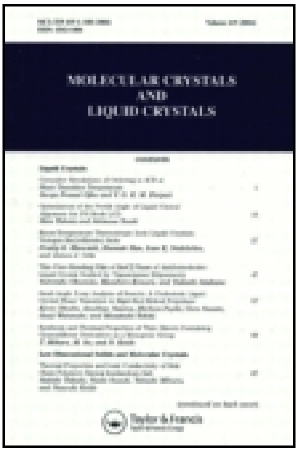

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Steric Effects in Polar Nematic Liquid Crystals

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Version of record first published: 30 Jun 2011

To cite this article: F. Bisi (2011): Steric Effects in Polar Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 541:1, 132/[370]-141/[379]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.570182

Mol. Cryst. Liq. Cryst., Vol. 541: pp. 132/[370]–141/[379], 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.570182

Steric Effects in Polar Nematic Liquid Crystals

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Recent measurements in a nematic liquid crystal formed by polyester compounds have given evidence of spontaneous macroscopic polar ordering. A mean-field theory for liquid crystals is built combining short-range, repulsive, steric forces with the average electric dipolar energy exchanged between molecules sharing the same excluded region. Such model is capable of identifying both uniaxial and biaxial polar phases. Under the assumption of a spheroidal shape for the molecules, and through a numerical bifurcation analysis, we assess the stability of phases upon two interaction parameters: the degree of intrinsic biaxiality, and the relative orientation of the permanent electric dipoles.

Keywords Ferroelectricity; nematic liquid crystal; polar nematics; steric tensor

1. Introduction

The development of ferroelectric nematic phases has been a goal of fundamental and practical importance, pursued for long time [1,2]. Ferroelectric liquid crystal smectic phases from chiral or from banana-shaped molecules were reported in the literature (see, e.g., references in [3]); however, because of their layered structure, such phases lack the high fluidity characteristics typical of nematic liquid crystals used in electro-optical devices. From a theoretical point of view, the existence of a simple uniaxial nematic with polar order is not forbidden, however it was classically ruled out, and in any case a debate existed [4].

However, recent experimental results have given evidence of spontaneous ferroelectric ordering in nematic liquid crystals: Koike et al. [5] performed second harmonic generation measurements on a polymer commercially available (Vectra), capable of forming nematic liquid crystals [6]. Although no electric poling is made, polar ordering is spontaneously formed in the nematic liquid crystal. Furthermore, the phase appears to possess C_s packing symmetry, i.e., it is a biaxial phase.

These recent experimental results prompt the development of a model to explain the formation of such polar phases and to give a hint on how to engineer new molecules capable of exhibiting polar phases also at high temperatures, to avoid crystallization or transition to more ordered phases, such as smectic ones. We will go

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along the avenue of a mean-field model, which seems capable of explaining results measurements based on second harmonic generation in nematics [7].

It has been recently shown that purely polar steric interactions have the potential of inducing unexpected orientationally ordered states [8]. Electric dipolar forces in the structure of classical fluids can play a role, which has been explored for long time; general reviews on these issues can be found in [9] and [10]; furthermore, a shorter account on liquid crystals is also in [2] and another one on computer simulation with Gay-Berne mesogens can be found in [11].

However, in this paper we build a model for nematic liquid crystals only; our goal is to show how an interaction potential based on short-range, repulsive, steric forces can be combined with a second potential based on long-range, globally attractive, dispersion forces. In particular, we observe that in real molecules anisotropies both in shape and in polarisability coexist; it has been shown that an interaction potential originating from dispersion forces can be combined with a hard-core repulsion potential in a formal theory, based on a so-called "steric" tensor [12]. Starting from this, we build an interaction Hamiltonian incorporating the average electric dipolar energy exchanged between molecules sharing the same excluded region.

For a more detailed survey on the literature dedicated to explore how the possible dipolar nature of molecules has been incorporated in other model fluids, see [13], and references cited therein.

2. Interaction Potential

We report here the outline of the model describing the interaction between two molecules, each one endowed with a permanent dipole, surrounded by an inaccessible region. Details of the model, as well as a thorough description and analysis of all of the subtleties can be found in [13].

2.1. *Dipolar Interactions*

First, we need to describe the dipole-dipole interaction of two molecules; each molecule occupies a specific region in space, and is endowed with an intrinsic dipole moment. When we consider two electric dipoles, $\boldsymbol{p}$ and $\boldsymbol{p}'$, occupying in the space the position P_0 and P_0', respectively, we can write their interaction energy U_{dip} as

$$U_{\mathrm{dip}} = \frac{1}{4\pi\varepsilon_0 d^3}\boldsymbol{p}\cdot(\mathbf{I} - 3\boldsymbol{e}\otimes\boldsymbol{e})\boldsymbol{p}' \tag{1}$$

where $\mathbf{I}$ is the identity tensor, ε_0 is the vacuum dielectric constant, d is the distance between the dipoles and $\boldsymbol{e}$ is the unit vector oriented along the straight line joining the dipoles (see Fig. 1), i.e.,

$$d := |P_0 - P_0'| \quad \text{and} \quad \boldsymbol{e} := \frac{1}{d}(P_0 - P_0'). \tag{2}$$

We remark that, for given positions P_0, P_0', U_{dip} attains its absolute minimum in the parallel configuration, that is for both $\boldsymbol{p}$ and $\boldsymbol{p}'$ parallel to $\boldsymbol{e}$ and $\boldsymbol{p} = \boldsymbol{p}'$; in addition, in the antiparallel configuration ($\boldsymbol{p}' = -\boldsymbol{p}$, and $\boldsymbol{p} \perp \boldsymbol{e}$) U_{dip} attains a local minimum.

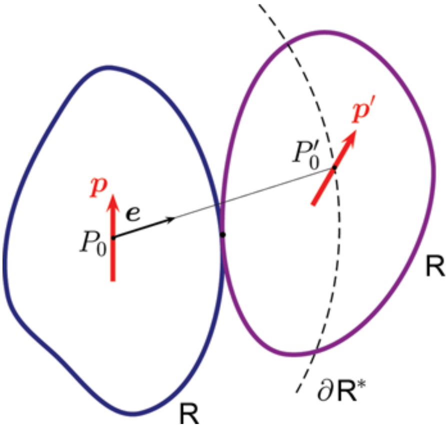

Figure 1. The regions R and R′ surrounding the charge centres P_0 and P'_0 of two interacting molecules. The unit vector $\boldsymbol{e}$ is directed from P_0 to P'_0. The excluded region R* is identified by its boundary, described as the envelope by P'_0 while ∂R* glides without rolling over ∂R. (Figure appears in color online.)

2.2. *Effective Hamiltonian*

As described in [12], the long-range interactions described above need being complemented by short-range repulsive forces, which represent the steric hindrance contribution to molecular interactions. Now, we imagine each dipole surrounded by a region R of space, inaccessible to all other dipoles; this region, called the van der Waals region, represents exactly the range of such repulsive forces. Therefore, when we consider a pair of molecules centred in (P, P'), endowed with dipoles $\boldsymbol{p}$ and $\boldsymbol{p}'$, respectively, and we fix a relative reciprocal orientation, there exists an excluded region R*, depending on R and R*, which can be seen as the region in space which is inaccessible to the dipole centre P'; in other words, the boundary of such excluded region ∂R* is enveloped by P' while the boundary ∂R′ of the second region glides without rolling on the boundary of the first region, ∂R. We can indeed consider R* as a shared excluded region, which depends only on the relative orientation (Fig. 1).

We want to take into account the presence of more than a pair of molecules in the system, therefore we imagine that an infinite system number of molecules are uniformly distributed in space, all equally oriented; the same number of molecules, N_{mac}, would be present in the same macroscopic volume V_{mac}. Let a probe molecule wander about the molecules of this system, while keeping its orientation unchanged: the total energy exchanged with the other molecules can be computed by imagining this latter exploring an influence ball $\mathrm{B_i}$ with radius R_i around the given molecule and then taking the limit as $R_i \to \infty$. The average energy is finally estimated by multiplying the total energy exchanged between a single molecule and its probe companion by the number density $\rho := N_{\mathrm{mac}}/V_{\mathrm{mac}}$.

Under these considerations, the effective Hamiltonian can be written in a compact form

$$H_{\mathrm{dip}} = \frac{\rho}{\varepsilon_0}\boldsymbol{p} \cdot \mathbf{S}_{\mathsf{R}^*}\boldsymbol{p}' \tag{3}$$

$$:= \frac{\rho}{4\pi\varepsilon_0} \lim_{\mathsf{R}_i \to \infty} \int_{S^2} dA(\boldsymbol{e}) \int_{u^*(\boldsymbol{e})}^{\mathsf{R}_i} \frac{1}{r} p \cdot (\mathbf{I} - 3\boldsymbol{e} \otimes \boldsymbol{e})\boldsymbol{p}' dr, \tag{4}$$

which defines the steric tensor $\mathbf{S}_{\mathsf{R}^*}$, where u^* $(\boldsymbol{e})$ describes a mapping of the unit sphere S^2 around P_0 into $\partial \mathsf{R}^*$.

3. Model Parameters for Spheroids

By adopting the description above for the excluded region, we have restricted our analysis to a star-shaped construction of R. Formally, the description of the excluded region can be given as

$$R^* := \{P^* : |P^* - P| < u^*(\boldsymbol{e}^*)\}, \tag{5}$$

$$\boldsymbol{e}^* := (P^{*^*} - P)/|P^* - P|. \tag{6}$$

where u^* $(\boldsymbol{e}^*)$ is an appropriate mapping of the unit sphere on the boundary $\partial \mathsf{R}^*$ of the excluded region. The effective Hamiltonian vanishes identically in a spherical molecule, which means in this case dipolar interaction effects would be masked by the steric contribution.

We then resort to a perturbative approach, and assume that the boundary $\partial \mathsf{R}$ of the region occupied by a molecule can be represented in spherical coordinates as a perturbation of a perfectly spherical surface:

$$u(\boldsymbol{e}) = R(1 + \varepsilon u_r(\boldsymbol{e})), \tag{7}$$

where R is the average molecular radius and ε a perturbation parameter.

To within the first order in ε, the steric tensor in Eq. (3) is

$$\mathbf{S}_{\mathsf{R}^*} = \frac{3}{8\pi^2} \varepsilon \int_{S^2 2} [u_r(\boldsymbol{e}) + u_r(-\mathbf{Q}^{\mathrm{T}}\boldsymbol{e})]\boldsymbol{e} \otimes \boldsymbol{e} + o(\varepsilon). \tag{8}$$

We assume now a quadrupolar shape for R; thus, we can introduce a symmetric shape tensor $\mathbf{E}$ such that

$$u_r(\boldsymbol{e}) = \boldsymbol{e} \cdot \mathbf{E}\boldsymbol{e}, \tag{9}$$

with

$$\mathbf{E} = \mathbf{E}^{\mathrm{T}} \quad \mathrm{tr}\mathbf{E} = 0; \tag{10}$$

with this choice, the effective Hamiltonian takes the form $(\mathbf{E}' = \mathbf{QEQ}^{\mathrm{T}})$:

$$H_{\mathrm{dip}} = \frac{\varepsilon\rho}{5\varepsilon_0} \boldsymbol{p} \cdot (\mathbf{E} + \mathbf{E}')\boldsymbol{p}' + o(\varepsilon). \tag{11}$$

We can introduce a unit vector $\boldsymbol{l} \in S^2$ along the permanent electric molecular dipole to describe the *molecular electric polarity*; in other words, we write $\boldsymbol{p} = p\ \boldsymbol{l}$, where p is the scalar electric dipole moment strength. If we neglect higher order terms, the effective hamiltonian in Eq. (11) thus takes the form

$$H = U_0(\mathbf{E}\boldsymbol{l} \cdot \boldsymbol{l}' + \mathbf{E}'\boldsymbol{l}' \cdot \boldsymbol{l}), \tag{12}$$

where $U_0 > 0$ is a constant that expresses the strength of the interaction.

Furthermore, we assume for the shape tensor in Eq. (9) a biaxial form

$$\mathbf{E} = \mathbf{q} + \lambda\mathbf{b}, \tag{13}$$

where

$$\mathbf{q} := \boldsymbol{m} \otimes \boldsymbol{m} - \frac{1}{3}\mathbf{I} \tag{14}$$

$$\mathbf{b} := \boldsymbol{n} \otimes \boldsymbol{n} - \boldsymbol{e}_\perp \otimes \boldsymbol{e}_\perp \tag{15}$$

are the traceless molecular tensors introduced in [14], and adopted for the assessment of biaxial phases for molecules endowed with D_{2h} symmetry [15–21].

The constitutive parameter in Eq. (13) λ ranges in $[-1, 1]$. For $\lambda = \pm 1$, the shape tensor $\mathbf{E}$ describes a disk-like molecule symmetric about $\boldsymbol{n}$ or $\boldsymbol{e}_\perp$. The largest biaxiality is attained for $\lambda = \pm\frac{1}{3}$.

In general, the dipole moment is not necessarily aligned with $\boldsymbol{m}$. Therefore, another model parameter is the angle α between the unit vectors $\boldsymbol{m}$ and $\boldsymbol{l}$. We place the unit vectors $\boldsymbol{l}$, $\boldsymbol{m}$, and $\boldsymbol{n}$ all in the same plane; thus the molecular electric polarity is

$$\boldsymbol{l} = \cos\alpha\boldsymbol{m} + \sin\alpha\boldsymbol{n}, \tag{16}$$

α can be assumed to range in $\left[0, \frac{\pi}{2}\right]$.

4. Mean Field Approximation

Following [22], we introduce two vector order parameters

$$\boldsymbol{M} := \langle \boldsymbol{m} \rangle \quad \text{and} \quad \boldsymbol{N} := \langle \boldsymbol{n} \rangle, \tag{17}$$

where $\langle \cdot \rangle$ denotes the appropriate ensemble average, computed relative to the one-particle distribution function ρ_0 of the mean-field approximation. These parameters describe a phase *uniaxial* if either $\boldsymbol{M} = 0$ or $\boldsymbol{N} = 0$, or if $\boldsymbol{M}$ and $\boldsymbol{N}$ are parallel, and *biaxial* if $\boldsymbol{M} \neq 0$ and $\boldsymbol{N} \neq 0$ and $\boldsymbol{M}$, $\boldsymbol{N}$ are not parallel. $\boldsymbol{M}$ and $\boldsymbol{N}$ define a plane, so we can identify this plane with $(\boldsymbol{e}_x, \boldsymbol{e}_z)$, and so we introduce four scalar order parameters (t, u, v, w) defined by

$$\boldsymbol{M} = t\, \boldsymbol{e}_x + u\, \boldsymbol{e}_z, \tag{18}$$

$$\boldsymbol{N} = v\, \boldsymbol{e}_x + w\, \boldsymbol{e}_z. \tag{19}$$

Correspondingly, the average polarisation is

$$\boldsymbol{P} = P_x\boldsymbol{e}_x + P_z\boldsymbol{e}_z, \tag{20}$$

where

$$P_x = t\cos\alpha + v\sin\alpha, \tag{21}$$

$$P_z = u\cos\alpha + w\sin\alpha. \tag{22}$$

Since both $\boldsymbol{m}$ and $\boldsymbol{n}$ are unit vectors, it is an easy consequence of (17) that all scalar order parameters (t, u, v, w) range in the interval $[-1, 1]$.

The assumption that neither $\boldsymbol{M}$ nor $\boldsymbol{N}$ can leave the plane $(\boldsymbol{e}_x, \boldsymbol{e}_z)$ in the different transitions possibly associated with phase transformations is to be confirmed *a posteriori* by computing the y-components M_y and N_y of $\boldsymbol{M}$ and $\boldsymbol{N}$ relative to the one-particle distribution function ρ_0 expressed in terms of (t, u, v, w): though finding M_y and E_y negligible will by no means be a proof of the validity of our assumption, it will provide evidence for the consistency of our model.

With these assumptions, the one-particle Hamiltonian H_0 becomes

$$\begin{aligned} H_0(\boldsymbol{M},\boldsymbol{N};\boldsymbol{m},\boldsymbol{n}) = {}& \frac{4}{3}\cos^2\alpha\boldsymbol{M}\cdot\boldsymbol{m} + \left(\lambda+\frac{1}{3}\right)\sin\alpha\cos\alpha\left(\boldsymbol{M}\cdot\boldsymbol{n}+\boldsymbol{E}\cdot\boldsymbol{m}\right) \\ & + 2\left(\lambda-\frac{1}{3}\right)\sin^2\alpha\boldsymbol{E}\cdot\boldsymbol{n} - \frac{1}{2}\left[\frac{4}{3}\cos^2\alpha\boldsymbol{M}^2\right. \\ & \left. + 2\left(\lambda+\frac{1}{3}\right)\sin\alpha\cos\alpha\boldsymbol{M}\cdot\boldsymbol{N} + 2\left(\lambda-\frac{1}{3}\right)\sin^2\alpha\boldsymbol{N}^2\right]. \end{aligned} \tag{23}$$

In terms of the order parameters the dimensionless mean-field free energy F_0 is described by the function:

$$\begin{aligned} f(t,u,v,w;\beta) = {}& -\left[\frac{2}{3}\cos^2\alpha(t^2+u^2) + \left(\lambda+\frac{1}{3}\right)\sin\alpha\cos\alpha(tv+uw)\right. \\ & \left. + \left(\lambda-\frac{1}{3}\right)\sin^3\alpha(v^2+w^2)\right] + \frac{1}{\beta}\ln\frac{1}{8\pi^2}\int_T^2 \mathrm{e}^{\beta g(t,u,v,w;\omega)}d\omega, \end{aligned} \tag{24}$$

Where the integral is performed on the toroidal manifold T, with

$$\begin{aligned} g(t,u,v,w;\omega) := {}& \frac{4}{3}\cos^2\alpha(t\cos\varphi\sin\vartheta + u\cos\vartheta) \\ & + \left(\lambda+\frac{1}{3}\right)\sin\alpha\cos\alpha[t(-\sin\psi\cos\varphi+\cos\psi\cos\varphi\cos\vartheta) \\ & - u\cos\psi\sin\vartheta + v\cos\varphi\sin\vartheta + w\cos\vartheta] \\ & + 2\left(\lambda-\frac{1}{3}\right)\sin^2\alpha[v(\cos\psi\cos\varphi\cos\vartheta - \sin\psi\sin\varphi) \\ & - w\cos\psi\sin\vartheta], \end{aligned} \tag{25}$$

and adopting

$$\beta := \frac{U_0}{k_B T}, \tag{26}$$

as the dimensionless inverse temperature (k_B is the Boltzmann constant).

The equilibrium equations obtained from the function in Eq. (24) suffer from a severe degeneracy, which can be removed by constraining the search for the critical points of f to $t = 0$ (i.e., by defining $\boldsymbol{e}_z$ as the direction of $\boldsymbol{M}$). This amounts to finding the free equilibrium points in (u, v, w) of the *extended* function

$$f_0^*(u, v, w; \beta) := f_0(u, v, w; \beta) + \mu \int_T^2 \cos\varphi \sin\vartheta e^{-\beta g_0(u,v,w;\omega)} d\omega, \tag{27}$$

where

$$g_0(u, v, w; \omega) := g(0, u, v, w; \omega), \tag{28}$$

and μ is a Lagrange multiplier to be determined.

The order parameter profiles have been obtained from a numerical bifurcation analysis of the equilibrium equations for Eq. (27), with the aid of MATCONT [24], a free software package, which integrates into Matlab [25]. We have performed the analysis starting from the trivial solution $u = v = w = 0$, which corresponds to the isotropic phase. Upon increasing β, we find a new stable solution branching off the trivial solution at

$$\beta = \beta_c(\lambda, \alpha) := \frac{3(\lambda - 1)\sin^2\alpha + 2 + \sqrt{3(3\lambda^2 - 2\lambda - 1)\sin^2\alpha + 4}}{(\lambda - 1)^2 \cos^2\alpha \sin^2\alpha}. \tag{29}$$

The minimum for the critical value is $9/8$, attained for $\lambda = -1$, $\alpha = \pi/2$, which corresponds to an oblate discotic molecule, with a permanent dipole moment $\boldsymbol{p}$ orthogonal to the disc (Fig. 2).

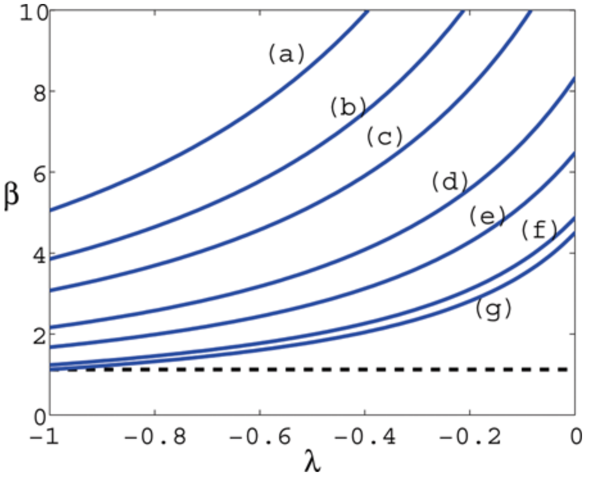

Figure 2. Plots of the critical value of dimensionless temperature β_c, as defined in Eq. 29, for $\lambda \in [-1, 0]$ and several values of α (from (a) to (g) $\alpha/\pi = 0.15, 0.175, 0.2, 0.25, 0.3, 0.4, 0.5$). The dashed line corresponds to $\beta_c = 9/8$, the minimum value attained for $\lambda = -1$ and $\alpha = \pi/2$ (a discotic molecule with the permanent dipole $\boldsymbol{p}$ orthogonal to the disc). (Figure appears in color online.)

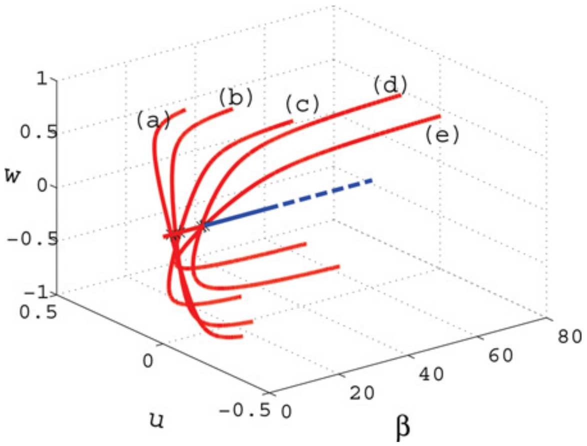

Figure 3. Bifurcation diagrams for the scalar order parameters u and w vs. β. Solid lines and dashed lines represent stable branches and unstable branches, respectively. A second order transition takes place for the critical value of dimensionless temperature β. (a) $\lambda = -0.9$, $\alpha = 0.25\pi$; $\beta_c = 2.35$, $\rho = 0.146$; (b) $\lambda = -0.5$, $\alpha = 0.25\pi$; $\beta_c = 3.58$, $\rho = 0.0554$; (c) $\lambda = 0$, $\alpha = 0.4\pi$; $\beta_c = 4.87$, $\rho = 0.132$; (d) $\lambda = 0.2$, $\alpha = 0.475\pi$; $\beta_c = 11.1$, $\rho = -0.149$; (e): $\lambda = 2/9$, $\alpha = 0.4375\pi$; $\beta_c = 11.9$, $\rho = -0.352$. (Figure appears in color online.)

The numerical evidence we collected suggests that the only equilibrium solutions for f are such that

$$t = \rho v \text{ and } u = \rho w, \tag{30}$$

and ρ can be computed under such assumption:

$$\rho(\lambda, \alpha) = -\frac{(3\lambda + 1)\sin\alpha\{9 + \beta_c[4\cos^2\alpha + 2(3\lambda - 1)\sin^2\alpha]\}}{4\cos\alpha\{9 + \beta_c[4\cos^2\alpha + \frac{1}{4}(3\lambda + 1)^2\sin^2\alpha]\}}, \tag{31}$$

This is confirmed by our numerical outcomes. In fact, we have found that along the bifurcated branch not only t, but also v vanishes to within our numerical precision, while the functions $u(\beta)$ and $w(\beta)$ are in a ratio ρ independent of β, to within the same numerical precision, but depending on different values for the model parameters (λ, α). Figure 3 shows typical bifurcation diagrams, obtained for different choices of (λ, α); they all show the classical pitchfork bifurcation with exchange of stability at $\beta = \beta_c$.

4. Conclusions

Within a mean-field model, we can predict the occurrence of a polar nematic phase for a system composed of polar molecules, with a biaxial shape. Steric effects have been introduced in the interaction potential through a second-rank tensor depending on the molecular excluded region R^*. An attractive potential is given by interactions due to permanent electric dipoles.

The synergy between the repulsive effect due to the presence of an excluded region and the dipolar interactions allows the prediction of uniaxial polar aligned states, once a biaxial shape for the molecule is assumed, even in the approximation of a spheroidal shape for the excluded region. Biaxial states are not explicitly ruled out by the theory, however for no choice of the model parameters such phases are attained; releasing the approximation of spheroidal shape for the molecules ought to allow overcoming this limitation.

We find a critical temperature T_c such that the equilibrium phase is isotropic for $T > T_c$ and nematic, (both polar and uniaxial), for $T < T_c$, via a second order transition. A single scalar order parameter is sufficient to describe the condensed phase. It can be shown that T_c is maximal when the constituting molecules are discotic, with their permanent dipole moment $\boldsymbol{p}$ along the symmetry axis. In such molecules, the occurrence of more ordered phases (e.g., smectic phases) is therefore less likely; this conclusion, which we made precise within a specific class of molecular shapes, is in agreement with what had already been anticipated in [23] through an intuitive reasoning, and it suggests a general strategy to build molecule capable of polar nematic phases.

Acknowledgment

This work refers to and partly resumes a more thorough paper written with Prof. A. M. Sonnet and Prof. E. G. Virga; the author is in debt with them. This work was partly supported by Grants Progetto Giovani 2008 "Modelli multiscala per fluidi nanostrutturati" and Progetto Giovani 2009 "Effetti sterici in fluidi nanostrutturati polari" by GNFM (Gruppo Nazionale per la Fisica Matematica), Italy.

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