University of
Strathclyde
Glasgow

Strathprints Institutional Repository

http://strathprints.strath.ac.uk/

Unified molecular field theory of nematic, smectic-*A*, and smectic-*C* phases

G. Pająk[1,2,3] and M. A. Osipov[1]

[1]*Department of Mathematics and Statistics, University of Strathclyde, Livingstone Tower, Richmond Street,*
Glasgow, Scotland, United Kingdom
[2]*Marian Smoluchowski Institute of Physics, Department of Statistical Physics and Mark Kac Center for Complex Systems Research,*
Jagiellonian University, Reymonta 4, Kraków, Poland
[3]*Faculty of Physics, Mathematics and Computer Science, Tadeusz Kościuszko Cracow University of Technology,*
Podchorążych 1, Kraków, Poland

A unified mean-field molecular theory of nematic (N_U), smectic A (Sm*A*), and smectic C (Sm*C*) liquid crystal phases, composed of uniaxial nonpolar molecules, is developed taking into account the variation of all orientational and translational order parameters in these phases. Numerical results, obtained by direct global minimization of the free energy, are presented in the form of three typical phase diagrams of different topology. Temperature variation of the relevant order parameters in different sequences of phases is analyzed for various cross sections of the phase diagrams. The present model enables one to reproduce all possible sequences of phase transitions between the given phases including isotropic (Iso)-N_U-Sm*A*-Sm*C*, Iso-N_U-Sm*C*, Iso-Sm*A*-Sm*C*, and Iso-Sm*C*. The properties of the NAC point, where the N_U, Sm*A*, and Sm*C* structures coexist, are considered in detail and the shape of the phase diagram in the vicinity of the NAC point is compared with existing experimental data.

I. INTRODUCTION

Smectic liquid crystals (LCs) are characterized by orientational and partial translational order of anisotropic molecules. In the simplest case the translational order manifests itself in the form of the one-dimensional density wave while the predominant orientation of primary molecular axis is specified by the director **n**. In the smectic A (Sm*A*) phase the director is parallel to the wave vector of the density wave (i.e., to the smectic layer normal). In contrast, in the smectic C (Sm*C*) phase the director is tilted at an angle Θ with respect to the layer normal, and as a result the Sm*C* phase appears to be biaxial. Smectic ordering exists also in other anisotropic soft systems including mesogenic polymers, lamellar phases, and smectic elastomers [1–3]. One notes that smectic soft matter systems are very interesting from both fundamental and application points of view because of the unique sequences of phase transitions, unusual combinations of different types of ordering, and rich phase diagrams.

The existing molecular theory of Sm*A* LCs is mainly based on the McMillan-Kobayashi approach [4,5], which has been used and developed by several authors [6–9] and which yield a number of results which are in qualitative agreement with experiment. On the other hand, the McMillan-Kobayashi approach cannot be used to distinguish between different mechanisms of smectic ordering because it is based on an oversimplified phenomenological interaction potential. It has been shown [10–14] that the model potential used in McMillan-Kobayashi theory does not include terms which describe a coupling between the intermolecular vector and long molecular axes. Without these terms in the interaction potential, the resulting free energy is not sensitive to the orientation of the director and thus this class of theories cannot be directly generalized to the Sm*C* phase.

A more general form of the model interaction potential has been used in advanced theories of the nematic-Sm*A* transition [10–12,15], which also enable one to determine the

smectic periodicity by minimization of the free energy. In particular, in Ref. [15] the coupling constants in the effective pair interaction potential have been calculated numerically as functions of molecular model parameters using both the standard Gay-Berne potential and the potential which takes into account strong repulsion and attraction between particular molecular fragments.

A number of molecular models for the Sm*A*-Sm*C* transition have been proposed by different authors [16–23], taking into account different intermolecular interactions. One notes that the first theories of the Sm*C* phase [16–18] are based on the assumption that the tilt of the director is induced by the ordering of short molecular axes including the biaxial ordering of permanent dipoles. Molecular models based on biaxial interactions have also been proposed by Wulf [17], who considered an interaction between biaxial zigzag shaped molecules, and by Somoza and Tarazona [18], who have taken into account the repulsion between rigid molecules of biaxial shape. One notes that these models are not supported by existing experimental data as there is no evidence of strong biaxial order in the Sm*C* phase. On the other hand, it is also known that the tilt may occur due to interactions between uniaxial molecules, and one may expect this mechanism to be generally predominant because the coupling between long axes of strongly anisotropic molecules is expected to be stronger than that between the short axes [24].

Uniaxial intermolecular interactions, which may promote the tilt, have been taken into consideration by van der Meer and Vertogen [19]. These authors have considered an induction interaction between a permanent off-center dipole of one molecule and the polarizability of an adjacent molecule. Such an induction interaction becomes uniaxial (but still promotes the tilt) after averaging over all orientations of both molecules about their long axes. This theory is based on the approximation of the perfect orientational order which results in an oversimplified scenario of the Sm*A*-Sm*C* transition. Indeed, in this approximation the Sm*A*-Sm*C* is reduced to a simultaneous

tilt of parallel molecules which is not accompanied by any entropy change. Poniewierski and Sluckin [21] have shown that the tilt in the SmC phase can be stabilized by an interaction between uniaxial quadrupoles, which also emphasizes the importance of interactions between long molecular axes.

The predominant role of uniaxial intermolecular interactions is also supported by recent computer simulations of the SmC phase [25,26] which indicate that the SmA-SmC transition can indeed be induced by interaction between uniaxial molecular quadrupoles [25] or by interaction between pairs of longitudinal dipoles [26]. In contrast, transverse dipoles appear to be less important.

The next step has been made by Govind and Madhusudana [22,23], who have developed a molecular theory of smectics with partial orientational and translational order based on the interaction between off-axis dipoles. This theory provides a more detailed description of the SmA-SmC transition compared to the previous models and enables one to obtain more detailed phase diagrams which contain the NAC point. One notes that the theory employs a strongly simplified pair potential and takes into consideration only the basic terms in the free energy which depend on few decoupled order parameters.

Recently, a detailed molecular field theory of the SmA-SmC transition in the system of uniaxial molecules has been developed [27–30] using the general expansion of the pair interaction potential. The coefficients of such an expansion have been calculated numerically using different molecular models based on the Gay-Berne potential supplemented by

specific interactions which account for the tilt. The theory enables one to describe SmC phases with both conventional and anomalously weak layer contraction [28,29] and to study the effect of the shape of the orientational distribution function on the properties of the SmA-SmC transition [30]. The drawback of this theory is related to the use of the approximation of the perfect smectic order which does not allow for a description of the N-SmA and N-SmC phase transitions.

In this paper we present a more general mean-field molecular theory of SmA and SmC LCs which uses the same expansion of the pair interaction potential as in [15,28] but does not employ the approximation of perfect orientational or translational order. We present three qualitatively different types of phase diagrams which contain the isotropic, nematic, SmA, and SmC phases. Two of these diagrams contain the NAC triple point, which is investigated in detail. In this general case the SmC phase is characterized by seven orientational, translational, and mixed scalar order parameters. All of these order parameters have been calculated numerically by direct minimization of the free energy for different sequences of phase transitions including I-SmC, I-N-SmC, and I-N-SmA-SmC ones.

II. FREE ENERGY FUNCTIONAL

In the so-called generalized van der Waals approximation [31,32] the free energy of a smectic LC phase composed of uniaxial molecules can be written in the form

$$F = \frac{1}{2}\rho^2 \int f(\mathbf{r}_1,\mathbf{a}_1)\, \Omega(|\mathbf{r}_1 - \mathbf{r}_2| - \boldsymbol{\xi}_{1,2})\, U_{\text{att}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_1 - \mathbf{r}_2)\, f(\mathbf{r}_2,\mathbf{a}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{a}_1\, d\mathbf{a}_2$$

$$+ \frac{1}{2}\lambda k_B T \rho^2 \int f(\mathbf{r}_1,\mathbf{a}_1)\, [1 - \Omega(|\mathbf{r}_1 - \mathbf{r}_2| - \boldsymbol{\xi}_{1,2})]\, f(\mathbf{r}_2,\mathbf{a}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{a}_1\, d\mathbf{a}_2$$

$$+ k_B T \rho \int f(\mathbf{r}_1,\mathbf{a}_1)\ln[f(\mathbf{r}_1,\mathbf{a}_1)]\, d\mathbf{r}_1\, d\mathbf{a}_1, \tag{1}$$

where ρ is the molecular number density and the one-particle distribution function $f(\mathbf{r},\mathbf{a})$ depends on the molecule position $\mathbf{r}$ and orientation of its long axis $\mathbf{a}$. The distribution function f is normalized as

$$\frac{1}{V}\int f(\mathbf{r},\mathbf{a})\, d\mathbf{r}\, d\mathbf{a} = 1, \tag{2}$$

where V is the volume of the LC system. In Eq. (1) the first term is the internal energy of the system in the mean-field approximation which is determined by the attraction interaction potential $U_{\text{att}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12})$, where $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, modulated by anisotropic steric repulsion. The second term in Eq. (1) describes the packing entropy in the system of rigid molecules which is determined by excluded volume effects. Here the step function $\Omega(|\mathbf{r}_{12}| - \boldsymbol{\xi}_{1,2}) = 0$ if the molecular cores penetrate each other and $\Omega(|\mathbf{r}_{12}| - \boldsymbol{\xi}_{1,2}) = 1$ otherwise, where $\boldsymbol{\xi}_{1,2}$ is the minimal touching distance between two molecules at a given mutual orientation. The density dependent factor $\lambda = \lambda(\rho) \sim 1$ and increases with the increasing volume fraction of hard

molecules. Finally, the third term is the orientational entropy which depends only on the one-particle distribution function. In the SmA and SmC phases the one-particle distribution function $f(\mathbf{r},\mathbf{a})$ possesses the one-dimensional periodicity; i.e., it is a periodic function of the coordinate z, where the z axis is parallel to the wave vector $\mathbf{q}$ of the smectic density wave. Thus, $f(z,\mathbf{a}) = f(z + d,\mathbf{a})$, where d is the period and $q = 2\pi/d$. The free energy (1) can also be expressed in a more compact form,

$$F = \frac{1}{2}\rho^2 \int f(\mathbf{r}_1,\mathbf{a}_1)\, U_{\text{eff}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12})\, f(\mathbf{r}_2,\mathbf{a}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{a}_1\, d\mathbf{a}_2$$

$$+ k_B T \rho \int f(\mathbf{r}_1,\mathbf{a}_1)\ln[f(\mathbf{r}_1,\mathbf{a}_1)]\, d\mathbf{r}_1\, d\mathbf{a}_1, \tag{3}$$

where we have introduced the following effective potential:

$$U_{\text{eff}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12}) = U_{\text{att}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12})\Omega(|\mathbf{r}_{12}| - \boldsymbol{\xi}_{1,2})$$

$$+ \lambda k_B T\, [1 - \Omega(|\mathbf{r}_{12}| - \boldsymbol{\xi}_{1,2})]. \tag{4}$$

Minimizing the functional (3) with respect to the distribution function $f(\mathbf{r},\mathbf{a})$, one obtains the self-consistency equation for the distribution function

$$f(\mathbf{r},\mathbf{a}) = \frac{1}{Z} \exp\left[-\frac{U_{MF}(\mathbf{r},\mathbf{a})}{k_B T} \right], \qquad (5)$$

where

$$Z = \frac{A}{V} \int \exp\left[-\frac{U_{MF}(\mathbf{r},\mathbf{a})}{k_B T} \right] d\mathbf{r} d\mathbf{a}, \qquad (6)$$

and where $U_{MF}(\mathbf{r},\mathbf{a})$ is the mean-field potential which is expressed as

$$U_{MF}(\mathbf{r}_1,\mathbf{a}) = \rho \iint f(\mathbf{r}_2,\mathbf{a}_2) \int U_{\text{eff}}(\mathbf{a},\mathbf{a}_2,\mathbf{r}_{12}) d\mathbf{r}_2 d\mathbf{a}_2. \qquad (7)$$

The one-particle distribution function f depends on the position $\mathbf{r}$ along the wave vector $\mathbf{q}$, on the unit vector $\mathbf{a}$ in the direction of the long molecular axis, and on the order parameters of a smectic phase.

III. ORDER PARAMETERS OF THE SMECTIC C PHASE

Let us first consider the uniaxial SmA phase. It is well known since the pioneering work by McMillan [4] that the scalar order parameters of the SmA are given by the following equations:

$$\psi = \langle \cos qz \rangle, \qquad (8)$$

$$S_k = \langle P_2(\cos\gamma) \rangle, \qquad (9)$$

and

$$\Sigma_k = \langle P_2(\cos\gamma) \cos qz \rangle, \qquad (10)$$

where the averaging $\langle (\cdots) \rangle$ is performed with the one-particle distribution function and γ is an angle between the long molecular axis $\mathbf{a}$ and the unit vector $\mathbf{k}$ which is parallel to the wave vector $\mathbf{q}$. The subscript k in S_k and Σ_k indicates that these order parameters are calculated with respect to the layer normal $\mathbf{k}$ which coincides with the director $\mathbf{n}$ in the SmA phase (but not in the SmC phase). The order parameters ψ and Σ_k describe different types of smectic ordering in the SmA phase. The order parameter ψ characterizes the positional ordering of molecular centers regardless of the degree of the orientational order. In contrast, the parameter Σ characterizes simultaneous positional and orientational ordering of anisotropic molecules.

One notes that the two primary tensor order parameters of the uniaxial SmA phase [15] can be expressed in terms of the scalar order parameters S_k and Σ_k in the following way:

$$Q_{ij} = \langle (a_i a_j - \tfrac{1}{3}\delta_{ij}) \rangle = S_k(k_i k_j - \tfrac{1}{3}\delta_{ij}),$$
$$\Sigma_{ij} = \langle (a_i a_j - \tfrac{1}{3}\delta_{ij}) \cos(\mathbf{q}\cdot\mathbf{r}) \rangle = \Sigma_k(k_i k_j - \tfrac{1}{3}\delta_{ij}). \qquad (11)$$

In contrast, the SmC phase is biaxial and therefore the tensor order parameters must contain biaxial contributions. The tensors Q_{ij} and Σ_{ij} can always be expressed in the diagonal (director) reference frame as

$$Q_{ij} = S(n_i n_j - \tfrac{1}{3}\delta_{ij}) + P(m_i m_j - l_i l_j) \qquad (12)$$

and

$$\Sigma_{ij} = \Sigma(n'_i n'_j - \tfrac{1}{3}\delta_{ij}) + \Pi(m'_i m'_j - l_i l_j). \qquad (13)$$

In Eq. (12) the unit vectors $\mathbf{n}$, $\mathbf{m}$, and $\mathbf{l}$ are the primary axes of the tensor $\mathbf{Q}$. Here $\mathbf{n}$ is the director and $\mathbf{l}$ is parallel to the C_2 symmetry axis of the SmC phase which is normal to the tilt plane. In Eq. (13) the unit vectors $\mathbf{n}'$, $\mathbf{m}'$, and $\mathbf{l}$ are the primary axes of the tensor $\boldsymbol{\Sigma}$. In the general case the principal axes of the tensor $\boldsymbol{\Sigma}$ do not coincide with those of the tensor $\mathbf{Q}$ because they are not fixed by symmetry. Only the axis $\mathbf{l}$ must be the same for all second rank macroscopic tensors in the SmC phase because $\mathbf{l}$ is parallel to the symmetry axis of the phase. Thus, even in the SmC phase composed of uniaxial molecules it is possible to define two different directors (based on primary axes of $\mathbf{Q}$ and $\boldsymbol{\Sigma}$) and, therefore, two different tilt angles Θ and θ. Here Θ is the angle between the director $\mathbf{n}$ (the primary axis of the tensor $\mathbf{Q}$) and the layer normal $\mathbf{k}$, while θ is the angle between the director $\mathbf{n}'$ (the primary axis of the tensor $\boldsymbol{\Sigma}$ and $\mathbf{k}$).

The definition of the director becomes even more opaque in the SmC phase composed of biaxial molecules. In this case one introduces a number of tilt angles which may differ significantly [33]. Thus, the use of the director frame in the SmC phase is not very convenient. The concept of the director which defines a unique tilt angle is also not very good from the experimental point of view because the tilt angle generally depends on the experimental technique used and may even depend on the wavelength of light which is used to measure it [34].

Taking into account that the two terms in the right hand sides of Eqs. (12) and (13) are orthogonal, the order parameters S, P, Σ, and Π can be expressed as

$$S = \langle P_2(\mathbf{a}\cdot\mathbf{n}) \rangle, \quad P = \tfrac{1}{2}\langle (\mathbf{a}\cdot\mathbf{m})^2 - (\mathbf{a}\cdot\mathbf{l})^2 \rangle \qquad (14)$$

and

$$\Sigma = \langle P_2(\mathbf{a}\cdot\mathbf{n}') \cos(\mathbf{q}\cdot\mathbf{r}) \rangle,$$
$$\Pi = \tfrac{1}{2}\langle ((\mathbf{a}\cdot\mathbf{m}')^2 - (\mathbf{a}\cdot\mathbf{l})^2) \cos(\mathbf{q}\cdot\mathbf{r}) \rangle. \qquad (15)$$

Here S is the uniaxial orientational order parameter with respect to the director $\mathbf{n}$, Σ is the uniaxial orientational-translational order parameter defined with respect to the director $\mathbf{n}'$ (which may be different from $\mathbf{n}$ in the SmC phase), and P and Π are the corresponding biaxial order parameters which describe biaxial distribution of long molecular axes in the SmC phase. One notes that in the SmC phase these order parameters can be defined explicitly only if the primary axes of the tensors $\mathbf{Q}$ and $\boldsymbol{\Sigma}$ are known, which is inconvenient from the practical point of view.

As discussed in detail in [15] it is more consistent to express the tensor order parameters of the SmC phase in the $(\mathbf{k},\mathbf{c},\mathbf{l})$ frame which is based on the symmetry of the phase as $\mathbf{k}$ is parallel to the layer normal and $\mathbf{l}$ is normal to the tilt plane. In this frame both tensors $\mathbf{Q}$ and $\boldsymbol{\Sigma}$ are not diagonal but can be expressed in a similar way,

$$Q_{ij} = S_k(k_i k_j - \delta_{ij}/3) + \tfrac{1}{2}P_k(c_i c_j - l_i l_j) + \tfrac{1}{2}V(k_i c_j + c_i k_j) \qquad (16)$$

and

$$\Sigma_{ij} = \Sigma_k(k_i k_j - \delta_{ij}/3) + \tfrac{1}{2}\Pi_k(c_i c_j - l_i l_j)$$
$$+ \tfrac{1}{2}\Lambda(k_i c_j + c_i k_j), \qquad (17)$$

where S_k, P_k, and V are the three independent orientational order parameters and Σ_k, Π_k, and Λ are the corresponding orientational-translational order parameters of the SmC phase which can be explicitly expressed as the following statistical averages of the corresponding molecular quantities:

$$S_k = \langle P_2(\cos\gamma)\rangle, \tag{18}$$

$$P_k = \langle \sin^2\gamma \cos 2\varphi\rangle, \tag{19}$$

$$V = \langle \sin 2\gamma \cos\varphi\rangle, \tag{20}$$

$$\Sigma_k = \langle P_2(\cos\gamma)\cos(\mathbf{q}\cdot\mathbf{r})\rangle, \tag{21}$$

$$\Pi_k = \langle \sin^2\gamma \cos 2\varphi \cos(\mathbf{q}\cdot\mathbf{r})\rangle, \tag{22}$$

$$\Lambda = \langle \sin 2\gamma \cos\varphi \cos(\mathbf{q}\cdot\mathbf{r})\rangle, \tag{23}$$

where φ is the azimuthal angle of the axis $\mathbf{a}$ in the smectic plane (that is in the plane perpendicular to $\mathbf{k}$). Here the order parameter S_k characterizes the degree of the orientational order with respect to the smectic layer normal $\mathbf{k}$. The order parameter P_k describes the biaxial distribution of long molecular axes in the smectic plane. Finally, the tilt order parameter V in the nondiagonal term of the $\mathbf{Q}$ tensor describes the tilt of its main axis with respect to the layer normal $\mathbf{k}$. In the SmA phase $V = 0$ and the tensor becomes diagonal. Thus, another advantage of this representation of the tensor order parameters is that the tilt order parameters V and Λ are explicitly expressed as statistical averages of molecular quantities in contrast to the corresponding tilt angles Θ and θ.

The sets of order parameters S_k, P_k, V and Σ_k, Π_k, Λ are equivalent to the sets S, P, Θ and Σ, Π, θ. As shown in [15], the parameters S_k, P_k, V can be directly related to the conventional order parameters of the SmC phase appearing in the diagonal representation of the tensor $\mathbf{Q}$:

$$\tan 2\Theta = \frac{V}{S_k - \frac{1}{2}P_k}, \tag{24}$$

$$S = \frac{1}{4}S_k + \frac{3}{8}P_k + \frac{3}{4}\frac{V}{\sin 2\Theta}, \tag{25}$$

$$P = \frac{1}{2}S_k + \frac{3}{4}P_k - \frac{V}{2\sin 2\Theta}. \tag{26}$$

The order parameters Σ_k, Π_k, Λ are related to Σ, Π, θ by the similar equations

$$\tan 2\theta = \frac{\Lambda}{\Sigma_k - \frac{1}{2}\Pi_k}, \tag{27}$$

$$\Sigma = \frac{1}{4}\Sigma_k + \frac{3}{8}\Pi_k + \frac{3}{4}\frac{\Lambda}{\sin 2\theta}, \tag{28}$$

$$\Pi = \frac{1}{2}\Sigma_k + \frac{3}{4}\Pi_k - \frac{\Lambda}{2\sin 2\theta}. \tag{29}$$

Thus, the SmC phase composed of uniaxial molecules is characterized by seven orientational and translational scalar order parameters $\{\psi, S_k, P_k, V, \Sigma_k, \Pi_k, \Lambda\}$ or $\{\psi, S, P, \Theta, \Sigma, \Pi, \theta\}$.

In the uniaxial SmA phase both the tilt order parameters V, Λ (or Θ, θ) and the biaxial order parameters P, P_k, Π, and Π_k vanish, $S = S_k$, $\Sigma = \Sigma_k$, and the system is characterized by three order parameters, ψ, S_k, and Σ_k, which appear already in the McMillan theory. Finally, in the uniaxial nematic phase only the orientational order parameter $S = S_k$ is nonzero.

One notes that it is generally important to distinguish between the translational order parameter ψ and the mixed orientational-translational order parameter Σ_k because either of them can be the primary order parameter of the transition into the SmA phase depending on the microscopic mechanism of such a transition [15].

The first mixed orientational-translational order parameter Σ_k has been introduced by McMillan in the molecular theory of the SmA phase [4]. In the past, several authors (see, for example, [9]) have decoupled the mixed parameter Σ_k as the product of S_k and ψ, i.e., $\Sigma_k \approx S_k\psi$ in order to simplify calculations in the McMillan theory. It may seem that the decoupling of the other mixed order parameter Π_k and Λ may lead to a much simpler description of the SmC phase. One notes, however, that it results in a very small computational advantage for modern PCs but may lead to significant qualitative mistakes and misinterpretations. The decoupling of the order parameter Σ_k has been analyzed in detail in [15], in which all coupling constants in the free energy of the SmA phase have been calculated numerically for different types of interaction potentials. It has been shown that in the case of smooth interaction potentials of Gay-Berne type the nematic order parameter S is larger than both ψ and Σ. In this case the decoupling of the mixed parameter Σ leads to small quantitative mistakes. In contrast, in smectics with nanoscale segregation between different molecular fragments the mixed parameter Σ is larger than both S and ψ. In this case the decoupling of $\Sigma \approx S\psi$ results in a strong underestimation of Σ because the product $S\psi$ is smaller than both $S < 1$ and $\psi < 1$ while the actual value of Σ is larger than both S and ψ. This underestimation strongly effects other properties of SmA.

As discussed in detail in [15] such a behavior is typical for de Vries type smectics which are characterized by abnormally weak orientational order and very strong translational order. In this case the decoupling approximation is qualitatively incorrect because these materials do not possess the nematic phase, and the primary order parameter of the I-SmA transition appears to be the orientational-density wave with the amplitude equal to the mixed order parameter Σ_k. Another example is the $B2$ smectic phase in which the primary order parameter appears to be the tilt density wave according to Lorman and Mettout [35]. Thus, essential physics may be lost as a result of the oversimplification of the order parameters. In this paper we do not use the decoupling approximation and calculate all the order parameters numerically by minimization of the free energy. The meaning of various order parameters of the SmC phase are illustrated in Fig. 1.

IV. MEAN-FIELD POTENTIAL

The one-particle distribution function of the SmC phase can be expanded in terms of all order parameters considered in the previous section. Keeping the first order terms, one obtains

$$\begin{aligned} f((\mathbf{q}\cdot\mathbf{r}),\mathbf{a}) = {} & \text{const} + \tfrac{5}{2}S_k P_2(\cos\gamma) + \tfrac{8}{3}P_k\sin^2\gamma\cos 2\varphi \\ & + 4V\sin 2\gamma\cos\varphi \\ & + \cos(\mathbf{q}\cdot\mathbf{r})\big[2\psi + \tfrac{5}{2}\Sigma_k P_2(\cos\gamma) \\ & + \tfrac{8}{3}\Pi_k\sin^2\gamma\cos 2\varphi + 4\Lambda\sin 2\gamma\cos\varphi\big] + \cdots. \end{aligned} \tag{30}$$
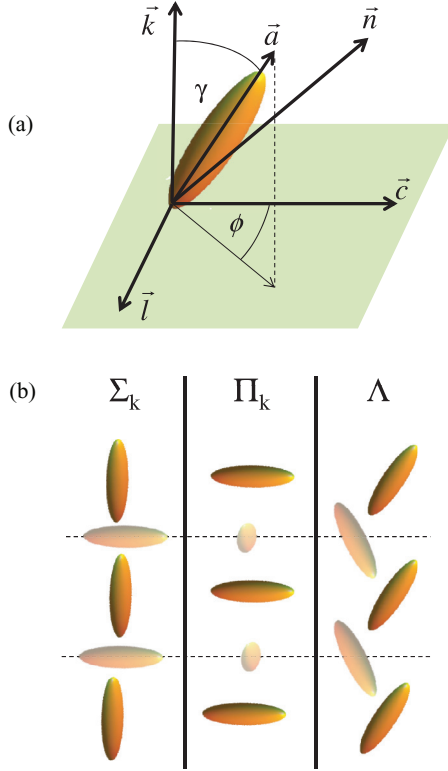
FIG. 1. (Color online) Schematic representation of the distribution of long molecular axes in the SmC phase (a) and the three density waves (b) which correspond to the orientational-translational order parameters Σ_k, Π_k, and Λ. The average width of the orientational distribution around the layer normal **k** in (a) is specified by the nematic order parameter S_k, the nonpolar asymmetry of the distribution is characterized by the biaxial order parameter P_k and the tilt order parameter V describes the shift of the distribution away from the layer normal. Panel (b) illustrates the fact that for sufficiently large values of the order parameter Σ_k local orientational distribution of molecules may depend on the position along the layer normal **k** [15] and may even be characterized by negative local order parameters for positions "between the layers."

One notes that the same one-particle distribution function $f((\mathbf{q} \cdot \mathbf{r}),\mathbf{a})$ is expressed in two different ways by Eqs. (30) and (5). These two expressions, however, are not in contradiction with each other. Indeed, expansion of Eq. (5) yields the same terms as in the expansion (30), and the coefficients in the corresponding terms appear to be equal according to the self-consistency equations for the order parameters. For example, the second term in the expansion of the distribution function Eq. (5) with the mean-field potential (46) in Legendre polynomials $P_{2n}(\cos\gamma)$ has the same form $\frac{5}{2}a_2 P_2(\cos\gamma)$ where the coefficient a_2 is expressed as

$$a_2 = \frac{1}{ZV}\int P_2(\cos\gamma)\exp(-\beta U_{MF}((\mathbf{q}\cdot\mathbf{r}),\gamma,\varphi))d\cos\gamma\,d\varphi\,d^3\mathbf{r},$$

where $\beta = 1/(k_B T)$ and where V is the system volume. One can readily see that a_2 is equal to the order parameter S_k, which is the coefficient in the the corresponding term in Eq. (30) in virtue of the well known self-consistency equation $S_k = \langle P_2(\cos\gamma)\rangle$ for the uniaxial nematic order parameter.

Substituting Eq. (30) into Eq. (7) one obtains the following expression for the mean-field potential:

$$U_{MF}(\mathbf{r}_1,\mathbf{a}) = U_N(\mathbf{r}_1,\mathbf{a}) + U_S(\mathbf{r}_1,\mathbf{a}), \tag{31}$$

where the first term is the homogeneous nematiclike contribution,

$$U_N(\mathbf{a}_1) = \rho \iint g_1(\gamma_2,\varphi_2)\, U_{\text{eff}}(\mathbf{a}_1 \cdot \mathbf{a}_2)\, d\mathbf{a}_2, \tag{32}$$

and the second term is positionally dependent,

$$U_S(\mathbf{r}_1,\mathbf{a}_1) = \rho \iint g_2(\gamma_2,\varphi_2)\int U_{\text{eff}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12})$$
$$\times \cos(\mathbf{q}\cdot\mathbf{r}_2)\,d\mathbf{a}_2 d\mathbf{r}_2. \tag{33}$$

Here $U_{\text{eff}}(\mathbf{a}_1 \cdot \mathbf{a}_2)$ is the averaged intermolecular interaction potential:

$$U_{\text{eff}}(\mathbf{a}_1 \cdot \mathbf{a}_2) = \int U_{\text{eff}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12})d\mathbf{r}_{12}, \tag{34}$$

and

$$g_1(\gamma,\varphi) = \tfrac{5}{2}S_k P_2(\cos\gamma) + \tfrac{8}{3}P_k \sin^2\gamma \cos 2\varphi$$
$$+ 4V \sin 2\gamma \cos\varphi, \tag{35}$$

$$g_2(\gamma,\varphi) = \left[2\psi + \tfrac{5}{2}\Sigma_k P_2(\cos\gamma) + \tfrac{8}{3}\Pi_k \sin^2\gamma \cos 2\varphi\right.$$
$$\left. + 4\Lambda \sin 2\gamma \cos\varphi\right]. \tag{36}$$

Let us first consider the homogeneous part of the mean-field potential. The integrated interaction potential in Eq. (32) can be expanded in Legendre polynomials:

$$U_{\text{eff}}(\mathbf{a}_1 \cdot \mathbf{a}_2) = \sum_n I_n P_n(\mathbf{a}_1 \cdot \mathbf{a}_2). \tag{37}$$

Substituting this expansion together with Eq. (35) into Eq. (32) and integrating over $\mathbf{a}_2$ one obtains

$$U_N(\mathbf{a}_1) = \rho I_2 S_k P_2(\cos\gamma) + \tfrac{3}{4}\rho I_2 P_k \sin^2\gamma \cos 2\varphi$$
$$+ \tfrac{3}{4}\rho I_2 V \sin 2\gamma \cos\varphi. \tag{38}$$

Equation (33) for the periodic part of the potential contains the function $\cos(\mathbf{q}\cdot\mathbf{r})$, which can be rewritten as $\cos(\mathbf{q}\cdot\mathbf{r}_2) = \cos((\mathbf{q}\cdot\mathbf{r}_{12}) + (\mathbf{q}\cdot\mathbf{r}_1)) = \cos(\mathbf{q}\cdot\mathbf{r}_{12})\cos(\mathbf{q}\cdot\mathbf{r}_1) + \sin(\mathbf{q}\cdot\mathbf{r}_{12})\sin(\mathbf{q}\cdot\mathbf{r}_1)$, where $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$. Now the integral over $\mathbf{r}_2$ in Eq. (33) can be expressed as an integral over $\mathbf{r}_{12}$ and split into the following two parts:

$$\int U_{\text{eff}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12})\cos(\mathbf{q}\cdot\mathbf{r}_2)d\mathbf{r}_2$$
$$= \cos(\mathbf{q}\cdot\mathbf{r}_1)\int U_{\text{eff}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12})\cos(\mathbf{q}\cdot\mathbf{r}_{12})d\mathbf{r}_{12}$$
$$+ \sin(\mathbf{q}\cdot\mathbf{r}_1)\int U_{\text{eff}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12})\sin(\mathbf{q}\cdot\mathbf{r}_{12})d\mathbf{r}_{12}. \tag{39}$$

One notes that the second term in Eq. (39) vanishes because the function $\sin(\mathbf{q}\cdot\mathbf{r}_{12})$ is odd in $\mathbf{r}_{12}$ while the interaction potential $U_{\text{eff}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12})$ is even (at least in the system of nonchiral molecules). As a result the periodic part of the mean-field potential can be written in the form

$$U_S(\mathbf{r}_1,\mathbf{a}_1) = \rho \cos(\mathbf{q}\cdot\mathbf{r}_1)\iint g_2(\gamma_2,\varphi_2)K(\mathbf{a}_1,\mathbf{a}_2,\mathbf{q})\,d\mathbf{a}_2,$$
$$\tag{40}$$

where

$$K(\mathbf{a}_1, \mathbf{a}_2, \mathbf{q}) = \int U_{\text{eff}}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_{12}) \cos(\mathbf{q} \cdot \mathbf{r}_{12}) d\mathbf{r}_{12}. \quad (41)$$

In the general case the interaction potential can be expanded in terms of the so-called spherical invariants,

$$U_{\text{eff}}(\mathbf{a}_1, \mathbf{r}_{12}, \mathbf{a}_2) = \sum_{lmk} J_{lmk}(r_{12}) T^{lmk}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2), \quad (42)$$

where $\mathbf{u}_{12} = \mathbf{r}_{12}/r_{12}$. The set $T^{lmk}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2)$ is a complete orthogonal set of basis functions [36] that contains the vector $\mathbf{a}_1$ to the power l, the vector $\mathbf{u}_{12}$ to the power m, and the vector $\mathbf{a}_2$ to the power k. The explicit expressions for the lower order invariants have been given, for example, in [37]. The invariants with one zero index are just Legendre polynomials. For example, $T^{202}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2) = P_2(\mathbf{a}_1 \cdot \mathbf{a}_2)$. The functions $T^{lmk}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2)$ possess a number of interesting properties. In particular,

$$\int T^{lmk}(\mathbf{a}, \mathbf{b}, \mathbf{c}) f(\mathbf{b} \cdot \mathbf{x}) d\mathbf{x}$$
$$= T^{lmk}(\mathbf{a}, \mathbf{x}, \mathbf{c}) \int P_m(\mathbf{b} \cdot \mathbf{x}) f(\mathbf{b} \cdot \mathbf{x}) d\mathbf{b}, \quad (43)$$

where $f(\mathbf{b} \cdot \mathbf{x})$ is an arbitrary function and $\mathbf{x}$ is a unit constant vector.

Substituting the expansion Eq. (42) into Eq. (41) and using Eq. (43) one obtains

$$K(\mathbf{a}_1, \mathbf{a}_2, \mathbf{q}) = \sum_{lmk} u_{lmk}(q) T^{lmk}(\mathbf{a}_1, \mathbf{k}, \mathbf{a}_2), \quad (44)$$

where the coefficients $u_{l,m,k}(q)$ are expressed as

$$u_{lmk}(q) = \int J_{lmk}(r_{12}) \cos(r_{12}(\mathbf{q} \cdot \mathbf{u}_{12})) P_m(\mathbf{u}_{12} \cdot \mathbf{k}) d\mathbf{u}_{12} r_{12}^2 dr_{12}. \quad (45)$$

As shown in Appendix, substitution of Eq. (44) into Eq. (40) and integration over $\mathbf{a}_2$ yields the following final expression for the mean-field potential:

$$U_{MF}((\mathbf{q} \cdot \mathbf{r}), \gamma, \varphi) = u\left(S_k P_2(\cos\gamma) + \tfrac{3}{4} P_k \sin^2\gamma \cos 2\varphi + \tfrac{3}{4} V \sin 2\gamma \cos\varphi\right)$$
$$+ w_0 \psi \cos(\mathbf{q} \cdot \mathbf{r}) + w_1[\psi P_2(\cos\gamma)\cos(\mathbf{q} \cdot \mathbf{r}) + \Sigma_k \cos(\mathbf{q} \cdot \mathbf{r})]$$
$$+ w_2 \Sigma_k P_2(\cos\gamma)\cos(\mathbf{q} \cdot \mathbf{r}) + w_3 \Pi_k \sin^2\gamma \cos 2\varphi \cos(\mathbf{q} \cdot \mathbf{r}) + w_4 \Lambda \sin 2\gamma \cos\varphi \cos(\mathbf{q} \cdot \mathbf{r}). \quad (46)$$

Finally, the free energy can be expressed as

$$F/V = -\tfrac{1}{2}\rho\left[u\left(S_k^2 + \tfrac{3}{4}P_k^2 + \tfrac{3}{4}V^2\right) + w_0\psi^2 + 2w_1\psi\Sigma_k + w_2\Sigma_k^2 + w_3\Pi_k^2 + w_4\Lambda^2\right] - k_B T \rho \ln Z, \quad (47)$$

where Z is given by Eq. (6), in which the mean-field potential is given by Eq. (46). Equation (47) is a general expression for the mean-field free energy of the SmC phase composed of uniaxial molecules which depends on coupling constants $u, w_0, w_2, w_3,$ and w_4 which characterize different types of intermolecular interactions responsible for different kinds of ordering. In particular, the coupling constant u is the Maier-Saupe constant which determines the isotropic-nematic transition temperature. The theory presented here obviously reduces to the standard Maier-Saupe molecular theory when all other coupling constants $w_0, w_2, w_3,$ and w_4 vanish. The coupling constants w_0 and w_2 characterize the energy associated with the smectic ordering and determine the transition temperature into the SmA phase. The terms proportional to w_1 describes a coupling between orientational and translational ordering both in the SmA and the SmC phase. This term is absent in the McMillan theory, which leads to an instability of the SmA phase with respect to a tilt of the director as discussed by many authors before [10–14]. This term is also responsible for the induction of tilt in the SmC phase which arises with the decreasing temperature. Finally, the constants w_4 and w_3 characterize the energy associated with the tilt and the inherent biaxiality of the SmC phase, respectively.

V. RESULTS

Numerical results have been obtained by direct minimization of the mean-field free energy Eq. (47) and include the phase diagrams and temperature profiles of all orientational and translational order parameters introduced above for various sequences of phase transitions. Phase diagrams are presented using the $T - w_2$ coordinates in order to maintain a link with the original McMillan paper [4] on the molecular theory of SmA. One notes that in [4] the analogous coupling constant, which mainly determines the transition into the SmA phase, is denoted by α (here $\alpha = -w_2$). In the context of the present theory a number of phase diagrams of different topology can be obtained which contain isotropic, nematic, and SmA and SmC phases. In all calculations the coupling constant u, which determines the isotropic-nematic transition temperature, has been used to rescale the temperature and all other coupling constants. We have also limited the analysis to the case when $w_0 = w_1$ and $w_3 = w_4$. Here the first condition is implemented to guarantee that the mean-field free energy is bounded from below, which is achieved when the two coupling constant are of the same order of magnitude. The relation $w_3 = w_4$ is used to simplify the description of the tilting transition (for details of calculations, see the Appendix). All phase diagrams are presented using the variables t and $-w_2$, where $t = \frac{k_B T}{u}$ is the dimensionless temperature.

First, in Fig. 2, we present the phase diagram which does not contain the NAC point. In this case the system undergoes the direct isotropic (Iso)-SmC phase transition at sufficiently large values of the coupling constant $|w_2|$. At lower values of $|w_2|$ there is the direct Iso-SmA transition, and the Iso and the SmC phases are separated by a region of the stable SmA phase. All
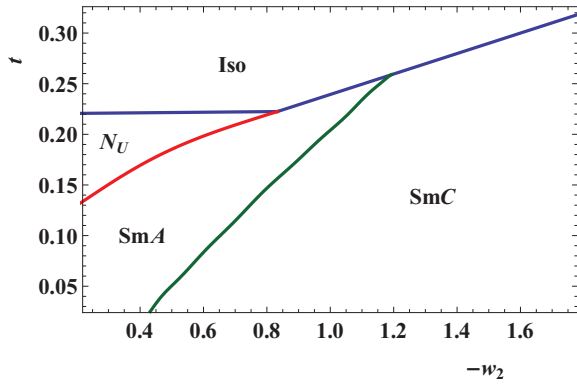
FIG. 2. (Color online) Phase diagram for $u = -1$, $w_0 = w_1 = -0.04$, $w_3 = w_4 = -0.0273 + 0.7575 w_2$. The blue line is the line of transitions from the isotropic phase (Iso), while the red and green lines represent the N_U-SmA and SmA-SmC phase transitions, respectively.

order parameters, defined in the **k** frame, have been calculated and presented as functions of temperature for $w_2 = -0.95$, which corresponds to the direct transition from the isotropic phase into the SmA phase (see Fig. 3) and for $w_2 = -1.6$, which corresponds to the direct transition into the SmC phase (see Fig. 4). One notes that the transitions from the isotropic phase to the nematic, SmA, and SmC phases are first order while the SmA-SmC phase transition is always of the second order in this model. The variation of all orientational order parameters, defined both in the **k** frame and in the director frame, are presented in panels (b) of Figs. 3 and 4. Here the order parameters S_k, P_k, and V are defined in the **k** frame while the parameters Θ, S, and P are defined in the director reference frame. The two sets of order parameters are related by Eqs. (24)–(26). It is interesting to note that the biaxial order parameter (P_k), which characterizes the biaxial distribution of uniaxial molecules with respect to the layer normal, is always nonzero in the SmC while the corresponding biaxial order parameter P, defined in the director reference frame, vanishes at all temperatures. Finally, the temperature variation of the mixed orientational-translational order parameters is presented in Figs. 3(c) and 4(c). Here the order parameters Σ_k, Π_k, and Λ, defined in the **k** frame, are related to the order parameters Σ, Π, and, θ, defined in the director frame, by Eqs. (27)–(29). Similar to the orientational biaxial order parameter P, the orientational-translational biaxial parameter $\Pi = 0$ in the director reference frame. One notes also that the two tilt angles Θ and θ, calculated using the Eqs. (24) and (27), respectively, appear to be exactly the same; that is $\Theta = \theta$ for all temperatures. This means that in the system composed of uniaxial molecules there is only one director and consequently only one tilt angle in the SmC phase despite the phase biaxiality.

The phase diagrams presented in Figs. 5 and 6 contain the NAC point. In the diagram 5 one finds a region where the system undergoes a sequence of first order phase transitions Iso-N_U-SmC, which is absent in the phase diagram presented in Fig. 2. Temperature variation of the corresponding order parameters for this sequence of phase transitions is shown in Fig. 7. Temperature variation of all order parameters along
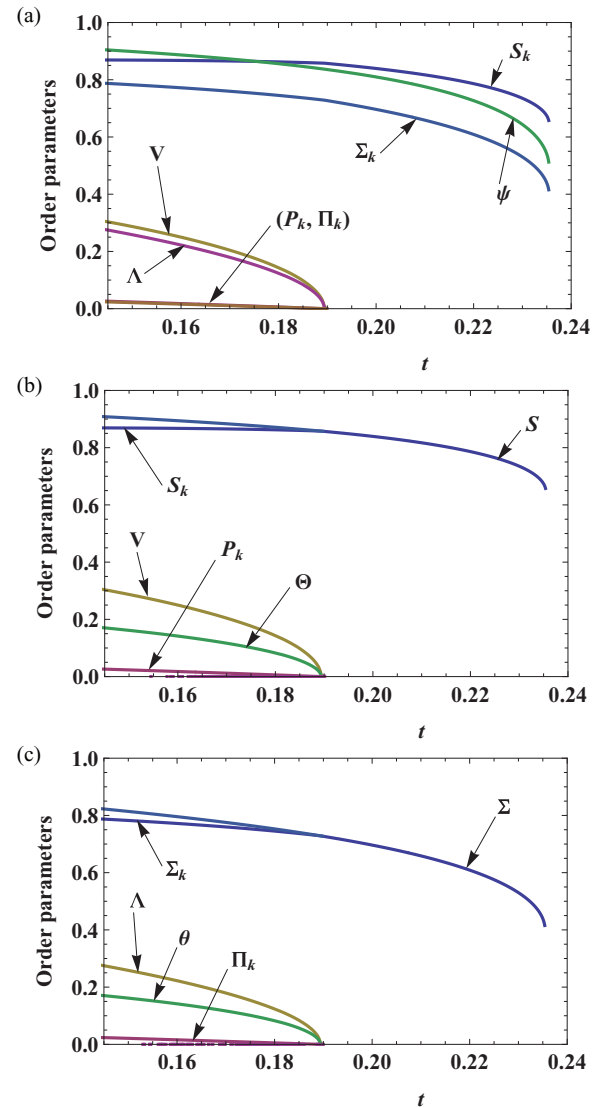

FIG. 3. (Color online) Temperature variation of the whole set of orientational and translational order parameters defined with respect to the smectic layer normal **k** in the case of the direct Iso-SmA phase transition (a), variation of the orientational (b), and the orientational-translational order parameters (c) defined both in the **k** frame and in the director reference frame. The parameters Θ, S, P, θ, Σ, and Π, defined in the director frame, have been calculated using Eqs. (24), (25), (26), (27), (28), and (29), respectively. Order parameter profiles have been obtained by minimization of the free energy Eq. (47) for $w_2 = -0.95$. The values of other coupling constants are the same as in Fig. 2.

another cross section of the same phase diagram is presented in Fig. 8(a). This cross section corresponds to the sequence of transitions between all four possible phases including Iso, N_U, SmA, and SmC. These phases are stable in different temperature ranges for the same values of the model parameters. For comparison, temperature variation of higher-order parameters, that is the orientational and orientational-translational averages of the forth Legendre polynomial, is presented in Fig. 8(b). As expected, the higher order parameters are smaller than the leading order parameters in all stable phases. The phase diagram of a different type is presented in Fig. 6. This diagram
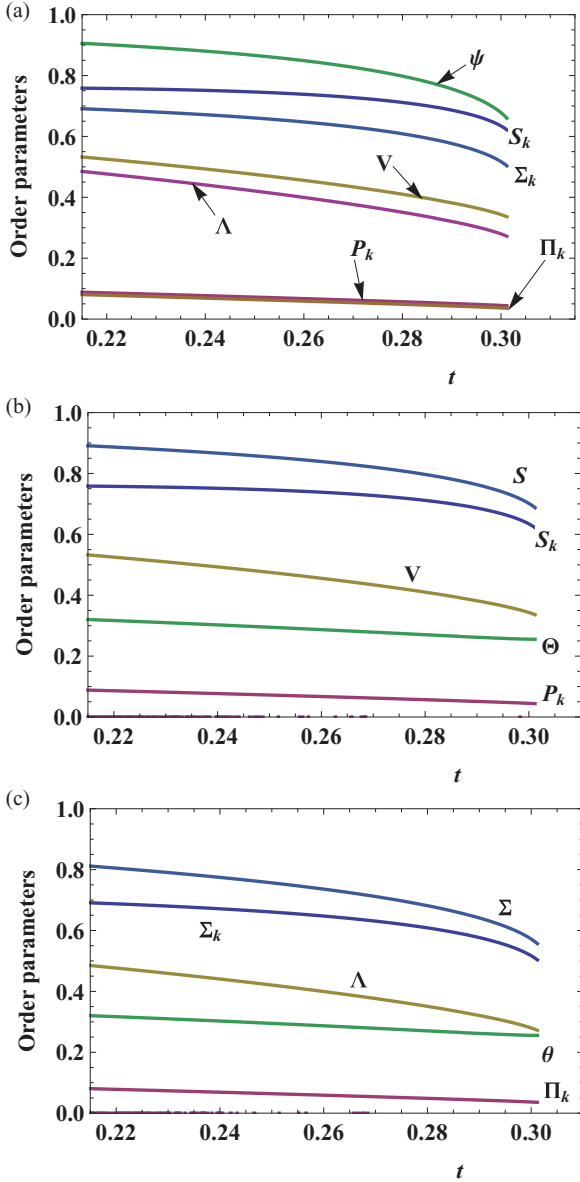
FIG. 4. (Color online) Temperature variation of the whole set of orientational and translational order parameters defined with respect to the smectic layer normal **k** in the case of the direct Iso-SmC phase transition (a), variation of the orientational (b), and the orientational-translational order parameters (c) defined both in the **k** frame and in the director reference frame. The order parameter profiles have been calculated for $w_2 = -1.6$, while the values of other coupling constants are the same as in Fig. 2.

also comprises the NAC point, but in this case there is no direct transition into the SmC phase from the isotropic phase. Temperature variation of all relevant order parameters across all four different phases is presented in Fig. 9. One notes that here the N_U-SmA phase transition is of the first order. Temperature variation of orientational order parameters, defined both in the **k** frame and in the director reference frame is presented in Fig. 9(b), while the orientational-translational order parameter profiles, defined in both frames, are presented in Fig. 9(c). One concludes once again that $P = \Pi = 0$ and $\Theta = \theta$; i.e., the tilt of the orientational ordering tensor appears
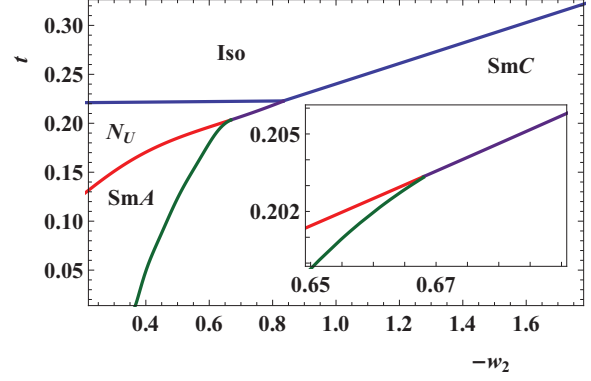

FIG. 5. (Color online) Phase diagram for $u = -1$, $w_0 = w_1 = -0.04$, $w_3 = w_4 = -0.0221 + 0.7725w_2$. The violet line represents the line of N_U-SmC phase transitions, and the colors of the other curves have the same meaning as in Fig. 2. The inset shows the magnified area around the NAC point.

to be the same as that of the orientational-translational tensor order parameter everywhere in the SmC phase.

VI. DISCUSSION

In this paper we have developed a molecular-field theory of the phase transitions between isotropic (Iso), uniaxial nematic (N_U), SmA, and SmC phases in the system composed of uniaxial particles using the general expansion of the pair interaction potential and the full set of order parameters. This enables one to undertake a more realistic study of the topology of the phase diagrams in the vicinity of the NAC point, where N_U, SmA, and SmC phases coexist.

In this approach the ordering of uniaxial molecules in the uniaxial SmA phase is characterized by the three scalar order parameters, introduced by McMillan, including the nematic order parameter S, the translational order parameter ψ, and the mixed orientational-translational order parameter Σ. In the SmC phase the two ordering tensors are biaxial and as a result the system is characterized by seven scalar order parameters including one translational, three orientational, and three mixed ones, which are discussed in detail in Sec. III. All
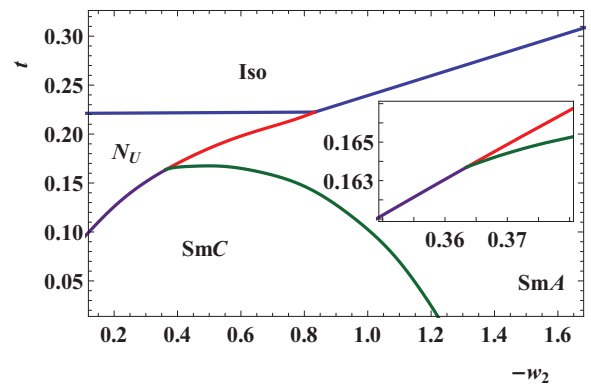

FIG. 6. (Color online) Phase diagram for $u = -1$, $w_0 = w_1 = -0.04$, $w_3 = w_4 = -0.0393 + 0.7425w_2$. The colors of the transition lines has the same meaning as in Figs. 2 and 5. The inset shows the magnified behavior in the vicinity of the NAC point.
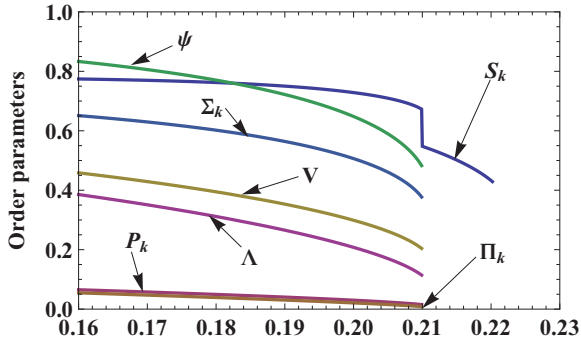
FIG. 7. (Color online) Temperature variation of the whole set of orientational and translational order parameters in the case of the Iso-N_U-SmC sequence of phase transitions for $w_2 = -0.72$; the values of other coupling constants are the same as in Fig. 5.

of these order parameters are defined in the so-called **k** frame [28–30] based on the density wave vector **k**. For instance, the nematic order parameter S_k describes the orientational order of uniaxial molecules with respect to **k**, the biaxial order parameter P_k specifies the biaxial order in the plane of the smectic layers and the tilt order parameter V indicates the average tilt of uniaxial molecules in the SmC phase. the meaning of these order parameters is illustrated in Fig. 1.

One notes that the advantage of using the **k** frame is related to the fact that in this frame all order parameters can be
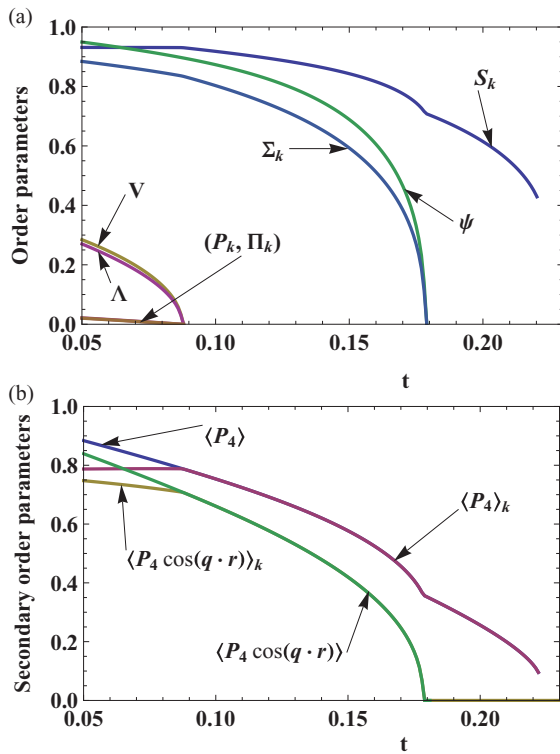

FIG. 8. (Color online) (a) Variation of the whole set of orientational and translational order parameters for $w_2 = -0.45$, which corresponds to the Iso-N_U-SmA-SmC sequence of phase transitions. The values of other coupling constants are the same as in Fig. 5. (b) Temperature variation of the higher-order parameters along the same cross section of the phase diagram.
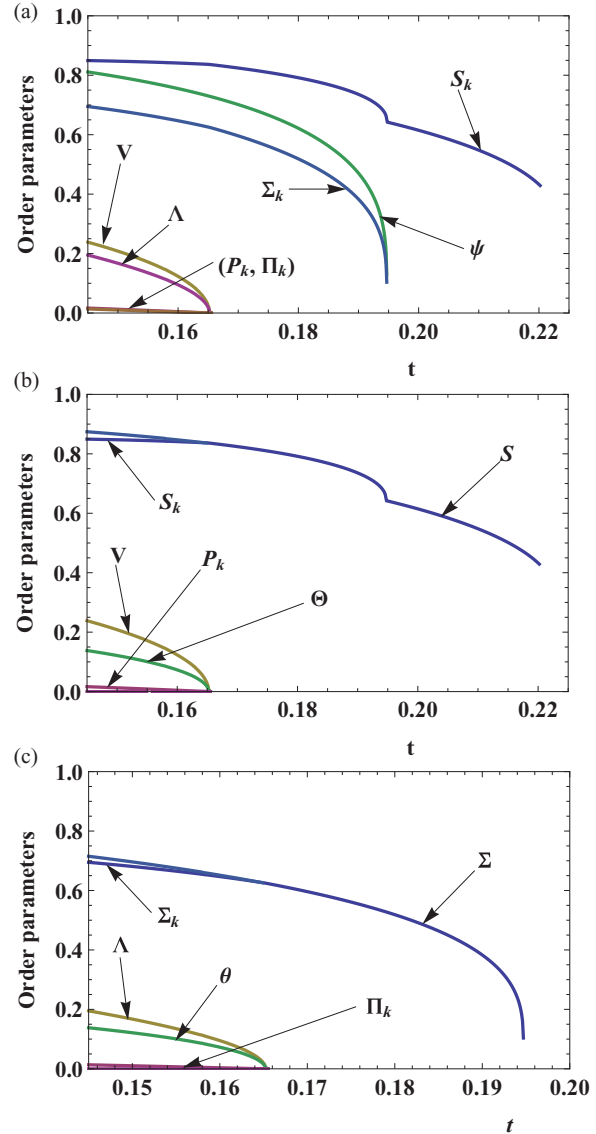

FIG. 9. (Color online) Temperature variation of the orientational and translational order parameters defined with respect to the smectic layer normal **k** along the cross section of the phase diagram in Fig. 6 for $w_2 = -0.575$ (a). Variation of the orientational (b) and the orientational-translational (c) order parameters defined both in the **k** frame and in the director reference frame along the same cross section of phase diagram.

expressed as explicit statistical averages of some molecular quantities. The use of the order parameters defined in the **k** frame is also favorable from the experimental point of view and from the standpoint of computer simulations because the orientation of the director is often not known experimentally while the orientation of smectic layers is usually fixed by the experimental geometry or by the simulation box, or it can be readily determined. It is also important to note that the orientation of the director in the SmC phase is not fixed by the symmetry of the phase, as the symmetry only requires that the director is parallel to the mirror (tilt) plane. The director is defined as the principal axes of some macroscopic second rank tensor, and thus the orientations of the directors, obtained from different tensors, should generally be different

in the SmC phase (in particular in the system of biaxial molecules). In practice the director tilt angle may even depend on the experimental procedure, that is, for example, on the wavelength of light as shown in [34]. Additionally, in contrast to the tilt order parameter V, the tilt angle Θ has more of a geometrical meaning and cannot be expressed as an explicit statistical average which is very inconvenient from the theoretical point of view. At the same time the conventional order parameters defined in the director frame including the tilt angle can always be calculated using Eqs. (24)–(26) and (27)–(29), which establish the exact relationship between the two equivalent sets of order parameters.

Order parameters in the **k** reference frame have been calculated numerically as functions of temperature for different values of the coupling constants by direct minimization of the free energy, and the results are summarized in three typical phase diagrams which have different topology. The temperature variation of all order parameters across different sequences of phase transitions is also presented for a number of cross sections of the diagrams.

In the phase diagrams presented in Figs. 2 and 5 one finds the direct transition from the isotropic to the SmC phase at large values of the coupling constant $|w_2|$. Such a direct transition has been observed in a number of materials, and it is well characterized experimentally as a strong first order transition [38,39]. For example, the direct Iso-SmC transition has been observed recently in the series of 2-(4-alkyloxyphenyl)-5-alkyloxypyrimidines with long alkoxy chains [40,41]. The compounds with $n = 6, 8, 9, 10$, and 14 methylene units have been studied, and the Iso-SmC transition is observed for $n = 14$ and 10. One notes that materials with shorter chains ($n = 8,9$) undergo the direct transition from the Iso to the SmA phase while the material with $n = 6$ undergoes the Iso-N_U transition. This is exactly the sequence of direct transitions from the isotropic phase which is found in the phase diagram in Fig. 2 when the constant $|w_2|$ is decreased. Thus, at least in some cases the absolute values of the parameters w_2 and w_3 can be correlated with the length of the chain.

Recently, the direct Iso-SmC phase transition has also been observed in a chiral three ring material with a fluorinated chain [42]. In both cases the LC materials are characterized by nano-scale segregation between chains and rigid cores which promotes the smectic ordering. This is consistent with the results of the theory as it has been shown before [15] that systems with strong nano-scale segregation correspond to large values of w_2 and w_3. It is interesting to note also that the Iso-SmC transition is often observed in main-chain smectic elastomers [43–45].

Two of the phase diagrams obtained in this paper contain the NAC triple point at which the N_U, SmA, and SmC phases coexist. The properties of a system in the vicinity of the NAC point has been an issue of debate since the pioneering theoretical works [46] and [47]. The results of the present molecular theory can shed some light on the behavior of LCs around the NAC point. One notes that in both phase diagrams the line of the N_U-SmC phase transitions splits into the N_U-SmA and SmA-SmC lines at the NAC point without any visible discontinuity of the slopes of all the lines. As a result the temperature interval of the SmA is expected to be relatively small in the vicinity of the NAC point. This

topology of the phase diagram in the vicinity of the NAC point has indeed been observed experimentally in the binary mixture of two materials with the same rigid core and different chains lengths [41] and in another mixture of two smectic LCs of similar structure [48]. A similar behavior has also been observed by taking into account that the strongly chiral LC mixture, studied in [49], may exhibit the twist grain boundary phase (*TGB*) instead of the conventional SmA phase.

Systematic experimental investigation of the phase diagrams in several binary mixtures indicate [50] that the behavior of the system at the NAC point can be interpreted as a splitting of the N_U-SmC line but the slopes of all three transition lines, which meet at the triple point, appear to be different. A similar behavior has also been observed in one-component smectic LCs by varying the pressure [51,52]. One notes that in few LC systems the behavior at the NAC point is different; i.e., the N_U-SmA line splits into the N_U-SmC and SmA-SmC lines at the NAC point [53]. It should be noted, however, that the direct comparison with the experimental phase diagrams is hardly possible at this stage because the latter are obtained by varying pressure or the concentration of components in a mixture. The existing molecular theory, however, has been developed for incompressible LCs. On the other hand, the change of concentrations of the components in a mixture of LCs should generally result in a nonlinear variation of all effective coupling constants and thus the experimental phase diagrams may correspond to very complex paths in the parameter space.

A number of phase diagrams which contain Iso, N, SmA, and SmC have also been obtained in [23]. Those diagrams are qualitatively similar to the ones presented in Figs. 2 and 5 but not to the diagram in Fig. 6. One notes also that in the model of Ref. [23] the SmA-SmC transition may be of both second and first order while in the present theory the transition is always second order.

It is interesting to note that even in the system of uniaxial molecules the SmC phase is characterized by two different tensor order parameters [the orientational and the mixed one, see Eqs. (11)], which are discussed in detail in Sec. III. In the uniaxial SmA phase the principal axes of the two tensors coincide with the smectic wave vector **k** and thus there is a unique director. In contrast, in the biaxial SmC phase the principal axes of the two tensors are not necessarily parallel, and thus one may define two different directors and two different tilt angles. Nonetheless, the results of numerical calculations presented in this paper strongly indicate that the two tilt angles are the same, at least in the context of our simple model of uniaxial particles. It was shown in our earlier paper [33] using the approximation of the perfect smectic order that if the molecules are biaxial, then there exist three different tilt angles in the SmC which specify the tilt of the primary axes of the three ordering tensors including the uniaxial one, the biaxial one and the mixed one, respectively. However, the generalization of the present theory to the case of biaxial molecules presents a significant computational challenge related to additional integrations.

Finally, one notes that molecular chirality has not been taken into account in the present theory. It is well known that chiral nematics are characterized by the macroscopic helical structure but the Iso-N_U transition is generally weakly affected

by molecular chirality. On the other hand, in many materials additional phases are observed which are induced by strong molecular chirality and which are not present in the theoretical phase diagrams presented in this paper. The most well studied chiral phases of this kind are the blue phases, which are characterized by three-dimensional director distribution and regular defect structure (see, for example, the review [54]) and the (*TGB*) phases (see, for example, [55–57]). In some mixtures these chiral phases are stable over a large temperature range [57,58]. *TGB* phases may either replace the conventional Sm*A* or Sm*C* phases or coexist with them on the same phase diagram. Some strongly chiral materials may exhibit more than one *TGB* phase [49].

A rich variety of interesting chiral phases is observed in some tilted smectic LCs. In the conventional Sm*C* phase the orientation of the tilt plane is the same in all smectic layers (if the helical structure in chiral systems is unwound). In contrast, in other chiral tilted smectic phases the orientation of the tilt plane differs from layer to layer. The incommensurate SmC_α phase is sometimes observed in the vicinity of the Sm*A*-Sm*C* transition, and chiral phases with two-, three-, four-, and six-layer periodicity have also been observed [59–62]. During the past decade a phenomenological theory of these novel smectic phases has been developed [63–66] using the models based on a coupling between different smectics layers. However, there is no unified molecular theory which enables one to obtain phase diagrams containing all of these chiral phases.

APPENDIX: DERIVATION OF THE MEAN-FIELD POTENTIAL

Truncating the series in Eq. (42) at $l = k = 2$ and taking into account nonpolar and achiral terms, the intermolecular interaction potential can approximately be expressed as

$$U_{\text{eff}}(\mathbf{a}_1, \mathbf{r}_{12}, \mathbf{a}_2) = J_{202}(r_{12}) P_2(\mathbf{a}_1 \cdot \mathbf{a}_2) + J_{220}(r_{12}) P_2(\mathbf{a}_1 \cdot \mathbf{u}_{12})$$
$$+ J_{022}(r_{12}) P_2(\mathbf{u}_{12} \cdot \mathbf{a}_2)$$
$$+ J_{222}(r_{12}) T^{222}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2)$$
$$+ J_{242}(r_{12}) T^{242}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2), \tag{A1}$$

where

$$T^{222}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2) = \tfrac{9}{2}(\mathbf{a}_1 \cdot \mathbf{a}_2)(\mathbf{a}_1 \cdot \mathbf{u}_{12})(\mathbf{u}_{12} \cdot \mathbf{a}_2)$$
$$- \tfrac{3}{2}(\mathbf{a}_1 \cdot \mathbf{a}_2)^2 - \tfrac{3}{2}(\mathbf{a}_1 \cdot \mathbf{u}_{12})^2$$
$$- \tfrac{3}{2}(\mathbf{u}_{12} \cdot \mathbf{a}_2)^2 + 1, \tag{A2}$$

$$T^{242}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2) = \tfrac{35}{8}(\mathbf{u}_{12} \cdot \mathbf{a}_2)^2(\mathbf{a}_1 \cdot \mathbf{u}_{12})^2$$
$$- \tfrac{5}{2}(\mathbf{a}_1 \cdot \mathbf{a}_2)(\mathbf{a}_1 \cdot \mathbf{u}_{12})(\mathbf{u}_{12} \cdot \mathbf{a}_2) + \tfrac{1}{4}(\mathbf{a}_1 \cdot \mathbf{a}_2)^2$$
$$- \tfrac{5}{8}(\mathbf{a}_1 \cdot \mathbf{u}_{12})^2 - \tfrac{5}{8}(\mathbf{u}_{12} \cdot \mathbf{a}_2)^2 + \tfrac{1}{8}. \tag{A3}$$

Substituting Eqs. (A2) and (A3) into Eq. (44) one obtains

$$K(\mathbf{a}_1, \mathbf{a}_2, \mathbf{q}) = v_0 + v_1[P_2(\mathbf{a}_1 \cdot \mathbf{k}) + P_2(\mathbf{a}_2 \cdot \mathbf{k})]$$
$$+ v_2 P_2(\mathbf{a}_1 \cdot \mathbf{a}_2)$$
$$+ v_3(\mathbf{a}_1 \cdot \mathbf{a}_2)(\mathbf{a}_1 \cdot \mathbf{k})(\mathbf{k} \cdot \mathbf{a}_2)$$
$$+ v_4 P_2(\mathbf{a}_1 \cdot \mathbf{k}) P_2(\mathbf{k} \cdot \mathbf{a}_2), \tag{A4}$$

where $v_0 = u_{222}/2 + 7u_{242}/36$; $v_1 = u_{220} - u_{222} + 5u_{242}/9$; $v_2 = u_{202} - u_{222} + u_{242}/6$; $v_3 = 9u_{222}/2 - 5u_{242}/2$; $v_4 = 35u_{242}/18$ and where the constants u_{nmk} are given by the general Eq. (45).

Finally, substitution of Eq. (A4) into Eq. (40) and integration over $\mathbf{a} = (\cos\gamma, \sin\gamma \cos\varphi, \sin\gamma \sin\varphi)$ yields the following expression for the periodic part of the mean-field potential:

$$U_S((\mathbf{q} \cdot \mathbf{r}), \gamma, \varphi)$$
$$= w_0 \psi \cos(\mathbf{q} \cdot \mathbf{r}) + w_1[\psi P_2(\cos\gamma) \cos(\mathbf{q} \cdot \mathbf{r})$$
$$+ \Sigma_k \cos(\mathbf{q} \cdot \mathbf{r})] + w_2 \Sigma_k P_2(\cos\gamma) \cos(\mathbf{q} \cdot \mathbf{r})$$
$$+ w_3 \Pi_k \sin^2\gamma \cos 2\varphi \cos(\mathbf{q} \cdot \mathbf{r})$$
$$+ w_4 \Lambda \sin 2\gamma \cos\varphi \cos(\mathbf{q} \cdot \mathbf{r}), \tag{A5}$$

where $w_0 = v_0$, $w_1 = v_1$ and $w_2 = v_2 + (4/9)v_3 + v_4$, $w_3 = (3/4)v_2$, $w_4 = (3/4)v_2 + (1/2)v_3$.

[1] W. Lehmann, H. Skupin, C. Tolksdorf, E. Gebhard, R. Zentel, P. Krüger, M. Lösche, and F. Kremer, Nature (London) **410**, 447 (2001).

[2] V. M. Kaganer, H. Möhwald, and P. Dutta, Rev. Mod. Phys. **71**, 779 (1999).

[3] J. P. F. Lagerwall and F. Giesselmann, ChemPhysChem **7**, 20 (2006).

[4] W. L. McMillan, Phys. Rev. A **4**, 1238 (1971).

[5] K. Kobayashi, Mol. Cryst. Liq. Cryst. **13**, 137 (1971).

[6] F. T. Lee, H. T. Tan, Y. M. Shih, and C.-W. Woo, Phys. Rev. Lett. **31**, 1117 (1973).

[7] P. J. Photinos and A. Saupe, Phys. Rev. A **13**, 1926 (1976).

[8] M. R. Kuzma and D. W. Allender, Phys. Rev. A **25**, 2793 (1982).

[9] G. F. Kventsel, G. R. Luckhurst, and H. B. Zewdie, Mol. Phys. **56**, 589 (1985).

[10] L. Mederos and D. E. Sullivan, Phys. Rev. A **39**, 854 (1989).

[11] B. Tjipto-Margo and D. E. Sullivan, J. Chem. Phys. **88**, 6620 (1978).

[12] J. Stecki and A. Kloczkowski, Mol. Phys. **42**, 51 (1981).

[13] L. Senbetu and C.-W. Woo, Phys. Rev. A **17**, 1529 (1978).

[14] M. D. Lipkin and D. W. Oxtoby, J. Chem. Phys. **79**, 1939 (1983).

[15] M. V. Gorkunov, M. A. Osipov, N. Kapernaum, D. Nonnenmacher, and F. Giesselmann, Phys. Rev. E **84**, 051704 (2011).

[16] R. J. Meyer and W. L. McMillan, Phys. Rev. A **9**, 899 (1974).

[17] A. Wulf, Phys. Rev. A **11**, 365 (1975).

[18] A. M. Somoza and P. Tarazona, Phys. Rev. Lett. **61**, 2566 (1988).

[19] B. W. Van der Meer and G. Vertogen, J. Phys. Colloq. **40**, C3-222 (1979).

[20] W. J. A. Goosens, J. Phys. (France) **46**, 1411 (1985).

[21] A. Poniewierski and T. J. Sluckin, Mol. Phys. **73**, 199 (1991).

[22] A. S. Govind and N. V. Madhusudana, Eur. Phys. Lett. **55**, 505 (2001).

[23] A. S. Govind and N. V. Madhusudana, Eur. Phys. J. E **9**, 107 (2002).

[24] M. A. Osipov, M. V. Gorkunov, H. F. Gleeson, and S. Jaradat, Eur. Phys. J. E **26**, 395 (2008).

[25] M. P. Neal and A. J. Parker, Chem. Phys. Lett. **294**, 277 (1998).

[26] R. Berardi, S. Orlandi, and C. Zannoni, Phys. Rev. E **67**, 041708 (2003).

[27] M. V. Gorkunov, F. Giesselmann, J. P. F. Lagerwall, T. J. Sluckin, and M. A. Osipov, Phys. Rev. E **75**, 060701 (2007).

[28] M. V. Gorkunov, M. A. Osipov, J. P. F. Lagerwall, and F. Giesselmann, Phys. Rev. E **76**, 051706 (2007).

[29] M. V. Gorkunov and M. A. Osipov, J. Phys.: Condens. Matter **22**, 362101 (2010).

[30] M. Osipov and G. Pająk, Phys. Rev. E **85**, 021701 (2012).

[31] M. A. Osipov, in *Handbook of Liquid Crystals*, 2nd ed., edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spies, and V. Vill, Vol. 1 (Wiley-VCH, Weinheim, 1998).

[32] W. M. Gelbart and B. Barboy, Acc. Chem. Res. **13**, 290 (1980).

[33] M. V. Gorkunov and M. A. Osipov, J. Phys. A: Math. Theor. **41**, 295001 (2008).

[34] F. Giesselmann, A. Langhoff, and P. Zugenmaier, Liq. Cryst. **23**, 927 (1997).

[35] V. L. Lorman and B. Mettout, Phys. Rev. E **69**, 061710 (2004).

[36] L. Blum and A. J. Torruella, J. Chem. Phys. **56**, 303 (1972).

[37] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids*, Vol. 1 (Clarendon, Oxford, 1984).

[38] S. Lakshminarayana, C. R. Prabhu, D. M. Potukuchi, N. V. S. Rao and V. G. K. M. Pisipati, Liq. Cryst. **20**, 177 (1996).

[39] G. Cordoyiannis, L. F. V. Pinto, M. H. Godinho, C. Glorieux, and J. Thoen, Phase Trans. **82**, 280 (2009).

[40] N. Kapernaum, C. S. Hartley, J. C. Roberts, R. P. Lemieux, and F. Giesselmann, Beilstein J. Org. Chem. **5**, 65 (2009).

[41] N. Kapernaum, C. S. Hartley, J. C. Roberts, F. Schoerg, D. Krueerke, R. P. Lemieux, and F. Giesselmann, ChemPhysChem **11**, 2099 (2010).

[42] J. M. Czerwiec, R. Dąbrowski, M. Żurowska, D. Ziobro, and S. Wróbel, Acta Phys. Pol. A **117**, 553 (2010).

[43] A. Sánchez-Ferrer and H. Finkelmann, Macromolecules **41**, 970 (2008).

[44] K. Hiraoka, W. Sagano, T. Nose, and H. Finkelmann, Macromolecules **38**, 7352 (2005).

[45] K. Hiraoka, M. Kobayasi, R. Kazama, and H. Finkelmann, Macromolecules **42**, 5600 (2009).

[46] J. Chen and T. C. Lubensky, Phys. Rev. A **14**, 1202 (1976).

[47] K. C. Chu and W. L. McMillan, Phys. Rev. A **15**, 1181 (1977).

[48] D. Johnson, D. Allender, R. deHoff, C. Maze, E. Oppenheim, and R. Reynolds, Phys. Rev. B **16**, 470 (1977).

[49] V. Manjuladevi and N. V. Madhusudana, Liq. Cryst. **32**, 1071 (2005).

[50] D. Brisbin, D. L. Johnson, H. Fellner, and M. E. Neubert, Phys. Rev. Lett. **50**, 178 (1983).

[51] R. Shashidhar, B. R. Ratna, and S. K. Prasad, Phys. Rev. Lett. **53**, 2141 (1984).

[52] S. Krishna Prasad, Ph.D. thesis, Raman Research Institute, Bangalore, 1985.

[53] G. Sigaud, F. Hardouin, and M. F. Achard, Solid State Commun. **23**, 35 (1977).

[54] T. Seideman, Rep. Prog. Phys. **53**, 659 (1990).

[55] J. W. Goodby, M. A. Waugh, S. M. Stein, E. Chin, R. Pindak, and J. S. Patel, Nature (London) **337**, 449 (1989).

[56] K. J. Ihn, J. A. N. Zasadzinski, R. Pindak, A. J. Slaney, and J. Goodby, Science **258**, 275 (1992).

[57] R. Shao, J. Pang, N. A. Clark, J. A. Rego, and D. M. Walba, Ferroelectrics **147**, 255 (1993).

[58] H. J. Coles and M. N. Pivnenko, Nature (London) **436**, 997 (2005).

[59] P. Mach, R. Pindak, A.-M. Levelut, P. Barois, H. T. Nguyen, C. C. Huang, and L. Furenlid, Phys. Rev. Lett. **81**, 1015 (1998).

[60] L. S. Hirst, S. J. Watson, H. F. Gleeson, P. Cluzeau, P. Barois, R. Pindak, J. Pitney, A. Cady, P. M. Johnson, C. C. Huang, A.-M. Levelut, G. Srajer, J. Pollmann, W. Caliebe, A. Seed, M. R. Herbert, J. W. Goodby, and M. Hird, Phys. Rev. E **65**, 041705 (2002).

[61] P. M. Johnson, S. Pankratz, P. Mach, H. T. Nguyen, and C. C. Huang, Phys. Rev. Lett. **83**, 4073 (1999).

[62] Shun Wang, Li Dong Pan, R. Pindak, Z. Q. Liu, H. T. Nguyen, and C. C. Huang, Phys. Rev. Lett. **104**, 027801 (2010).

[63] M. Cepic and B. Zeks, Phys. Rev. Lett. **87**, 085501 (2001).

[64] A. V. Emelyanenko and M. A. Osipov, Phys. Rev. E **68**, 051703 (2003).

[65] P. V. Dolganov, V. M. Zhilin, V. K. Dolganov, and E. I. Kats, Phys. Rev. E **83**, 061705 (2011).

[66] P. V. Dolganov, V. M. Zhilin, V. K. Dolganov, and E. I. Kats, Phys. Rev. E **67**, 041716 (2003).