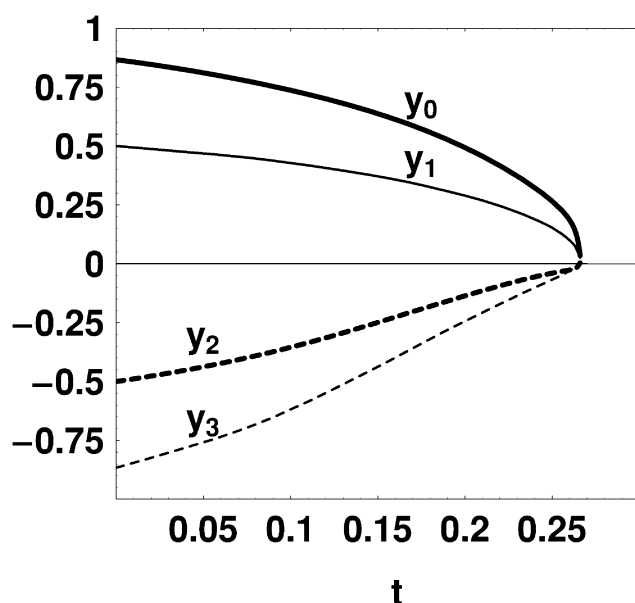


Figure 6. Exemplary calculations of the $\{y_0, y_1, y_2, y_3\}$ -parameters that are used to build the \mathbf{Q} and \mathbf{R} tensors. Interaction parameters chosen correspond to the model (9) with $\lambda = \frac{1}{\sqrt{6}}$.

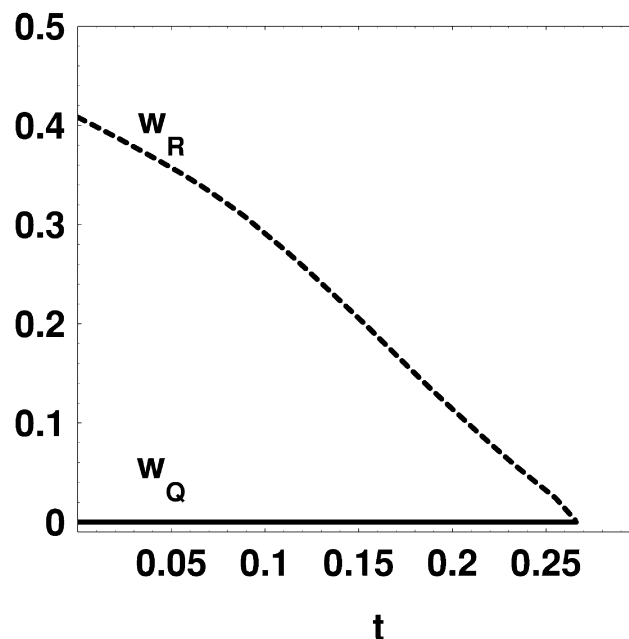


Figure 7. Exemplary calculations of the uniaxiality parameter (3) for \mathbf{Q} and \mathbf{R} , equation (18).

ary tensors. This is important, especially when a Landau expansion based upon molecular order parameters is constructed [15, 16]. We conclude that the analysis as given offers a simple scheme with which to study the stability of the biaxial ordering in model systems. The direct phase transitions from the isotropic phase are well captured by just the two effective parameters $\{v_0, v_2\}$ as the relevant information about I –(U,B) bifurcation is contained in the expansion (6). Note also that primary features of the phenomenological phase diagrams, figures 2–4, are recovered in the $\{v_0, v_2\}$ parameter space. In this sense the Luckhurst–Romano model seems generic for the class of phase transitions studied.

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Appendix: relevant symmetry-adapted irreducible tensors vs directional cosines

Here we list all relevant Δ -functions of $L=2$ and irreducible \mathbf{L}_m and \mathbf{B}_m tensors. Also we give their relation to directional cosines:

$$\Delta_{0,0}^{(2)}(\tilde{\Omega}) = \mathbf{L}_0 \cdot \mathbf{B}_0 = \frac{1}{4} + \frac{3 \cos(2\tilde{\beta})}{4} = -\frac{1}{2} + \frac{3}{2} (\mathbf{b}_3 \cdot \mathbf{l}_3)^2 \quad (A1)$$

$$\begin{aligned} \Delta_{0,2}^{(2)}(\tilde{\Omega}) &= \mathbf{L}_0 \cdot \mathbf{B}_2 = \frac{\sqrt{3}}{2} \cos(2\tilde{\gamma}) \sin(\tilde{\beta})^2 \\ &= \frac{\sqrt{3}}{2} [(\mathbf{b}_1 \cdot \mathbf{l}_3)^2 - (\mathbf{b}_2 \cdot \mathbf{l}_3)^2] \end{aligned} \quad (A2)$$

$$\begin{aligned} \Delta_{2,0}^{(2)}(\tilde{\Omega}) &= \mathbf{L}_2 \cdot \mathbf{B}_0 = \frac{\sqrt{3}}{2} \cos(2\tilde{\alpha}) \sin(\tilde{\beta})^2 \\ &= \frac{\sqrt{3}}{2} [(\mathbf{b}_3 \cdot \mathbf{l}_1)^2 - (\mathbf{b}_3 \cdot \mathbf{l}_2)^2] \end{aligned} \quad (A3)$$

$$\begin{aligned} \Delta_{2,2}^{(2)}(\tilde{\Omega}) &= \mathbf{L}_2 \cdot \mathbf{B}_2 = \frac{1}{4} \cos(2\tilde{\alpha}) [3 + \cos(2\tilde{\beta})] \cos(2\tilde{\gamma}) \\ &\quad - \cos(\tilde{\beta}) \sin(2\tilde{\alpha}) \sin(2\tilde{\gamma}) \\ &= (\mathbf{b}_1 \cdot \mathbf{l}_1)^2 + (\mathbf{b}_2 \cdot \mathbf{l}_2)^2 - \frac{1}{2} (\mathbf{b}_3 \cdot \mathbf{l}_3)^2 - \frac{1}{2} \end{aligned} \quad (A4)$$

$$\Delta_{2,0}^{(2)}(\tilde{\Omega}) + \Delta_{0,2}^{(2)}(\tilde{\Omega}) = \sqrt{3} [(\mathbf{b}_2 \cdot \mathbf{l}_2)^2 - (\mathbf{b}_1 \cdot \mathbf{l}_1)^2] \quad (A5)$$

where $\mathbf{L}_m = \mathbf{T}_m^{(2)}(\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3)$, $\mathbf{B}_m = \mathbf{T}_m^{(2)}(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3)$. For arbitrary right-handed orthonormal tripod $\{\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}\}$ the tensors $\mathbf{T}_m^{(2)}(\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}) \equiv \mathbf{T}_m^{(2)}$ are

$$\mathbf{T}_0^{(2)} = \frac{1}{\sqrt{6}} (3\hat{\mathbf{z}} \otimes \hat{\mathbf{z}} - 1) \quad (A6)$$

$$\mathbf{T}_2^{(2)} = \frac{1}{\sqrt{2}} (\hat{\mathbf{x}} \otimes \hat{\mathbf{x}} - \{\hat{\mathbf{y}} \otimes \hat{\mathbf{y}}\}). \quad (A7)$$

Note that for $L=2$ there are only two irreducible tensors consistent with D_{2h} symmetry: uniaxial $\mathbf{T}_0^{(2)}$ ($w=1$) and biaxial $\mathbf{T}_2^{(2)}$ of maximal biaxiality ($w=0$). Using irreducible basis and identifying $\{\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}\}$ with $\{\hat{\mathbf{t}}, \hat{\mathbf{m}}, \hat{\mathbf{n}}\}$ one

can write the alignment tensor \mathbf{Q} , equation (1), in an equivalent form as

$$\mathbf{Q} = q_0 \mathbf{T}_0^{(2)}(\hat{\mathbf{l}}, \hat{\mathbf{m}}, \hat{\mathbf{n}}) + q_2 \mathbf{T}_2^{(2)}(\mathbf{l}, \mathbf{m}, \mathbf{n}) \quad (A8)$$

with

$$\begin{aligned} \text{Tr } \mathbf{Q}^2 &= q_0^2 + q_2^2 \\ \text{Tr } \mathbf{Q}^3 &= \frac{q_0(q_0^2 - 3q_2^2)}{\sqrt{6}} \end{aligned} \quad (A9)$$

where $q_0 = \frac{(2S-P)}{\sqrt{6}}$ and $q_2 = \frac{-P}{\sqrt{2}}$.