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K. Trojanowski [a], D. W. Allender [b], L. Longa [a] & Ł. Kuśmierz [a]

[a] Department of Statistical Physics, Jagellonian University, Marian Smoluchowski Institute of Physics, and Mark Kac Complex Systems Research Center, Kraków, Poland

[b] Department of Physics and Liquid Crystal Institute, Kent State University, Kent, OH, USA

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Theory of Phase Transitions of a Biaxial Nematogen in an External Field

K. TROJANOWSKI,[1] D. W. ALLENDER,[2] L. LONGA,[1] AND Ł. KUŚMIERZ[1]

[1]Department of Statistical Physics, Jagellonian University, Marian Smoluchowski Institute of Physics, and Mark Kac Complex Systems Research Center, Kraków, Poland
[2]Department of Physics and Liquid Crystal Institute, Kent State University, Kent, OH, USA

Landau-de Gennes (LdeG) theory and a microscopic model of interacting quadrupolar tensors, also known as the dispersion model, are used to analyze the effect of an external field on a nematogenic liquid crystal material having the zero field phase sequence biaxial nematic-uniaxial nematic-isotropic liquid as temperature increases. Although both approaches give qualitatively the same results the dispersion model does not reproduce all features of the phenomenological phase diagrams. For example, the biaxial-uniaxial transition for positive uniaxial anisotropic susceptibility is found to shift with field to either higher or lower temperature, depending on the values of the coefficients in the LdeG expansion, while the molecular model shows only the first type of behavior.

Keywords Biaxial nematic; Landau-de Gennes theory; liquid crystal phase transitions; molecular modeling

1. Introduction

Gramsbergen, Longa and de Jeu [1] analyzed the effect of an electric or magnetic field on the uniaxial nematic-isotropic and on the uniaxial nematic-biaxial nematic phase transitions. In addition to using Landau theory to explain basic effects induced by external fields, they cited the experimental evidence available at the time. Their work is extended here to consider further effects of an external field not only at the level of phenomenological LdeG theory but also using a microscopic model of interacting quadrupoles on a cubic lattice, also known as the dispersion model [2,3]. More specifically, the case of positive uniaxial dielectric (diamagnetic) anisotropy, where $\varepsilon_{\|} > \varepsilon_{\perp}$, is considered in detail by (a) including terms in the Landau theory out to sixth order in the order parameter and (b) by applying the mean field approximation and Monte Carlo simulations to the dispersion model. The results are that the field dependence of the uniaxial-isotropic transition temperature has the same features both in the Landau theory and in the microscopic model: (i) the

Address correspondence to D. W. Allender, Department of Physics and Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA. Tel.: (330) 672 0345; Fax: (330) 672 2959; E-mail: dallende@kent.edu

isotropic phase becomes a paranematic phase with a very weak field-induced uniaxial order; (ii) a shift of the uniaxial nematic-paranematic transition temperature with increasing field strength, until (iii) the transition terminates at a critical point when the field reaches the critical value. It is worth noting that all three of these features occur for the well-known nematogen 5CB placed in an electric field, according to the landmark experiment of Lelidis and Durand [4], which found $T_{UP}(E_c) - T_{UP}(0) \approx 0.6\,K$ and $E_c \approx 13\,V/\mu m$, where $T_{UP}(E)$ is the uniaxial nematic - paranematic transition temperature, E is the electric field and E_c is its value at the critical point. Conversely the biaxial-uniaxial transition temperature, T_{BU}, is found to not have a universal shift with field strength in LdeG theory: T_{BU} may increase or decrease depending on the values of the coefficients in the LdeG free energy. Within the dispersion model only a slight decrease of the transition temperature is observed. The case of negative uniaxial dielectric anisotropy shows that the biaxial-uniaxial transition is destroyed and the uniaxial-isotropic transition becomes a weak biaxial- weak uniaxial (paranematic) transition. The LdeG analysis is only qualitative for this case.

2. Landau-de Gennes Free Energy

The Landau order parameter for both the uniaxial and biaxial nematic phases is taken to be the anisotropic part of the dielectric (diamagnetic) tensor [5]: $Q_{ij} = \varepsilon_{ij} - \delta_{ij}\,(1/3)\,\varepsilon_{kk}$, where δ_{ij} is the identity tensor and repeated indices are summed over. Q_{ij} is traceless. The principal axes of the tensor ε_{ij} are taken to be the triad of unit vectors $\hat{\boldsymbol{a}}$, $\hat{\boldsymbol{b}}$, and $\hat{\boldsymbol{c}}$ with corresponding principal values $\varepsilon_a \geq \varepsilon_b \geq \varepsilon_c$. The isotropic phase corresponds to $\varepsilon_a = \varepsilon_b = \varepsilon_c$, a uniaxial nematic with positive anisotropy to $\varepsilon_{\parallel} \equiv \varepsilon_a > \varepsilon_b = \varepsilon_c \equiv \varepsilon_{\perp}$, a uniaxial nematic with negative anisotropy to $\varepsilon_{\perp} \equiv \varepsilon_a = \varepsilon_b > \varepsilon_c \equiv \varepsilon_{\parallel}$, and a biaxial nematic to $\varepsilon_a > \varepsilon_b > \varepsilon_c$. The Q_{ij} tensor can then be expressed as $Q_{ij} = q_a\, a_i a_j + q_b\, b_i b_j + q_c\, c_i c_j$, where $q_a = (2\varepsilon_a - \varepsilon_b - \varepsilon_c)/3$, $q_b = (2\varepsilon_b - \varepsilon_a - \varepsilon_c)/3$, and $q_c = (2\varepsilon_c - \varepsilon_a - \varepsilon_b)/3$. Note that $q_a - q_b = \varepsilon_a - \varepsilon_b \equiv \Delta_{ab}$, and $q_b - q_c = \varepsilon_b - \varepsilon_c \equiv \Delta_{bc}$. When $\Delta_{ab} \geq \Delta_{bc}$, the relationship with the positive anisotropy uniaxial nematic suggests that it is useful to define $S \equiv q_a$ and $P \equiv \Delta_{bc}$. This leads to the familiar form $Q_{ij} = S\ a_i a_j + (1/2)(-S+P)\ b_i b_j + (1/2)(-S-P)\, c_i c_j$, and the conditions $S \geq P \geq 0$. Similarly, when $\Delta_{ab} < \Delta_{bc}$ the identifications $S \equiv q_c$ and $P \equiv -\Delta_{ab}$ lead to $Q_{ij} = (1/2)(-S-P)\ a_i a_j + (1/2)(-S+P)\ b_i b_j + S\, c_i c_j$, with $0 \geq P \geq S$ and a clear connection to a negative uniaxial anisotropy when $P \to 0$.

The field independent terms in the LdeG free energy [1,6] are the scalar invariants of $\mathrm{Tr}(\mathbf{Q}^2)$ and $\mathrm{Tr}(\mathbf{Q}^3)$. Furthermore, the electric (magnetic) field and Q_{ij} dependent term in the LdeG free energy is given by:

$$F_E = -(1/2) E_i Q_{ij} E_j \tag{1}$$

For a bulk sample, the field will establish the orientation of the $\hat{\boldsymbol{a}}$, $\hat{\boldsymbol{b}}$, and $\hat{\boldsymbol{c}}$ axes. To minimize F_E, the field will always be along the $\hat{\boldsymbol{a}}$ axis since we assumed that $q_a > q_b > q_c$. Thus $F_E = -(1/2)\, E^2\, q_a$. Lastly, it is useful to make the variable changes: $S \equiv q\cos(\theta)$ and $P \equiv \sqrt{3}\, q \sin(\theta)$ where $0 \leq \theta \leq \pi/6$, and $q > 0$ for $\Delta_{ab} > \Delta_{bc}$ (positive uniaxial anisotropy), but $q < 0$ for $\Delta_{ab} < \Delta_{bc}$(negative uniaxial anisotropy). Now $\mathrm{Tr}(\mathbf{Q}^2) = (3/2)\, q^2$ and $\mathrm{Tr}\,(\mathbf{Q}^3) = (3/4)\, q^3 \cos(3\theta)$, which leads to the following form for the LdeG free energy [1,6]:

$$F = \frac{1}{2}aq^2 - \frac{1}{3}bq^3\cos(3\theta) + \frac{1}{4}cq^4 + \frac{1}{5}dq^5\cos(3\theta) + \frac{1}{6}eq^6 + \frac{1}{6}\varphi q^6[\cos(3\theta)]^2 - \frac{1}{2}E^2 q_{\pm}, \tag{2}$$

where $q_+ = q\cos(\theta)$ (for positive uniaxial anisotropy), $q_- = -q\cos(\theta - \pi/3)$ (for negative uniaxial anisotropy), a, b, c, d, e and $\varphi \equiv f - e$ are Landau coefficients, and a is linear in temperature. For stability, $f > 0$ and $e > 0$ are required, but the additional condition $f > e$ is necessary to have a stable biaxial nematic when $E = 0$ [6]. In the absence of a field, a wide variety of sequences of transitions are possible as a function of decreasing a (i.e., temperature), depending on the specific values of b, c, d, e, and f [6]. Rather than consider all possibilities, which are left to our forthcoming publication, in this work generic values of the parameters will be chosen such that the sequence is a first order isotropic to uniaxial nematic transition at T_{UI} followed by a second order uniaxial nematic to biaxial nematic transition at T_{BU} as temperature is reduced. The phase diagrams of reference [6] reveal that effectively this means that c and d may be either positive or negative, as long as b is sufficiently positive and $f > e > 0$.

2.1. *Calculations for $\Delta_{ab} > \Delta_{bc}$*

The first feature of interest is to examine the N_U-N_P transition when $\Delta_{ab} > \Delta_{bc}$. For the uniaxial phase $\theta = 0$ and F reduces to $F = \frac{1}{2}aq^2 - \frac{1}{3}bq^3 + \frac{1}{4}cq^4 + \frac{1}{5}dq^5 + \frac{1}{6}fq^6 - gq \equiv F_U$. Here $g \equiv E^2/2$. The equilibrium value of q (labeled q_e) is the one of the five possible q's satisfying $\partial F/\partial q = 0$ that has the lowest value of F. It is assumed that b, c, d, and f have values such that for $g = 0$, there is a single transition from $q_e = 0 \equiv q_I$ to $q_e \equiv q_U > 0$ as a decreases. When $g > 0$, one finds a single transition in q_e from q_P to q_U where $0 < q_P < q_U$. The transition occurs when $F(q_P) = F(q_U)$. Technically of course q_P now represents a uniaxial paranematic phase with weak anisotropy rather than a true isotropic phase.

The critical point where the N_U-N_P transition ends is labeled by the critical values q_c, a_c, and g_c. They can be obtained from the additional conditions that $\partial^2 F/\partial q^2 = 0$ and $\partial^3 F/\partial q^3 = 0$ at the critical point: $q_c^3 + \frac{3d}{5f}q_c^2 + \frac{3c}{10f}q_c - \frac{b}{10f} = 0$, $a_c = \frac{1}{2}q_c[3b - 3cq_c - 2dq_c^2]$, $g_c = \frac{1}{5}q_c^2[3b - 4cq_c - 3dq_c^2]$. Trivially this gives $q_c = b/3c$, $a_c = b^2/3c$, and $g_c = b^3/27c^2$ when $d = f = 0$, which reproduces the critical point in the fourth order Landau theory of reference [1], although a stable biaxial nematic no longer exists. When $E = 0$, the N_U-I transition occurs at $a_0 = bq_0 - cq_0^2 - dq_0^3 - fq_0^4$, where q_0 satisfies $2fq_0^3 + \frac{9}{5}dq_0^2 + \frac{3}{2}cq_0 - b = 0$.

The second feature of interest is to analyze the effect of E on the N_B–N_U transition. Since the biaxial nematic has $\theta \neq 0$, it is convenient to define $\cos(\theta) = 1 - x$, which leads to $\cos(3\theta) = 1 - 9x + 12x^2 - 4x^3$. Now $F = F_U + F_B$ with

$$F_B = xP_1 + x^2P_2 + x^3P_3 + q^6\varphi\left[36x^4 - 16x^5 + \frac{8}{3}x^6\right], \tag{3}$$

where $P_1 = q\left[g + 3bq^2 - \frac{9}{5}dq^4 - 3\varphi q^5\right]$, $P_2 = 4q^3\left[-b + \frac{3}{5}dq^2 + \frac{35}{8}\varphi q^3\right]$, and $P_3 = \frac{4}{3}q^3\left[b - \frac{3}{5}dq^2 - 28\varphi q^3\right]$. A second order N_B–N_U transition occurs when $x = 0$ satisfies both $\partial F_B/\partial x = 0$ (i.e., $P_1 = 0$), and $\partial F_U/\partial q = 0$. $P_1 = 0$ is linear in g and does not explicitly involve a while $\partial F_U/\partial x = 0$ is linear in both g and a. Denoting the values of q and a at which the second order N_B–N_U transition occurs by q_B and a_B, one finds $3\varphi q_B^5 + \frac{9}{5}dq_B^4 - 3bq_B^2 - g = 0$, and $a_B = -2bq_B - cq_B^2 + \frac{4}{5}dq_B^3 + (2f - 3e)q_B^4$. Let a_{B0} and q_{B0} be the corresponding values when $g = 0$. Having obtained the equations for a_c, q_c, g_c, a_B and q_B, it is necessary to select illustrative values of b, c, d, e, and f to demonstrate the effect of E. For simplicity of calculation, assume $c = d = 0$.

The results are: $a_0 = f(b/2f)^{4/3}$, $a_c = 3a_0/5^{1/3} = 1.75\, a_0$, $g_c = 6f(b/10f)^{5/3}$, $q_{B0} = (b/\varphi)^{1/3}$, and $a_{B0} = -(be/\varphi)q_{B0} = -ef^{1/3}(2/\varphi)^{4/3}a_0$. The expression for a_B is the fifth order polynomial $(a_B/a_{B0})^5 - (a_B/a_{B0})^2 = (g/g_c)([1 - e/f]/10)^{2/3}/5$. To further simplify, values of e and f must be selected, although it is clear that scaling a_c by a_0, a_B by a_{B0} and g by g_c renders the choice of b irrelevant. For $e = 1$ and $f = 1.5$, $a_{B0} = -7.27a_0$ and as g/g_c increases from 1 to 10 to 20, a_B/a_{B0} increases from 1.0068 to 1.058 to 1.103. However, for $e = 1$ and $f = 2$, $a_{B0} = -3.17a_0$ and as g/g_c increases from 1 to 10 to 20, a_B/a_{B0} decreases from 0.991 to 0.910 to 0.824. The conclusion to be reached from these examples is that the shift of a_B with changing E is sensitive to the parameters e and f: T_{BU} may move to lower temperature or higher temperature as E increases. It should also be noted that because the only known measurement [4] of a_c/a_0 corresponds to a $T_c - T_{NP}$ of only 0.6 K, that sets the scale for the field dependent transition temperatures and suggests the shifts will be small. However if the a_{B0}/a_0 ratio is a large negative number, the shift may be large.

2.2. *Discussion of the Case* $\Delta_{ab} < \Delta_{bc}$

As shown by Gramsbergen *et al.* [1] the effect of E on the N_U-N_P transition in fourth order Landau theory is much more striking for negative uniaxial anisotropy than for positive uniaxial anisotropy (see Figure 17 in reference [1]). Specifically, the isotropic phase becomes a weakly anisotropic paranematic phase, but the uniaxial nematic becomes weakly biaxial. That is, the field induces biaxiality in a phase that is uniaxial at zero field. Experimentally, the phenomenon of field induced biaxiality has also been observed [7,8]. The N_B-N_P transition line in the E^2 – a phase space does not end in a critical point as for N_U-N_P transition, but changes from first order to second order at a tricritical point. What happens in the sixth order Landau theory that also includes a N_B-N_U transition at zero field? Qualitatively, one expects similar behavior for the N_B-N_P transition as in the fourth order Landau theory, but some quantitative shifts due to the extra parameters. However a second order N_B-N_U transition at zero field is likely to simply disappear at nonzero field [1]. Biaxiality is expected to smoothly increase from weak to strong order as temperature decreases [1] (see Fig. 22 in [1]), analogous to the behavior of a zero field second order ferromagnetic transition in a metal when a magnetic field is applied. If the Landau parameters are such that the N_B-N_U transition is first order in zero field (see Figs. 8, 9, and 11 in [6]) then in the presence of a field, a N_B-N_B transition is expected, which should terminate in a critical point when the field becomes strong enough.

3. Quadrupolar Model in an External Field

It is often useful to establish the connection between the macroscopic Q_{ij} tensor and the microscopic order parameters that describe the time-averaged orientational order of the molecules, as is discussed in section 2.1.3. of de Gennes and Prost [5] and in [1]. However, that connection is not expected to be very direct in general. For example, in the case of the dielectric tensor the macroscopic polarization is not simply the sum of the polarizations of individual molecules caused by the applied field. The diamagnetic tensor is somewhat simpler to interpret at the molecular level [1], but note that even in this case there might not be a unique Landau expansion for a given material: there can be a different one for each choice of which tensor is the order parameter. More specifically, the coefficients weighting terms with odd power of $\mathrm{Tr}(\boldsymbol{Q}^3)$ can

acquire different signs when we have materials that have different anisotropies for different properties. Clearly, as discussed above, the action of an external field conjugate to a given susceptibility will contribute to the interaction energy with an overall plus or minus sign, consistent with the sign of the anisotropy. The molecular model studied here is the simplest one which accounts for nematic phases and for which predictions of molecular and LdeG theories can be directly compared. We take a system composed of N molecules that occupy the sites of a simple three dimensional cubic lattice. The molecules are assumed to be nonpolar and to have anisotropic intermolecular interactions as well as electric and magnetic susceptibilities. The dimensionless interaction energy, H, of the system is given by

$$H\bar{\epsilon} = -\bar{\epsilon} \sum_{<i,j>} \mathrm{Tr}[\boldsymbol{Q}(\boldsymbol{\Omega}_i)\boldsymbol{Q}(\boldsymbol{\Omega}_j)] - \sum_{i=1}^{N} \Delta\varepsilon h^2 e_\alpha Q_{\alpha\beta}(\Omega_i) e_\beta, \tag{4}$$

where the first term represents anisotropic intermolecular interactions. They are expressed in terms of a molecular (symmetric and traceless) quadrupolar tensor $\boldsymbol{Q}$, which is composed of uniaxial ($\boldsymbol{T}_0^{(2)}$) and biaxial ($\boldsymbol{T}_2^{(2)}$) parts of $D_{\infty h}-$ and $D_{2h}-$ symmetry, respectively. It reads

$$\boldsymbol{Q}(\boldsymbol{\Omega}_i) = \boldsymbol{T}_0^{(2)}(\boldsymbol{\Omega}_i) + \sqrt{2}\lambda \boldsymbol{T}_2^{(2)}(\boldsymbol{\Omega}_i), \tag{5}$$

where $\boldsymbol{T}_0^{(2)}(\boldsymbol{\Omega}_i) = \sqrt{\frac{3}{2}}(\hat{\boldsymbol{c}}_i \otimes \hat{\boldsymbol{c}}_i - \frac{1}{3}\mathbf{1})$ and $\boldsymbol{T}_2^{(2)}(\boldsymbol{\Omega}_i) = \sqrt{\frac{1}{2}}(\hat{\boldsymbol{a}}_i \otimes \hat{\boldsymbol{a}}_i - \hat{\boldsymbol{b}}_i \otimes \hat{\boldsymbol{b}}_i))$ are built out of the orthonormal tripod $\{\hat{\boldsymbol{a}}_i, \hat{\boldsymbol{b}}_i, \hat{\boldsymbol{c}}_i\}$ of vectors defining the orientational degrees of freedom of the i-th molecule ($\boldsymbol{T}_m^{(L)}(\boldsymbol{\Omega}_i) \equiv \boldsymbol{T}_m^{(L)}(\{\hat{\boldsymbol{a}}_i, \hat{\boldsymbol{b}}_i, \hat{\boldsymbol{c}}_i\})$). The term proportional to $\Delta\varepsilon h^2$ represents interaction of molecules with an external field $\boldsymbol{E}$ ($h = |\boldsymbol{E}|$, $|\boldsymbol{e}| = 1$, $\boldsymbol{e} \parallel \boldsymbol{E}$). Summation in (4) runs over nearest neighbors and $\boldsymbol{\Omega}$ represents orientation of principal axes of $\boldsymbol{Q}$.

One possible interpretation of $\boldsymbol{Q}$ is in terms of the anisotropic part of the molecular polarizability tensor $\boldsymbol{\alpha}$ in which case the model is referred to as the dispersion model. Then the interaction energy (4) accounts for the leading order of point dispersive interactions [9] with the parameters $\bar{\epsilon}$ and λ being dependent on the diagonal elements $\{\alpha_{xx}, \alpha_{yy}, \alpha_{zz}\}$ of $\boldsymbol{\alpha}$: $\bar{\epsilon} = \epsilon_0(2\alpha_{zz} - \alpha_{xx} - \alpha_{yy})^2$ and $\lambda = \sqrt{\frac{3}{2}}\frac{\alpha_{xx}-\alpha_{yy}}{(2\alpha_{zz}-\alpha_{xx}-\alpha_{yy})}$. The parameter λ 'measures' the deviation of $\boldsymbol{\alpha}$ from cylindrical molecular symmetry and $\Delta\epsilon$ is the anisotropy of $\boldsymbol{\alpha}$. With this interpretation, for an electric case, $\boldsymbol{E}$ would be the local field equal to the applied field plus the fields produced by all induced dipole moments in the system. In the simplest approximation where both fields are assumed just proportional to each other (Lorentz-Lorentz or isotropic approximation [10]) the proportionality coefficient can be absorbed by the factor $\Delta\varepsilon h^2$ and $\boldsymbol{E}$ treated as the applied field. In the magnetic case the local and the applied fields are the same.

Special cases of the model (4) have already been studied. For $\mathrm{h} = \lambda = 0$ the potential in Eq. (4) reduces to the well-known Maier-Saupe or Lebwohl-Lasher potential [11], which describes a phase diagram with isotropic and uniaxial nematic phases connected by a first-order phase transition. Second is the one where $\lambda \neq 0$ and $\mathrm{h} = 0$. Potential (4) then reduces to the model proposed by Luckhurst *et al.* [2], which was extensively studied by Biscarini *et al.* [3]. The model describes a phase diagram with uniaxial nematic and biaxial nematic phases connected by the second-order

phase transition. In addition to an isotropic (I) phase, the following phases are identified: nematic prolate (N_U^+) for positive anisotropy of $\boldsymbol{\alpha}$, nematic oblate (N_U^-) for negative anisotropy of $\boldsymbol{\alpha}$ and biaxial nematic (N_B) phases. The tensor $\boldsymbol{Q}$ exhibits maximal degree of biaxiality for $\lambda = 1/\sqrt{6}$ – the so called self-dual Landau point [12], for which a direct continuous N_B-I phase transition occurs. For $\lambda < 1/\sqrt{6}$ and $\lambda > 1/\sqrt{6}$ the biaxial phase is preceded by a uniaxial phase: N_U^+ and N_U^-, respectively. Further generalizations of the model are found in [12–14]. Our goal here is to investigate the effect of taking into account interaction of the molecules with an external field, which can be either electric or magnetic. We show that the results are consistent with LdeG theory discussed in the previous section.

3.1. *Order Parameters*

The primary order parameters, useful for identifying phases are the thermodynamic averages, $<\Delta^{(L)}_{mm'}>$, of symmetrized Wigner matrices $\Delta^{(L)}_{mm'} = \mathrm{Tr}[\boldsymbol{T}^{(L)}_m(\{\hat{\boldsymbol{l}}, \hat{\boldsymbol{m}}, \hat{\boldsymbol{n}}\}) \boldsymbol{T}^{(L)}_{m'}(\{\hat{\boldsymbol{a}}_i, \hat{\boldsymbol{b}}_i, \hat{\boldsymbol{c}}_i\})]$, where $\{\hat{\boldsymbol{l}}, \hat{\boldsymbol{m}}, \hat{\boldsymbol{n}}\}$ denotes the directors' tripod. The dominant of these are $<\Delta^{(2)}_{00}>$ and $<\Delta^{(2)}_{22}>$, which are non-zero in the nematic phases. The alignment tensor of Landau theory is proportional to $<\boldsymbol{Q}> = \sum_{m=0,2} \boldsymbol{T}^{(2)}_m(\{\hat{\boldsymbol{l}}, \hat{\boldsymbol{m}}, \hat{\boldsymbol{n}}\})$ $\mathrm{Tr}[\boldsymbol{T}^{(2)}_m(\{\hat{\boldsymbol{l}}, \hat{\boldsymbol{m}}, \hat{\boldsymbol{n}}\}) <\boldsymbol{Q}(\boldsymbol{\Omega}_i)>] = \sum_{m=0,2} \boldsymbol{T}^{(2)}_m(\{\hat{\boldsymbol{l}}, \hat{\boldsymbol{m}}, \hat{\boldsymbol{n}}\})$ $(<\Delta^{(2)}_{m0}> + \sqrt{2}\lambda < \Delta^{(2)}_{m2}>)$. Having determined $<\boldsymbol{Q}>$ the distinction between oblate and prolate ordering can be made by calculating $\mathrm{w}(<\boldsymbol{Q}>) = \frac{\sqrt{6}\mathrm{Tr}[<\boldsymbol{Q}>^3]}{Tr[<\boldsymbol{Q}>^2]^{3/2}}$, which equals $+1$ in the prolate uniaxial and -1 in the oblate uniaxial phase [1,6]. For the biaxial case $1 < w < -1$, with $w = 0$ corresponding to a biaxial state of maximal biaxiality. $\boldsymbol{Q}$ vanishes in the isotropic phase, hence w is undefined there.

3.2. *Results of Mean Field Analysis and Monte Carlo Simulations*

Thermodynamic properties of the system (4) are derived from the free energy $\beta F = -\ln Z$, where $Z = (\prod_{k=1}^{N} \int d\boldsymbol{\Omega}_k)\exp[-\frac{H}{t}]$ and where t is the reduced temperature. We will apply two methods to determine phase diagrams. The methods are the Metropolis Monte Carlo (MC) simulation and the mean field (MF) approximation. The first method allows to generate states out of the N-particle distribution function $\mathrm{P_N}(\boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2, \ldots, \boldsymbol{\Omega}_N) = \mathrm{Z}^{-1}\exp[-\frac{H}{t}]$ while the mean field theory makes use of the non-equilibrium free energy, F^{non}, expressed in terms of the one-particle distribution function $\mathrm{P_1}(\boldsymbol{\Omega}) \equiv \mathrm{P}(\boldsymbol{\Omega})$: $t^{-1}F^{non} = \frac{1}{2}N\,d\,t^{-1} \int \mathrm{d}\boldsymbol{\Omega}_1 \mathrm{d}\boldsymbol{\Omega}_2\ [P(\boldsymbol{\Omega}_1)P(\boldsymbol{\Omega}_2)\ \mathrm{H}(\boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2)] + N \int \mathrm{d}\boldsymbol{\Omega}\ P(\boldsymbol{\Omega}) \ln P(\boldsymbol{\Omega})$. As usual, the equilibrium properties are obtained by minimizing F^{non} with respect to P, subject to the normalization condition $\int \mathrm{d}\boldsymbol{\Omega}\ P(\boldsymbol{\Omega}) = 1$. Here $\mathrm{d} = 6$ is the number of nearest neighbors for each molecule and $\boldsymbol{\Omega}$ is the $SO(3)$-invariant parameterization of rotations either in terms of the Euler angles (MF) or quaternions (MC). As MF underestimates entropy, it gives overestimation of the transition temperature and therefore provides a good starting point for more accurate MC estimates.

The MF calculus and MC simulations presented in this paper aim at constructing the phase diagram in the variables $(t, \Delta\varepsilon h^2)$ for the prolate biaxial molecules of $\lambda = 0.3$ (i.e., $\mathrm{w}(\boldsymbol{Q}) = \frac{1-6\lambda^2}{(1+2\lambda^2)^{3/2}} \overset{\lambda=0.3}{\rightarrow} 0.36$). The simulations were carried out on a cubic $16 \times 16 \times 16$ lattice with periodic boundary conditions. A MC move is made by rotating a randomly chosen molecule with quaternion parameterization for rotations. Doing so N times is considered a sweep. Each run consisted of 50000–60000

MC lattice sweeps to thermalize the system from an initial, completely ordered, biaxial configuration and 80000–100000 sweeps of the production run. The acceptance ratio was tuned to vary between 30% and 40%. Every 10th sweep was considered for measurement of thermodynamic averages.

The applied field was chosen to be aligned along the z axis and both positive and negative values of $\Delta\epsilon h^2$ were considered for selected λ. The phase boundaries were identified from peaks of the specific heat and the phases were determined from w. Figure 1 reproduces the known result of a temperature scan in the case of zero field [3]. The high temperature phase is thus the isotropic (I) phase. As the temperature is lowered a first-order phase transition occurs and the nematic prolate (N_U^+) phase emerges. Lowering the temperature further causes a second-order phase transition to take place from the uniaxial to the biaxial nematic (N_B) phase. Figure 2 presents the full (t, $\Delta\epsilon h^2$) phase diagram in the regime of parameters where the qualitative differences in phase behavior were detected.

The effect of the field in the case of positive anisotropy of susceptibility is fully consistent with Landau-de Gennes theory. The results are presented in the upper part of the phase diagram in Figure 2. An exemplary temperature scan is presented in Figure 3. In the case of positive anisotropy, the interaction promotes aligning of the eigenvectors of the molecular $\boldsymbol{Q}$ tensors associated with the largest eigenvalue along the direction of the field. The isotropic (I) phase acquires a small (field-induced) long range order and is replaced by the paranematic prolate (N_P^+) phase. The phase transition from I to N_U^+ is replaced by N_P^+ to N_U^+ for sufficiently small

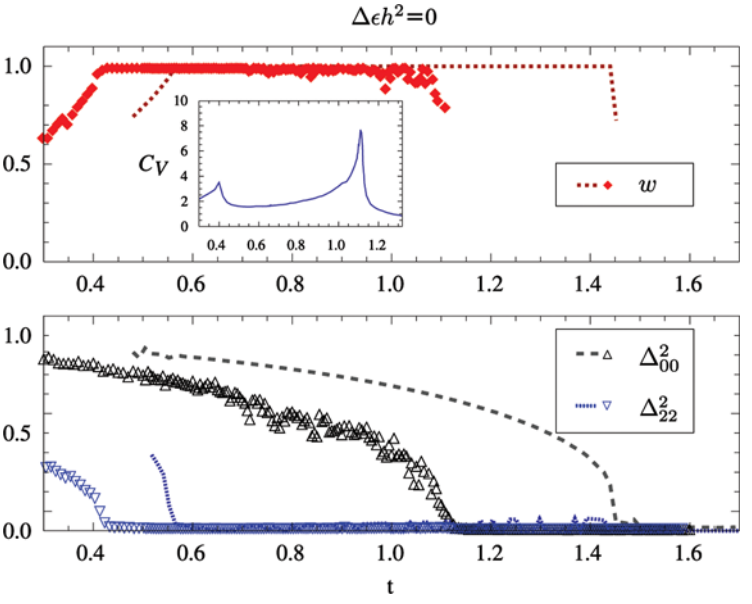

Figure 1. Temperature scan of the order parameters for $\lambda = 0.3$ in the case of zero field, reproducing the familiar sequence of phase transitions as known from Ref [2]. Points represent MC results, dashed lines correspond to MF calculations. Specific heat for this scan is plotted in the inset. The phase sequence is $I \rightarrow N_U^+ \rightarrow N_B$ as the temperature is decreased. Signatures of the phase transitions are peaks in the specific heat, as well as a rapid change in order parameters and w. The parameter w is not defined in the isotropic phase.

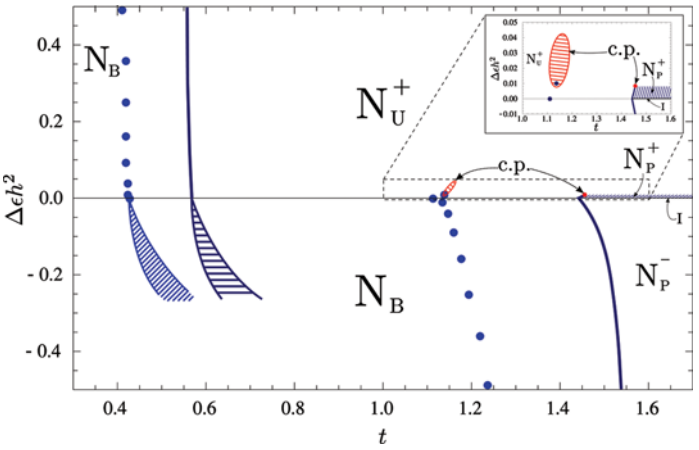

Figure 2. Mean Field (thick lines) and Monte Carlo results (points) for the phase diagram of the model with $\lambda = 0.3$ in $(t, \Delta\varepsilon h^2)$ plane. Also presented is the critical point for positive molecular anisotropy; it is indicated as a point for MF and as a dashed area for MC results. Inset is a zoom about the critical point. For negative anisotropy, the transition from uniaxial nematic (N_U^+) to biaxial nematic (N_B) occurring for zero field is replaced by an area, where spontaneous biaxiality is predominant. This is indicated as dashed areas with horizontal dashes for MF and slanted dashes for MC results.

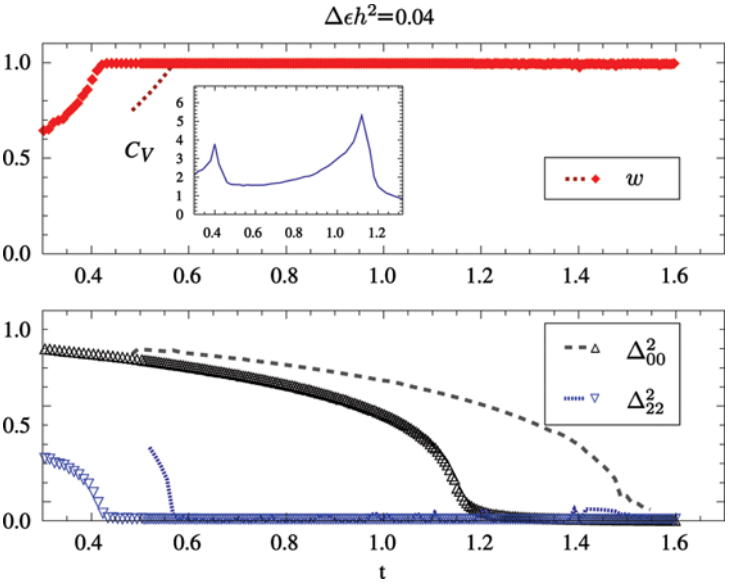

Figure 3. Temperature scan of the order parameters and w for $\Delta\epsilon h^2 = 0.04$ (above the critical point). Dashed lines correspond to Mean Field results while Monte Carlo data is presented as points. Specific heat for this scan is plotted in the inset. The phase sequence is $N_P^+ \rightarrow N_U^+ \rightarrow N_B$ as the temperature is decreased. Note that in the N_P^+ phase the uniaxial order parameter is small, however w clearly indicates prolate order. The phase transitions are detected from peaks of the specific heat and from a rapid change in order parameters and w.

fields and the transition temperature is slightly increased with increasing field. The transition line terminates at a critical point. Above that point the N_P^+ phase transforms into N_U^+ without a phase transition. MF calculations revealed this point to occur at $\Delta\epsilon h^2 \approx 0.1$, while MC results indicate the presence of the critical point for $\Delta\epsilon h^2$ somewhere in the range (0.01, 0.04). The field does not affect much the N_U^+ to N_B transition line; the transition temperature is only slightly lowered with the field.

The case of negative molecular susceptibility is less obvious, but nevertheless intuitive. The lower part of the phase diagram in Figure 2 presents the results for this case. An exemplary scan for $\Delta\epsilon h^2 = -0.04$ is given in Figure 4. The eigenvectors associated with the *lowest* of the eigenvalues of the $\boldsymbol{Q}$ tensors are promoted to align parallel to the field. Therefore, when the field is applied to the isotropic phase, it induces a small uniaxial oblate ordering in the sample (N_P^- phase). That is, in the plane perpendicular to the field, there is still residual $SO(2)$ symmetry. When the temperature is lowered, this uniaxial symmetry of N_P^- is broken and the biaxial nematic phase emerges. The temperature of the first order N_B to N_P^- transition initially increases, but saturates as the magnitude of the field is increased. At sufficiently high fields the N_B to N_P^- transition becomes second order. As the temperature is lowered, the field-induced biaxial order parameter is small until $t \gtrsim 0.5$. For $t \lesssim 0.5$, in the hatched

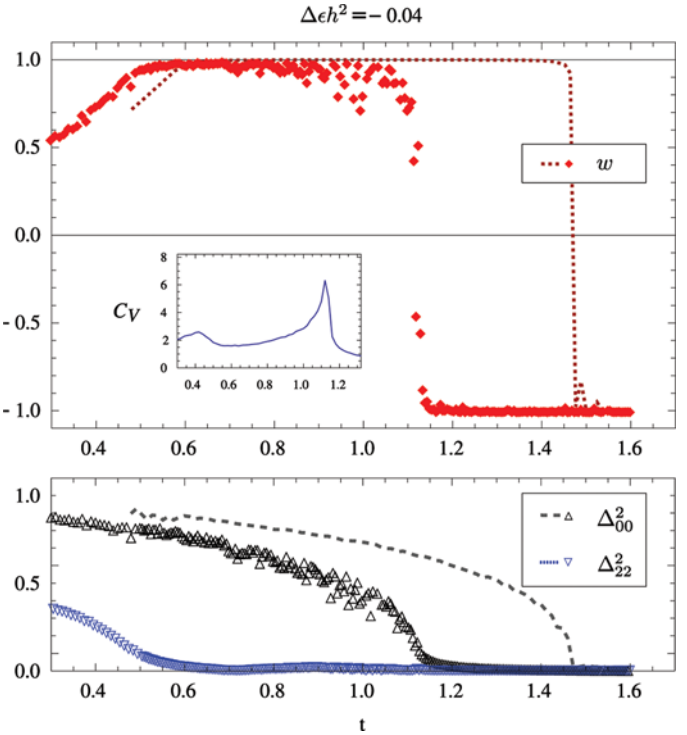

Figure 4. Similar as Figure 3 but for $\Delta\epsilon h^2 = -0.04$. The phase sequence is $N_P^- \rightarrow N_B$ as the temperature is decreased. The paranematic oblate (N_P^-) phase has very small, field induced nematic order, but the presence of ordering is evident from the fact that $w \approx -1$ in this phase. The phase transition is identified from a peak in the specific heat, as well as from a rapid change of w.

area of Figure 2, spontaneous biaxiality emerges. But, contrary to the case of $\Delta\epsilon h^2 > 0$, when the $N_B - N_U^+$ phase transition is observed, the peak in the specific heat disappears and there is no indication of any phase transition. The phases on both sides of this transient region are clearly the same N_B phase, differing only in the amount of ordering (see Figure 4).

4. Conclusions

Results of Landau theory to sixth order in the traceless tensor order parameter and molecular modeling have been used to theoretically analyze the effect of an external field on both the biaxial nematic-uniaxial nematic and the uniaxial nematic to para-nematic phase transitions. Quantitative calculations for the case of positive uniaxial anisotropy demonstrate that the shift of the N_B-N_U transition temperature with field strength, and even the sign of the shift, is sensitive to the empirical coefficients in the Landau free energy expansion. The N_U-N_P transition, as expected from Landau theory and molecular modeling, ends in a critical point and the transition from N_B to field- induced N_P^- crosses over from first to second order. Qualitatively, it is anticipated that for negative uniaxial anisotropy, a first order zero field N_B-N_U transition will become a N_B-N_B transition that ends in a critical point at sufficiently strong field, however this has not been demonstrated in the present modeling.

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