ON A MOLECULAR BASED Q-TENSOR MODEL FOR LIQUID CRYSTALS WITH DENSITY VARIATIONS

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Abstract. In this article, we study the new Q-tensor model previously derived from Onsager’s molecular theory by Han et al. [Arch. Rational Mech. Anal., (2014), DOI 10.1007/s00205-014-0792-3] for static liquid crystal modeling. Taking relative density and Q-tensor as order parameters, the new Q-tensor model not only characterizes important phases while capturing density variation effects, but also remains computationally tractable and efficient. We report the results of two numerical applications of the model, namely the isotropic–nematic–smectic-A–smectic-C phase transitions and the isotropic–nematic interface problem, in which density variations are indispensable. Meanwhile, we show the connections of the new Q-tensor model with classical models including generalized Landau-de Gennes models, generalized McMillan models, and Chen-Lubensky model. The new Q-tensor model is the pivot and an appropriate trade-off within the classical models in three scales.

1. Introduction

A proper choice of order parameters is the most important perspective building a sound model for liquid crystals. The order parameters should be simple and explanatory in terms of mathematics and physics, while efficient in computations. From the viewpoint of theoretical analysis, it is desirable to adopt the order parameters as simple as possible to capture essential phenomena of liquid crystals, with four phases the most important: isotropic(I), nematic(N), smectic-A(SA), and smectic-C(SC) phases. As for the aspect of computations, the order parameters should be discretely represented with reasonable dimensions while keeping energy functional well-posed, concise, and efficient.

The classical models for static liquid crystals can be classified into three scales: molecular models, tensor models, and vector models. Every model respectively shows its merits in some aspects as mentioned above; nevertheless, not all of these aspects.

The molecular model for liquid crystals is based on microscopic statistical physics. By means of cluster expansion, Onsager [2] pioneered the molecular field theory, in which the order parameter is the density function for molecules at given position and orientation. Onsager’s molecular model is established on sound physical theories, and contains no adjustable parameters. However, the molecular model is not sensitive to macroscopic properties, and the high dimension of the order parameter imposes considerable obstacles in computations.

On the contrary, a vector model for liquid crystals was phenomenologically proposed by Oseen [3], where the order parameter is a vector field n(x) representing the director. As a development of Landau-Ginzburg theory and Oseen-Frank theory, Chen and Lubensky [4] introduced the relative density as another order parameter to characterize N-SA-SC phase transitions. Chen-Lubensky model is famous for its conciseness. The internal coefficients can be measured through experiments. However, this model presumes liquid crystals to be uniaxial, and the director n is singular at defect points, which renders it difficult to characterize some small-scale phenomena, such as defects and interfaces.

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Overcoming the drawbacks of the molecular model and the vector models, the well-known Landau-de Gennes model \cite{5} was proposed with the energy functional

\begin{equation}
F^{LG}[Q] = \int_{\Omega} \left( \frac{A(T - T^*)}{2} \text{tr}(Q^2) - \frac{B}{3} \text{tr}(Q^3) + \frac{C}{4} (\text{tr}(Q^2))^2 \right) dx \\
+ \int_{\Omega} \left( L_1 |\nabla Q|^2 + L_2 \partial_j Q_{ik} \partial_k Q_{ij} + L_3 \partial_j Q_{ij} \partial_k Q_{ik} + L_4 Q_{lk} \partial_k Q_{ij} \partial_l Q_{ij} \right) dx,
\end{equation}

where $A$, $B$, $C$, and $L_i$ are constants. The order parameter is a $3 \times 3$ symmetric traceless tensor field $Q(x)$, which is the second moment of molecule’s orientation at every point.

The Q-tensor is a desirable order parameter providing information on both the preferred molecular orientation and the degree of orientational order on every given point, while capturing essential physical properties. Various phenomena were studied with the Landau-de Gennes model, e.g., phase transitions in confined geometries \cite{6} \cite{7}, wetting phenomena \cite{8} \cite{9}, surface-induced bulk alignment \cite{10} \cite{11}, and defects and disclinations \cite{12} \cite{13}.

The order parameter and the energy functional of Landau-de Gennes model are also simple enough to perform rigorous mathematical analysis. John Ball proved that the energy of Landau-de Gennes model is unbounded from below as $L_4 \neq 0$, and proposed to modify the entropy term from polynomial into a thermotropic one in order to avoid the unboundedness \cite{14}. Furthermore, John Ball proved that for simply-connected domains and in Sobolev space $W^{1,2}$ with corresponding boundary conditions, Landau-de Gennes theory and Oseen-Frank theory coincide \cite{15}.

Various generalizations of Landau-de Gennes model \cite{16} \cite{17} \cite{18} \cite{19} were proposed to include smectic phases. The work of Pajak and Osipov \cite{16} is a generalization of McMillan model \cite{20} and Landau-de Gennes model, which starts from self-consistent field theory and adopts the one mode approximation to parameterize the density function. This model is efficient in computations, but the order parameters are spatially invariant, failing to characterize some physical phenomena with confined geometry and spatial variance. The works of Mukherjee \cite{18} and Biscari et al. \cite{19} are also generalizations of the Landau-de Gennes theory. The Q-tensor is coupled with the complex smectic order parameter, and the spatial inhomogeneity of order parameters enables the model to characterize smectic phases. However, it is noteworthy that these theories were phenomenologically presented.

In a recent paper by Han et al. \cite{1}, a systematic way of modeling static liquid crystals with uniaxial molecules was proposed. To be more precise, starting from Onsager’s molecular theory, a new Q-tensor model was presented incorporating Bingham closure and Taylor expansion with truncation at low order moments. The coefficients in the new Q-tensor model were approximated in terms of the microscopic shape factor $\varepsilon = D/L$ by assuming the interaction potential to be the volume exclusion potential of rigid rod-like molecules. Three elastic constants $K_1$, $K_2$, and $K_3$ measuring the strains on liquid crystals in deformation were calculated analytically. Under the uniaxial assumption, some preliminary numerical results regarding $I$-$N$-$S_A$ phase transitions were presented.

The energy functional of the new Q-tensor model in a modified version reads

\begin{equation}
F[c, Q] = F_{\text{bulk}} + F_{\text{elastic}, 2} + F_{\text{elastic}, 4},
\end{equation}
where
\[
\beta F_{\text{bulk}} = c_0 \int_\Omega c(x) \left( \ln c(x) + B_Q : Q - \ln Z(x) \right) dx
\]
(1.3)
\[
\frac{c_0^2}{2} \int_\Omega \left[ A_1 c^2 - A_2 |cQ|^2 - A_3 |cQ_4|^2 \right] dx,
\]
\[
\beta F_{\text{elastic}, 2} = \frac{c_0^2}{2} \int_\Omega \left[ -G_1 \nabla c^2 + G_2 |\nabla (cQ)|^2 + G_3 \partial_i (cQ_{ik}) \partial_j (cQ_{jk}) - G_4 \partial_i (cQ_{ij}) \partial_j (c) \right] dx
\]
(1.4)
\[
+ G_5 |\nabla (cQ_4)|^2 + G_6 \partial_i (cQ_{4iklm}) \partial_j (cQ_{4jklm}) + G_7 \partial_i (cQ_{4ijkl}) \partial_j (cQ_{kl}) \right] dx,
\]
\[
\beta F_{\text{elastic}, 4} = \frac{c_0^2}{2} \int_\Omega \left[ H_1 |\nabla^2 c|^2 + H_2 |\nabla^2 (cQ)|^2 \right]
\]
(1.5)
\[
+ H_3 \partial_{ij} (cQ_{ij}) \partial_{kl} (cQ_{kl}) + H_4 \partial_{ik} (cQ_{ip}) \partial_{jk} (cQ_{jp}) \right] dx.
\]

The bulk energy $F_{\text{bulk}}$ contains the entropy and the quadratic terms of the order parameters. The second order elastic energy $F_{\text{elastic}, 2}$ contains the derivative terms of the order parameters; the fourth order elastic energy $F_{\text{elastic}, 4}$ contains the second order derivative terms of the order parameters. Note that here the fourth order elastic energy $F_{\text{elastic}, 4}$ is truncated: only the positive definite terms are preserved in order to ensure the lower boundedness of the energy functional. The detailed descriptions of the energy functional are presented in the main body of the paper.

In this paper, we focus on the density variation effects of the new Q-tensor model, and show its effectiveness in terms of mathematics, physics, and computations. The introduction of the relative density $c(x)$ as another order parameter exhibits many benefits. It empowers the model to characterize smectic phases, and to characterize the density variations in small-scale phenomena such as defects and interfaces. Since a few Fourier modes are enough to characterize the profiles of the order parameters, the model can be solved with low computational costs. Numerical experiments are performed to study $\mathbf{I-N-S_A-S_C}$ phase transitions, and the results agree well with experimental records. The $\mathbf{I-N}$ interface problem is also studied in the new Q-tensor model setup, where the numerical results are compared with previous results obtained by Onsager’s molecular theory [21] and Monte-Carlo simulations [22].

In addition, we will elaborate on the strong connections of the new Q-tensor model with the classical models of liquid crystals in three scales. Derived from Onsager’s molecular theory, the new Q-tensor model can generate all the other classical models with some assumptions and approximations. Figure 1 shows the classical models in three scales and their relations.

This paper is organized as follows. In section 2, we demonstrate the mathematical properties of the new Q-tensor model and the numerical methods to compute the energy functional. In section 3, the numerical results regarding $\mathbf{I-N-S_A-S_C}$ phase transitions and $\mathbf{I-N}$ interface are presented. In section 4, we compare the Q-tensor model with the classical models. We give several concluding remarks in section 5. Some detailed calculations involved in the paper are provided in the appendix.

2. Model

In this section, we review the new Q-tensor model previously derived from Onsager’s molecular theory in paper [1], and discuss the numerical methods. We will demonstrate the merits of relative density as the order parameter in terms of concise mathematics, efficient computations, and explanatory physics.
2.1. **Mathematical Properties.** The new Q-tensor model gives the free energy of liquid crystals as equation (1.2), with the definitions of notations as follows. Consider the rod-like liquid crystal molecules in domain $\Omega \subset \mathbb{R}^3$. The molecules take positional coordinate $x \in \Omega$, and orientational coordinate $m \in S^2$. We introduce the normalized relative density $c(x)$ and the Q-tensor $Q(x)$ as order parameters. The scalar function $c(x)$ is the relative density of molecules, with normalization $\frac{1}{|\Omega|} \int_{\Omega} c(x) dx = 1$. The tensor $Q(x)$ is the second moment of $m$ with respect to $\rho$,

$$Q(x) = \int_{S^2} (mm - \frac{1}{3} I) \rho(x, m) dm,$$

where $\rho$ is the probability density function of molecules with respect to orientation $m$ at given position $x$. This definition immediately requires the Q-tensor to be a symmetric, traceless $3 \times 3$ matrix whose eigenvalues $\{\lambda_i(Q)\}$ are constrained by the inequalities

$$-\frac{1}{3} < \lambda_i(Q) < \frac{2}{3}, \quad i = 1, 2, 3; \quad \sum_{i=1}^{3} \lambda_i(Q) = 0.$$

Bingham closure assumption is essential to the model reduction. Assume that the density function $\rho$ at given $x$ follows Bingham distribution,

$$\rho(x, m) = \frac{1}{Z(x)} \exp(\mathcal{B}_Q(x) : mm),$$

where

$$Z(x) = \int_{S^2} \exp(\mathcal{B}_Q(x) : mm) dm,$$

and $\mathcal{B}_Q(x)$ is any traceless symmetric matrix in $\mathbb{R}^{3\times3}$. It can be proved that $Q(x)$, $\mathcal{B}_Q(x)$ and $\rho(x, m)$ can be mutually determined under this assumption [23]. Therefore, under the
well-known Bingham closure, the dimension of probability density function \( \rho(x, m) \) reduces to five, the same as that of \( Q(x) \) and \( B_Q(x) \).

Let \( Q_4 \) be the fourth moment of \( m \) in terms of \( \rho \), which is defined as

\[
Q_{4ijkl}(x) = \int_{S^2} \left( m_i m_j m_k m_l - \frac{1}{7}(m_im_j\delta_{kl})_{\text{sym}} + \frac{1}{35}(\delta_{ij}\delta_{kl})_{\text{sym}} \right) \rho(x, m) \, dm,
\]

where \((\cdot)_{\text{sym}}\) means the symmetrization of the tensor. Since \( \rho(x, m) \) and \( Q(x) \) can be mutually determined, \( Q_4(x) \) is not an independent order parameter, and can be determined by the order parameter \( Q(x) \).

As a generalization of the Landau-de Gennes theory, the introduction of the relative density \( c(x) \) as another order parameter enables the model to characterize smectic phases and density variations in physical phenomena such as defects and interfaces. The major phases of rod-like molecule liquid crystals can be characterized by \( c(x) \) and \( Q(x) \) as

- \( \text{I phase: } c = \text{const}, \quad Q = 0. \)
- \( \text{N phase: } c = \text{const}, \quad Q = s(nn - \frac{1}{3}I) = \text{const}. \)
- \( \text{S}_A \) phase: \( c \) and \( Q \) are one-dimensional periodic and constant in the other two dimensions. The director \( n \), defined as the principle eigenvector of \( Q \)-tensor, is parallel to the layer normal \( \nabla c \).
- \( \text{S}_C \) phase: \( c \) and \( Q \) are one-dimensional periodic and constant in the other two dimensions. The director \( n \) and the layer normal \( \nabla c \) yield angle \( \theta \).

Biaxiality is often remarkable in smectic phases, and in other physical phenomena such as defects and interfaces. In this paper, biaxiality is given by a common mathematical definition

\[
B(x) = 1 - 6 \frac{(\text{tr}(Q(x)^3))^2}{(\text{tr}(Q(x)^2))^3}.
\]

This definition requires the biaxiality \( B(x) \) within the interval \([0, 1]\). If the \( Q \)-tensor is uniaxial, \( B(x) \) will be zero; if the \( Q \)-tensor shows strong biaxiality, \( B(x) \) will tend to one.

Other notations in the energy functional (1.2) gives: the scalar \( c_0 \) is the average density, and thermodynamic beta \( \beta = \frac{1}{k_B T} \). The 14 dimensionless coefficients \( A_i, G_i, \) and \( H_i \) are determined in terms of the microscopic molecule’s interaction potential, and are functions of temperature. We can infer their approximate interval by assuming the interaction potential to be the volume exclusion potential of rigid rod-like molecules \([1]\). To ensure the energy to be lower-bounded, it is necessary that \( H_1 \) and \( H_2 + \frac{2}{3}H_3 + \frac{4}{3}H_4 \) be positive. Otherwise, assuming the order parameters to be a series of highly oscillating functions, it is easy to show that the energy functional tends to negative infinity.

### 2.2. Numerical Methods

Consider the one-dimensional \( Q \)-tensor model, which states that the other two dimensions are considered homogeneous. Please note here that the one-dimensional case is significant and sufficiently representative, since all the four phases listed in the previous subsection enjoy periodicity in one dimension. For periodic boundary conditions, the spectral method is efficient and accurate enough to compute the energy functional, by representing the order parameters with a few Fourier modes. As another method, we can discretize the order parameters in nodal space and use finite difference method to calculate the derivatives.
Consider the reduced energy functional on the interval \([0, h]\), which takes the form (2.7)
\[
\beta F_h[c, Q] = c_0 \int_0^h c(x)(\ln c(x) + B_Q : Q - \ln Z(x))dx
\]
\[
+ \frac{c_3^2}{2} \left\{ \int_0^h \left[ A_1 c^2 - A_2 |cQ_{ij}|^2 - A_3 |cQ_{ijkl}|^2 \right] dx
+ \int_0^h \left[ -G_1 \frac{d}{dx}|c|^2 + G_2 \frac{d}{dx}(cQ_{ij})|^2 + G_3 \left( \frac{d}{dx}(cQ_{1k}) \right)^2 - G_4 \frac{d}{dx}(cQ_{11}) \frac{d}{dx}(c)
+ G_5 \left( \frac{d}{dx}(cQ_{ijkl}) \right)^2 + G_6 \left( \frac{d}{dx}(cQ_{1k1l}) \right)^2 + G_7 \frac{d}{dx}(cQ_{11kl}) \frac{d}{dx}(cQ_{kl}) \right] dx
+ \int_0^h \left[ H_5 \left( \frac{d^2}{dx^2}(c) \right)^2 + H_2 \left( \frac{d^2}{dx^2}(cQ_{pq}) \right)^2 + H_3 \left( \frac{d^2}{dx^2}(cQ_{11}) \right)^2 + H_4 \left( \frac{d^2}{dx^2}(cQ_{1p}) \right)^2 \right] dx \right\}
\]

For given \(x \in [0, h]\), \(Q(x)\) can be represented by five independent scalar variables. The Bingham assumption implies that \(B_Q, Q, \) and \(Q_4\) are mutually determined and can be diagonalized simultaneously. In practice, we use \(\lambda\) and \(d\) to characterize the eigenvalues of \(B_Q\), and use Euler angles \(\theta, \beta, \) and \(\gamma\) to characterize the orthogonal transformation matrix \(T\). The first angle \(\theta\) represents the angle between the principle eigenvector of \(Q\) and the x-axis. Let \(\hat{B}, \hat{Q}\), and \(\hat{Q}_4\) be the diagonal forms of the matrices, respectively, \(B_Q, Q, \) and \(Q_4\). Thus, \(Q\) and \(Q_4\) can be represented as
\[
Q_{mn} = \hat{Q}_{ij} T_{im} T_{jn},
Q_{4mnop} = \hat{Q}_{4ijkl} T_{im} T_{jn} T_{k0} T_{lp},
\]

where
\[
\hat{Q}_{ij} = \frac{1}{Z} \int_{S^2} (m_i m_j - \frac{1}{3} \delta_{ij}) \exp(\hat{B} : mm)dm,
\hat{Q}_{4ijkl} = \frac{1}{Z} \int_{S^2} \left( m_i m_j m_k m_l - \frac{1}{7} (m_i m_j \delta_{kl})_{sym} + \frac{1}{36} (\delta_{ij} \delta_{kl})_{sym} \right) \exp(\hat{B} : mm)dm,
\hat{B} = \text{diag}(-\frac{1}{2} \lambda + d, -\frac{1}{2} \lambda - d),
Z = \int_{S^2} \exp(\hat{B} : mm)dm,
\]

(2.10) \(T = \begin{pmatrix}
\cos \theta & -\sin \theta \cos \gamma & \sin \theta \sin \gamma \\
\sin \theta \cos \beta & \cos \theta \cos \gamma - \sin \beta \sin \gamma & -\cos \theta \sin \beta \sin \gamma - \sin \beta \cos \gamma \\
\sin \theta \sin \beta & \cos \theta \sin \gamma + \cos \beta \sin \gamma & -\cos \theta \sin \beta \sin \gamma + \cos \beta \cos \gamma
\end{pmatrix}.
\)

In practice, the double integrals with respect to \(m \in S^2\) can be precomputed to reduce the computational costs.
One way to represent the order parameters is to expand them by Fourier modes (2.11)
\[ c(x) = 1 + \sum_{j=1}^{n} c_j^{(1)} \cos jkx + c_j^{(2)} \sin jkx, \quad \lambda(x) = \lambda_0 + \sum_{j=1}^{n} \lambda_j^{(1)} \cos jkx + \lambda_j^{(2)} \sin jkx, \]
\[ d(x) = d_0 + \sum_{j=1}^{n} d_j^{(1)} \cos jkx + d_j^{(2)} \sin jkx, \quad \theta(x) = \theta_0 + \sum_{j=1}^{n} \theta_j^{(1)} \cos jkx + \theta_j^{(2)} \sin jkx, \]
\[ \beta(x) = \beta_0 + \sum_{j=1}^{n} \beta_j^{(1)} \cos jkx + \beta_j^{(2)} \sin jkx, \quad \gamma(x) = \gamma_0 + \sum_{j=1}^{n} \gamma_j^{(1)} \cos jkx + \gamma_j^{(2)} \sin jkx, \]
where \( \lambda_0, d_0, \theta_0, \beta_0, \gamma_0, c_j^{(i)}, \lambda_j^{(i)}, d_j^{(i)}, \theta_j^{(i)}, \beta_j^{(i)}, \gamma_j^{(i)}, \) and \( h = 2\pi/k \) are the arguments of the objective functional in the phase transition problem. Here \( h \) is also an argument since we aim to minimize the density of free energy. The dimension of variables is \( 12n + 6 \). The derivatives of \( c \cdot Q \) and \( c \cdot Q_4 \) are calculated using Fast Fourier transform (FFT). In the following section, we use this method in computing the phase transition problem; empirically, \( n = 6 \) is enough to characterize the profiles of the order parameters.

As another way to represent the order parameters, we can discretize the interval \([0, h]\) with \( N \) nodes. The dimension of variables is \( 6N \). The derivatives of the order parameters are computed using finite difference method. In the following section, we use this method in computing the I-N interface problem, and \( N = 50 \) is accurate enough empirically.

The minimum of the energy functional can be found by standard method, for example, the BFGS method. The overall computational cost is as moderate as the cost of the Landau-de Gennes model. Both the two problems discussed in the following section converge in about 100 steps with absolute precision of \( 1 \times 10^{-5} \).

3. Results and Discussions

In paper [1] where the new Q-tensor model was first introduced, the coefficients \( A_i, G_i, \) and \( H_i \) were expressed in terms of the molecule’s shape factor \( \varepsilon = D/L \), under the assumption that the interaction is the volume exclusion potential of the rod-like molecules without attraction effects, with \( D \) the diameter of semi-sphere at two ends of the rod and \( L \) the length of the rod. If we take account of the attraction effects between molecules, these coefficients would be functions of temperature, and alter within a few order of magnitudes as the temperature changes [21]. In this section, to testify this model conveniently, we assume that these coefficients are independent. We set these coefficients near the values deduced under the volume exclusion assumption. Fix
\[ A_1 = 0.22409, \quad A_2 = 0.14728, \quad A_3 = 0.09663, \]
\[ G_1 = 0.00884, \quad G_2 = 0.00182, \quad G_3 = 0.00680, \]
\[ G_5 = 0.00016, \quad G_6 = 0.00174, \quad G_7 = 0.01181, \]
\[ H_1 = 0.00028, \quad H_2 = H_4 = 0. \]
These coefficients are derived in terms of microscopic shape factor \( \varepsilon = D/L = 0.1 \), with modification to \( H_1 \) which has been multiplied by 2 in order to ensure the lower boundedness, and \( H_2 \) and \( H_4 \) ignored since they are order of magnitude smaller. Two remaining coefficients \( G_4 \) and \( H_3 \) are not fixed. Empirically, they are more important to determine the phases of liquid crystals. We will set these two coefficients near \( G_4^{(0)} = 0.02374 \) and \( H_3^{(0)} = 0.00063 \) within an order of magnitude.
We consider the phase transition problem and the I-N interface problem. The phase transition problem is to find the most stable phase of liquid crystals given the average density, to find the characterizations of the various phases, and to study the transition of phases from one to another as the average density increases. In some suitable environments, I and N phases will coexist and take up different regions in the liquid crystal materials. The I-N interface problem is to investigate the interfacial region between the I and N phases. The mathematical formulation of these two problems will be given below. Density variations are essential in both problems. In the phase transition problem, the density variation serves to lower the second order elastic energy $F_{\text{elastic,2}}$, which renders the smectic phase stable. In the I-N interface problem, given the chemical potential and the grand potential density, the density at I and N phases are different, which renders a natural variation of density at the interface.

3.1. Phase Transitions. First, we consider the phase transition problem. We need solve the optimization problem

$$
\min_{c(x), G(x), h} \left\{ \frac{F_h}{h} \right\}, \quad \text{subject to} \quad \frac{1}{h} \int_0^h c(x)dx = 1.
$$

where $F_h$ is defined in equation (2.7). Since I and N phases are spatially homogeneous, and $S_A$ and $S_C$ phases are layered, we presume the solution to be periodic to reduce the computational costs. Spectral methods are used to calculate the free energy. The period $h$, which is also a variable that needs to be optimized, represents the layer thickness in smectic phases. Figure 2 illustrates the microscopic configuration of molecules of smectic phase. The following phase transitions are found given various sets of $G_1$ and $H_3$.

- $G_4 = G_4^{(0)} \times 3.9, H_3 = H_3^{(0)} \times 1.7.$
  
  $I \leftrightarrow \approx 45.2 \leftrightarrow N \leftrightarrow \approx 46.5 \leftrightarrow S_A \leftrightarrow \approx 50.3 \leftrightarrow S_C.$

- $G_4 = G_4^{(0)}, H_3 = H_3^{(0)}.$
  
  $I \leftrightarrow \approx 45.2 \leftrightarrow N \leftrightarrow \approx 50.6 \leftrightarrow S_A.$

- $G_4 = G_4^{(0)} \times 2, H_3 = H_3^{(0)} \times 6.$
  
  $I \leftrightarrow \approx 45.2 \leftrightarrow N \leftrightarrow \approx 50.6 \leftrightarrow S_C.$

The one-dimensional phase diagrams of I-N-S$_A$-S$_C$ transitions are presented using $F_{\text{min}} - c_0$ coordinates in Figure 3 and using $\theta - c_0$ coordinates in Figure 4.

As the average density $c_0$ increases, the system exhibits I, N, S$_A$, and S$_C$ phases sequentially. As shown in Figure 3, I-N and N-S$_A$ phase transitions are first order. I and N phases coexist as $c_0$ is within 45.2 $\pm$ 0.2; N and S$_A$ phases coexist as $c_0$ is within 46.5 $\pm$ 0.2. Free energies of both phases in these regions are local minimum, and they cross at the critical average density. From the physical point of view, the average density $c_0 = 45.2$ states that averagely there are 45.2 liquid crystal molecules with shape factor $\varepsilon = 0.1$ in a cube with volume $L^3$, and the molecules take up roughly 35 percent the volume of the entire space.

As shown in Figure 4, the S$_A$-S$_C$ phase transition is second order. After $c_0$ exceeds 50.3, the tilt angle of director increases from 0 to 5 degrees continuously. In one layer, the centers of molecules align in order, but not exactly in a plane, which renders the layer thickness larger than the length of molecules. The optimized layer thickness for both S$_A$ and S$_C$ phases is roughly 1.81$L$, i.e. 1.81 times the length of molecule, and it varies slightly within the order $0.005L$ as the average density increases. The layer thickness is quite sensitive to coefficients $G_i$ and $H_i$. If $H_3$ decreases from $H_3^{(0)} \times 3.9$ to $H_3^{(0)} \times 3.6$, the layer thickness will decrease from...
Figure 2. Illustrations for smectic phases. The tilt angle $\theta$ and the layer thickness $h$ are their important characterizations.

Figure 3. An one-dimensional phase diagram with four phases presented. The small regions between the dashed line represents the bistable areas. The remaining coefficients are $G_4 = G_4^{(0)} \times 3.9$ and $H_3 = H_3^{(0)} \times 1.7$.

Figure 4. The tilt angle versus average density. The tilt angle of smectic phase increases continuously after the average density exceeds 50.3. The $S_A-S_C$ transition is second order.

1.81$L$ to 1.74$L$. This relation between the coefficients and the layer thickness is explained using the deduced vector model, with its details discussed in Section 4.3.

Figure 5 shows the components of the free energy as the average density increases, which exhibits the order of transitions more clearly. The definitions of these components are given as (1.3), (1.4), and (1.5), and the entropy is the first part of the bulk energy $F_{\text{bulk}}$. The entropy decreases at the beginning. It has positive leaps at $I-N$ and $N-S_A$ critical points, and finally increases gradually. The bulk energy increases gradually with a leap at $N-S_A$ critical point. The elastic energy $F_{\text{elastic},2}$ and $F_{\text{elastic},4}$ are zero in $I$ and $N$ phases. The second order elastic energy $F_{\text{elastic},2}$ drops and continuously decreases after reaching $N-S_A$ critical point, while the fourth order elastic energy $F_{\text{elastic},4}$ soars up and continuously increases after $N-S_A$ point.
with a smaller magnitude than $F_{\text{elastic},2}$. All these components at $S_A$-$S_C$ critical point are continuous. The total energy increases steadily without significant leaps.

The second order elastic energy $F_{\text{elastic},2}$ contains two parts: derivative terms of density $c(x)$ and Oseen-Frank energy which contains the derivative terms of director $\mathbf{n}$. This decomposition is further discussed in Section 4.3. In smectic phases, Oseen-Frank energy is zero for there is no distortion of the director. The derivative terms of density $c(x)$ in $F_{\text{elastic},2}$ with negative coefficients are the reason for the density-varied phases to have a lower free energy. The second order derivative terms of density in $F_{\text{elastic},4}$ with positive coefficients are the reason for the total energy to be stable.

According to liquid crystal experiments, the I-N transition is first order. Nevertheless, the N-S$_A$ transition could be either first or second order, depending on the liquid crystal materials. The study of 8CB-10CB (where CB represents cyanobiphenyl) mixtures [25] confirmed the prediction made by Halperin et al. that fluctuation lead the second order N-S$_A$ transition to a weak first order one. The study of 4-n-alkoxybenzylidene-4'-phenylazoaniline [26] drew the conclusion that decreasing length of the alkyl end chain drives the first order N-S$_A$ transition to be second order. According to Monte-Carlo simulation based on molecular theory, assuming the molecule’s shape to be spherocylindrical, McGrother et al. [27], Bolhuis et al. [28], and Lolson et al. [29] showed that the N-S$_A$ transition is a first order one, but it tends to be continuous as the shape factor $L/D \to \infty$.

For S$_A$-S$_C$ transition, the study of 4-n-pentyl-phenylthiol-4'-n-octyloxybenzoate [30] confirmed that it is a second order transition, and the tilt angle increases from 0 degree to 20 degree continuously. In the meantime, the study of 4- (trans-4'-n-Alkylcyclohexyl) Benzoates [31] showed that when molecules forming dimers, the layer thickness of smectic phase is larger than the length of molecules but within $2L$.

The representative use of the order parameters and the biaxiality characterizing the smectic phase is shown in Figure 6. The Q-tensor can be denoted as $Q = s(\mathbf{n}\mathbf{n} - \frac{1}{3}I) + b(\mathbf{n}'\mathbf{n}' - \frac{1}{3}I)$, where $\mathbf{n}'$ is perpendicular to the director $\mathbf{n}$; $s(x)$ is the principle nematic order parameter, and $b(x)$ characterizes biaxial effects. The biaxiality $B(x)$ is defined as equation (2.6). In smectic phase, the relative density $c(x)$ and order parameter $s(x)$ fluctuate within one layer. The

**Figure 5.** The components of free energy and the total free energy.
maximum point of \( c(x) \) and \( s(x) \) are identical, where the centers of molecules concentrate and the molecules are more likely to point to the preferred direction. In \( S_A \) phase, the biaxiality \( B(x) \) vanishes, which supports the uniaxial approximation often adopted in modeling \( S_A \). In \( S_C \) phase, \( B(x) \) vanishes when the relative density \( c(x) \) is large. At the region between two layers where the relative density \( c(x) \) is small, the biaxiality \( B(x) \) is large. This phenomena can be explained intuitively: the group of molecules at the vicinity region between two layers have more freedom of orientation and are less symmetric than the group of molecules at the center of one layer.

The I-N-S\textsubscript{A} transitions and I-N-S\textsubscript{C} transitions are presented given other sets of coefficients. The one-dimensional phase diagrams are presented using \( F_{\text{min}} - c_0 \) coordinates in Figure 7 characterizing I-N-S\textsubscript{A} transitions, and in Figure 8 characterizing I-N-S\textsubscript{C} transitions. In \( S_A \) phase, the layer thickness is roughly 1.52\( L \). In \( S_C \) phase, the layer thickness is roughly 1.92\( L \), and the tilt angle is 23 degree. The N-S\textsubscript{C} transition is also first order.

3.2. I-N Interface. Consider the liquid crystals in the entire space. I and N are at two opposite ends of the space, sharing the same chemical potential and the same grand potential density. Assume the I-N interface to be a plane, which states that the order parameters

**Figure 6.** The characterizations of smectic phase, with \( x \)-axis to be the relative position in one layer. (a) The relative density \( c \). (b) Denotes Q-tensor as \( Q = s(nn - \frac{1}{3}I) + b(n'n' - \frac{1}{3}I) \), where \( n' \) is perpendicular to \( n \); \( s \) is the principle nematic order parameter, and \( b \) characterizes biaxial effects. (c) The biaxiality is defined as \( B(x) = 1 - \frac{6}{(tr(Q^2))} \).
Figure 7. An one-dimensional phase diagram of I-N-SA transitions. The remaining coefficients are $G_4 = G_4^{(0)}$ and $H_3 = H_3^{(0)}$.

Figure 8. An one-dimensional phase diagram of I-N-SC transitions. The remaining coefficients are $G_4 = G_4^{(0)} \times 2$ and $H_3 = H_3^{(0)} \times 6$.

Figure 9. Snapshots of configurations in the immediate vicinity of the I-N interface, for the three different anchoring conditions. The configuration with tilt angle $\theta = \frac{\pi}{2}$ is the most stable.

vary in one dimension and are homogeneous in the other two dimensions. Given the angle $\theta$ between the interface normal and the director of nematic phase, the configuration of the interface is determined. The microscopic configuration of molecules of I-N interface is illustrated as Figure 9.
Consider the region $\Omega = [-h, h]$. We need to minimize the grand potential (3.3)

$$
\beta \Xi[c, Q] = \int_{-h}^{h} c(x)(\ln c(x) + B_Q : Q - \ln Z(x))dx
$$

$$
+ \frac{1}{2} \left\{ \int_{-h}^{h} \left[ A_1 c^2 - A_2 |cQ_{ij}|^2 - A_3 |cQ_{ijkl}|^2 \right] dx 
\right. 
+ \int_{-h}^{h} \left[ -G_1 \frac{d}{dx} c|^2 + G_2 \frac{d}{dx} (c Q_{ij})|^2 + G_3 (\frac{d}{dx} (c Q_{1k})|^2 - G_4 \frac{d}{dx} (c Q_{1i}) \frac{d}{dx} (c) 
\right. 
+ G_5 \frac{d}{dx} (c Q_{ijkl})|^2 + G_6 (\frac{d}{dx} (c Q_{1klm}))|^2 + G_7 \frac{d}{dx} (c Q_{1kl}) \frac{d}{dx} (c Q_{kl}) \right\} dx 
+ \int_{-h}^{h} \left[ H_5 (\frac{d^2}{dx^2} (c))^2 + H_2 (\frac{d^2}{dx^2} (c Q_{pq}))|^2 + H_3 (\frac{d^2}{dx^2} (c Q_{1i})|^2 + H_4 (\frac{d^2}{dx^2} (c Q_{1p})|^2 \right\} dx

- \mu \int_{-h}^{h} c(x)dx,
$$

under proper boundary conditions. The chemical potential is chosen to meet the coexistence condition, $\mu = 3.407$. The order parameters for stable isotropic phase are $c = 43.57$ and $Q = 0$; the order parameters for stable nematic phase are $c = 48.30$ and $Q = s (nn - \frac{1}{3} I)$ with $s = 0.667$. We anchor the angle $\theta$ between the director and the interface normal to be constant all over the space, and perform simulations with a series of $\theta$. Thus, the boundary conditions are

$$
\begin{align*}
  c_{x=-h} &= 43.57, & c_{x=h} &= 48.30, \\
  \lambda_{x=-h} &= 0, & \lambda_{x=h} &= 3.522, \\
  d_{x=-h} &= 0, & d_{x=h} &= 0, \\
  \beta_{x=-h} &= 0, & \beta_{x=h} &= 0, \\
  \gamma_{x=-h} &= 0, & \gamma_{x=h} &= 0, \\
  \theta &= \theta_0,
\end{align*}
$$

where $\theta_0 = 0, \pi/8, \pi/4, 3\pi/8, \pi/2$. The length $h$ is chosen large enough, which is $7L$ in our computations. The coefficients $A_i$, $G_i$, and $H_i$ are given in equations (3.1) with $G_1 = G_4^{(0)} = 0.02374$, $H_3 = H_3^{(0)} = 0.00063$. Note that the coefficients $G_i$ here are all deduced by assuming the interaction potential to be the volume exclusion potential of rigid rod-like molecules. The results are summarized as follows.

Figure 10 (a) shows the profile of density $c(x)$. The density profile for tilt angle $\theta$ greater than $\frac{\pi}{4}$ is a monotonically increasing function; nevertheless, for tilt angle smaller than $\frac{\pi}{4}$, it displays a shallow dip near the isotropic side of the interface, and a small oscillation near the nematic side of the interface. The shallow dip near isotropic side was captured by Chen [21] in numerical simulation of Onsager’s molecular theory, in which it was explained by the competition of the entropy and the excluded-volume interaction. The oscillating behavior was noticed by Allen [22] in Monte Carlo simulations; however, in Monte Carlo simulations, the oscillating behavior emerged for all cases of the tilt angle, and was explained as boundary effects. In the new Q-tensor model, the oscillating behavior can be explained by the negative coefficients of the derivative terms of density $c(x)$: with oscillation, the elastic energy $F_{\text{elastic},2}$ can be lower. On the contrary, the fourth order elastic energy $F_{\text{elastic},4}$ serves to stabilize the energy at interface. The interfacial width of the density is roughly $3L$. It is at its narrowest at $\theta = \frac{\pi}{4}$.
Figure 10. The profiles of the order parameters: a) The density $c(x)$; b) The principle nematic order parameter $s(x)$; c) The biaxial effect $b(x)$. The definitions of $s(x)$ and $b(x)$ are given by denoting $Q$-tensor as $Q = s(nn - \frac{1}{3}I) + b(n'n' - \frac{1}{3}I)$, where $n'$ is perpendicular to $n$. The centers of these profiles are shifted by 0.5 in order to clearly display them for different tilt angles.

Figure 10 (b) shows the principle nematic order parameter $s(x)$. Unlike the density profile, the profile of $s(x)$ is always a monotonic function. The centers of profiles for $c(x)$ and $s(x)$ are different. There is a “phase shift” for $s(x)$ to isotropic side with roughly $0.5L$ compared to the density profile. Unlike the density profile, the interfacial width of $s(x)$ remains identical at $3L$ as tilt angle $\theta$ increases.

The interfacial width is not sensitive to the coefficients $H_i$. No matter how we alter the coefficients $H_i$ with an order of magnitude, the interfacial width is always roughly $3L$; nevertheless, as $H_i$ increases, the oscillation near the nematic side is mitigated but still exists. Since the coefficients $A_i$ and $G_i$ are all mechanistically determined under the volume exclusion assumption, the calculated interfacial width is physically reliable. Liquid crystal experiments confirmed that the interfacial width is of order $L$.

Figure 10 (c) shows the biaxiality parameter $b(x)$. The biaxial effect only appears significantly in the interfacial region. It is opposite between the isotropic side and the nematic side, and is stronger at the isotropic side. The biaxiality is the strongest for $\theta = \frac{\pi}{2}$. There is no biaxiality for the $\theta = 0$ case because of the rotational symmetry. In general, the biaxial effect for $I$-$N$ interface is quite weak.

Figure 11 shows the dependence of the isotropic-nematic surface energy on the angle $\theta$. The surface energy is defined as the difference between the grand potential of the interface
Figure 11. The surface energy density versus the tilt angle $\theta$

and that of the isotropic phase. The surface energy is a monotonic function of the tilt angle and has a minimum at $\theta = \frac{\pi}{2}$. Therefore, the interface prefers to have a tilt angle of $\frac{\pi}{2}$, which is the configuration as Figure 9 (c). In another word, if we do not assume the tilt angle $\theta$ constant, but just anchor it at the boundary, it would tend to $\frac{\pi}{2}$ at the interface, which was the setup and situation in the study by Monte Carlo simulations [22].

In comparison with the previous studies of I-N interface problem investigated using Onsager’s molecular theory and Monte Carlo simulations, the study using the new Q-tensor model shares similar results. Since the dimension of order parameters of the new Q-tensor model is lower, it is much efficient in computations.

4. Comparison with Classical Models

In this section, we show the effectiveness of the new Q-tensor model by comparing it with classical models for liquid crystals in various scales.

4.1. Generalized Landau-de Gennes Models. De Gennes pioneered the Q-tensor, which provides information on both the preferred molecular orientation and the degree of orientational order, to describe nematics phases [5]. Later on, by exploiting an analogy between smectic liquid crystals and superconductors, de Gennes again proposed an independent, complex order parameter that allows for the description of nematic-smectic phase transitions [35]. Successive models were presented to couple the nematic order tensor with the complex smectic order parameter, such as the work of Mukherjee [18], in which the energy functional density contained the first and the second order derivative terms of order parameters, and the work of Biscari et al. [19], in which the energy functional contained only the first order derivative terms.

Landau-de Gennes model is famous for its tractability in mathematical analysis and computations. However, these generalized Landau-de Gennes models were proposed phenomenologically, with an unnatural coupling of complex smectic order parameter and the Q-tensor.

On the contrary, the new Q-tensor model is established on sound physical theories. The entropy term is in the thermotropic form defined by John Ball [14], but no longer the polynomial as in Landau-de Gennes model. Such an entropy term ensures the boundedness of the eigenvalues of Q-tensor, preserving the physical meaning of Q-tensor. If we assume $c(x)$
is constant, $F_{\text{bulk}} + F_{\text{elastic,2}}$ would degenerate to the energy functional of Landau-de Gennes model, which is able to characterize stable nematic phase \[14\].

Meanwhile, the introduction of $Q_4(x)$ is necessary, otherwise the elastic constant $K_1$ is equal to $K_3$, which is not always true. Moreover, if we need to model density variation phenomena in which $c(x)$ is not constant, $F_{\text{bulk}} + F_{\text{elastic,2}}$ would not be a lower-bounded energy functional, for the reason that the derivative terms of $c(x)$ in $F_{\text{elastic,2}}$ is negative. It is necessary to consider at least the second order derivative terms $F_{\text{elastic,4}}$ to stabilize the energy functional.

### 4.2. Generalized McMillan Models

Based on Onsager’s molecular theory, assuming a two particle interaction potential and introducing an orientational order parameter, Maier and Saupe proposed a molecular field theory to characterize I-N transition \[32\]. Adding a positional order parameter, McMillan extended the theory to include $S_A$ phase \[20\]. Successive improvements were made to account for more complicated potentials, such as the work of Mederos et al. \[33\] which incorporated the hard core interaction, and the work of Gorkunov et al. \[34\] which considered the fragments’ attraction and repulsion interaction.

Most recently, Pajak and Osipov \[16\] proposed a generalization of McMillan model including I-N-S_A-S_C phases. In smectic phase, let $\mathbf{k}$ be the unit layer normal, $\mathbf{l}$ be the unit normal of the tilt plane, and $\mathbf{c}$ be their unit orthogonal complement. The layer thickness is presumed to be $q$. The order parameters of the generalized McMillan model are $\tilde{\psi}$, $\tilde{Q}_{ij}$, and $\tilde{\Sigma}_{ij}$, defined in terms of the probability density function of molecules $\rho(\mathbf{x}, \mathbf{m})$ as

\[
\tilde{\psi} = \frac{1}{|\Omega|} \int_{\Omega} \int_{\mathbb{S}^2} \rho(\mathbf{x}, \mathbf{m}) \cos(q\mathbf{k} \cdot \mathbf{x}) d\mathbf{m} d\mathbf{x},
\]

\[
\tilde{Q}_{ij} = \frac{1}{|\Omega|} \int_{\Omega} \int_{\mathbb{S}^2} (\mathbf{m} \cdot \frac{1}{3} \mathbf{l}) \rho(\mathbf{x}, \mathbf{m}) d\mathbf{m} d\mathbf{x},
\]

\[
\tilde{\Sigma}_{ij} = \frac{1}{|\Omega|} \int_{\Omega} \int_{\mathbb{S}^2} (\mathbf{m} \cdot \frac{1}{3} \mathbf{l}) \rho(\mathbf{x}, \mathbf{m}) \cos(q\mathbf{k} \cdot \mathbf{x}) d\mathbf{m} d\mathbf{x}.
\]

In the $(\mathbf{k}, \mathbf{c}, \mathbf{l})$ framework, these order parameters have decomposition

\[
\tilde{Q}_{ij} = S(k_i k_j - \frac{\delta_{ij}}{3}) + \frac{1}{2} \rho_c (c_i c_j - l_i l_j) + \frac{1}{2} V(k_i c_j + c_i k_j),
\]

\[
\tilde{\Sigma}_{ij} = \Gamma(k_i k_j - \frac{\delta_{ij}}{3}) + \frac{1}{2} \Pi (c_i c_j - l_i l_j) + \frac{1}{2} \Lambda (k_i c_j + c_i k_j).
\]

The free energy of the generalized McMillan model can be expressed as

\[ F = -\frac{1}{2} c_0 [u(S^2 + \frac{3}{4} P^2 + \frac{3}{4} V^2) + \omega_0 \tilde{\psi}^2 + 2\omega_1 \tilde{\psi} \Gamma + \omega_2 \Gamma^2 + \omega_3 \Pi^2 + \omega_4 \Lambda^2] - k_B T c_0 \ln Z. \]

It is the summation of entropy term and quadratic terms of $\tilde{\psi}$, $S$, $P$, $V$, $\Gamma$, $\Pi$, and $\Lambda$. Here, $c_0$ is the average density, $u$ is the Maier-Saupe constant which determines the I-N transition temperature, $\omega_i$ are constants, and $Z$ is the partition function which can be represented by the order parameters.

The generalized McMillan model can be directly derived from the new Q-tensor model if we assume

\[ c(x) = 1 + \tilde{\psi} \cos(q \mathbf{k} \cdot \mathbf{x}), \]

\[ c(x) Q_{ij}(x) = \tilde{Q}_{ij} + \tilde{\Sigma}_{ij} \cos(q \mathbf{k} \cdot \mathbf{x}). \]

where $c(x)$ and $Q(x)$ are the order parameters of the new Q-tensor model, and $\tilde{\psi}$, $\tilde{Q}$, and $\tilde{\Sigma}$ are the order parameters of the generalized McMillan model. Intuitively, the order parameters
of the generalized McMillan model are the Fourier coefficients of the order parameters of the new Q-tensor model, and the generalized McMillan model can be interpreted as the one mode approximation of the new Q-tensor model.

The generalized McMillan models are mechanistic models based on self-consistent field theory. The coefficients are linked with microscopic quantities, i.e. the parameters in interaction potentials. Another advantage of the generalized McMillan model is its elegance and simplicity, where the energy functional can be expressed by several scaler parameters.

However, the order parameters of the generalized McMillan model are averaged over the entire space, failing to characterize some small-scale phenomena where the domain has confined geometry and spatial variance, for example, phase transitions in confined geometries, wetting phenomena, surface-induced bulk alignment, defects and disclinations, and interfaces.

4.3. Chen-Lubensky Model. Chen-Lubensky model \cite{4} is a vector model based on the Landau-Ginzburg theory, characterizing the $N$-$S_A$-$S_C$ transitions. The order parameters are the relative density $c(x)$ and the director $n(x)$. The corresponding free energy consists of two parts,

\begin{equation}
F_{CL} = F_c + F_{OF},
\end{equation}

where $F_c$ contains terms up to second order derivatives of the density $c(x)$,

\begin{equation}
F_c = \frac{1}{2\beta} \int_{\Omega} \left( ac^2 + D_1 [(n \cdot \nabla c)^2 - C_1(n \cdot \nabla c)^2 + \frac{C_2^2}{4D_1}c^2 
+ C_2(\delta_{ij} - n_i n_j)\nabla i c \nabla j c + D_2[(\delta_{ij} - n_i n_j)\nabla i c \nabla j c]^2 \right) dx,
\end{equation}

and $F_{OF}$ is the Oseen-Frank energy for distortions in terms of the nematic director $n(x)$,

\begin{equation}
F_{OF} = \frac{1}{2} \int_\Omega \left( K_1(\nabla \cdot n)^2 + K_2[\nabla \times (\nabla \times n)]^2 + K_3|\nabla \times (\nabla \times n)|^2 \right) dx.
\end{equation}

The coefficients $C_1$, $C_2$, $D_1$, $D_2$, $a$, and $K_i$ are determined through experiments. These coefficients are intuitive: $K_i$ are elastic constants; $C_1$ and $D_1$ determine the horizontal period; $C_2$ and $D_2$ determine the perpendicular period.

In paper \cite{11} where the new Q-tensor model was first introduced, assuming the Q-tensor uniaxial and $c(x)$ and $S_2(x)$ constant, the Oseen-Frank energy $F_{OF}$ was deduced and the elastic constants $K_1$, $K_2$, $K_3$ were expressed analytically. In the following paragraphs, making alternative assumptions that Q-tensor is uniaxial and constant, we will deduce a vector model similar to the free energy $F_c$.

Assume Q-tensor is uniaxial and spatially homogeneous,

\begin{equation}
Q_{ij} = S_2 \left( n_i n_j - \frac{1}{3}\delta_{ij} \right),
\end{equation}

\begin{equation}
Q_{ijkl} = S_4 \left( n_i n_j n_k n_l - \frac{1}{3}(n_i n_j \delta_{kl})_{sym} + \frac{1}{35}(\delta_{ij} \delta_{kl})_{sym} \right),
\end{equation}

where $S_2$, $S_4$, and $n$ are constant.

Under this assumption, the energy functional can be formulated as

\begin{equation}
\beta F[c(x), S_2, n] = c_0 \int_\Omega c \ln(c) dx + \frac{C_2^2}{2} \int_\Omega \left( \hat{A}_1 c^2 - \hat{G}_1|\nabla c|^2 - \hat{G}_2(n \cdot \nabla c)^2 + \hat{H}_1(\nabla^2 c : nn)^2
+ \hat{H}_2(\nabla^2 c : nn) \Delta c + \hat{H}_3(\Delta c)^2 + \hat{H}_4|n \cdot \nabla^2 c|^2 + \hat{H}_5|\nabla \cdot (\nabla^2 c)|^2 \right) dx,
\end{equation}
where $\hat{A}_i$, $\hat{G}_i$, and $\hat{H}_i$ are functions of $A_i$, $G_i$, $H_i$, $S_2$, and $S_4$, linear with respect to $A_i$, $G_i$, $H_i$, and quadratic with respect to $S_2$ and $S_4$. The expressions of $\hat{A}_i$, $\hat{G}_i$, $\hat{H}_i$ in terms of $A_i$, $G_i$, $H_i$, $S_2$, $S_4$ are listed in the appendix.

The deduced vector model is able to characterize $\mathbf{I-N-S_A-S_C}$ phase transitions. As $c_0$ is small, the entropy terms dominate, and the system exhibits isotropic phases. As $c_0$ increases, the interaction terms dominate, and the system transits to nematic and smectic phases.

Two quantities are important in smectic phases: layer thickness and tilt angle. To derive these quantities, assuming a given $S_2$, we plug a trial function $c(x) = 1 + c_1 \cos(qk \cdot x)$ into the energy functional, where $|k| = 1$, $k \cdot n = \cos \theta$, and $|c_1| < 1$. The free energy becomes

$$
\beta F(q^2, \cos^2 \theta, c_1) = c_0 \int_\Omega c \ln(c) d\mathbf{x} + \frac{c_0^2}{2} \int_\Omega \left\{ \hat{A}_1 c^2 + c_1^2 \cos^2(qk \cdot x) \left[ -(\hat{G}_1 \cos^2 \theta + \hat{G}_2)q^2 + (\hat{H}_1 \cos^4 \theta + \hat{H}_2 \cos^2 \theta + \hat{H}_3 + \hat{H}_4 \cos^2 \theta + \hat{H}_5)q^4 \right] \right\} d\mathbf{x},
$$

where $F$ is a quadratic function of $q^2$ and $\cos^2 \theta$. Minimizing the free energy over $q$, $\cos \theta$, and $c_1$, we obtain the minimizer $\hat{q}$, $\hat{\theta}$, and $\hat{c}_1$, with relations

$$
\hat{q}^2 = \frac{\hat{G}_1 + \hat{G}_2 \cos^2 \hat{\theta}}{2(\hat{H}_1 \cos^4 \hat{\theta} + \hat{H}_2 \cos^2 \hat{\theta} + \hat{H}_3 + \hat{H}_4 \cos^2 \hat{\theta} + \hat{H}_5)},
$$

$$
\cos^2 \hat{\theta} = 1 - \frac{\hat{q}^2(2\hat{H}_1 + \hat{H}_2 + \hat{H}_4) - \hat{G}_2}{2\hat{q}^2 \hat{H}_1}.
$$

These two equations can be solved iteratively, and $\hat{c}_1$ is easy to compute but cannot be expressed explicitly. The system will exhibit

- **$S_A$** phase, if $\hat{q}^2 > 0$, $\cos^2 \hat{\theta} \geq 1$, and $\hat{c}_1 \neq 0$. Let $\hat{q}_1 = (\hat{G}_1 + \hat{G}_2)/[2(\hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \hat{H}_4 + \hat{H}_5)]$. The layer thickness is $\hat{h} = L/\hat{q}_1$.

- **$S_C$** phase, if $\hat{q}^2 > 0$, $0 < \cos^2 \hat{\theta} < 1$, and $\hat{c}_1 \neq 0$. The layer thickness is $\hat{h} = L/\hat{q}$, and the tilt angle is $\hat{\theta}$.

- no smectic phase, otherwise.

The analytical derivation above can explain the relations between the coefficients $A_i$, $G_i$, $H_i$, and the tilt angle and layer thickness. It can also help to set the coefficients in the new Q-tensor model.

In comparison with the deduced vector model, Chen-Lubensky model lacks entropy terms which leads to its failure in characterizing isotropic phase. In Chen-Lubensky model, the Oseen-Frank energy and the derivative terms of $c(x)$ are added up directly. On the contrary, in the new Q-tensor model, the Oseen-Frank energy and the derivative terms of $c(x)$ are deduced based on different assumptions as discussed previously. If no assumptions are made, there will be cross terms incorporating the gradient of $\mathbf{n}$ and the gradient of $c(x)$. Furthermore, there are two extra terms in the deduced vector model, $\hat{H}_4|n \cdot \nabla^2 c|^2$ and $\hat{H}_5|\nabla^2 c|^2$. These two terms may lead to different phenomena in the subspace perpendicular to the director. Except for these differences, the deduced vector model agrees with Chen-Lubensky model.

5. **Summary**

In this work, we have investigated the new Q-tensor theory for liquid crystals focusing on density variations. The $\mathbf{I-N-S_A-S_C}$ phase transitions are discovered, and the $\mathbf{I-N}$ interface is investigated. We have also drawn comparison of the proposed model with the classical
models, and strong connections are found. We have shown that all these classical models can be derived from the new Q-tensor model for special cases.

In comparison, the high dimension of order parameter sets considerable obstacles in computations for the Onsager’s molecular model. The order parameter $n(x)$ adopted in Chen-Lubensky model fails to explain the degree of orientational order. Landau-de Gennes model is famous for its tractability in mathematical analysis and computations. However, generalizations of Q-tensor model are needed to include smectic phase. The generalized McMillan model is a good approximation of the Onsager’s theory, and efficient in computations. The weakness is in the ultimate energy functional which fails to reflect detailed physical understanding. On the other hand, the generalized Landau-de Gennes models were proposed phenomenologically.

On the contrary, the new Q-tensor model is established on sound physical theories. The introduction of relative density enables us to characterize smectic phases and the density variations in physical phenomena. The new Q-tensor model captures much of the essential physics while remaining mathematically tractable with efficient computations. Compared to all classical models, the new Q-tensor model is a good trade-off.

One notes that the new Q-tensor model studies the phase transitions as a function of the average density. It is difficult to consider the temperature-driven phase transitions, which needs to adopt the attraction interaction. This would be studied in future work. Defects are essential physical phenomena for liquid crystals. The effects of density variations in defects characterized by the new Q-tensor model would be studied in the future.

6. Appendix

The relations between $\hat{A}_i$, $\hat{G}_i$, $\hat{H}_i$ (the coefficients in vector model with energy functional (4.9)) and $A_i$, $G_i$, $H_i$ (the coefficients in the new Q-tensor model with energy functional (1.2)) are as follows. $S_2$ and $S_4$ are the principle nematic order parameters defined as (4.8).

$$
\begin{align*}
\hat{A}_1 &= A_1 + 2 \frac{3}{3} A_2 S_2^2 + 8 \frac{5}{35} A_3 S_4^2 \\
\hat{G}_1 &= G_1 - 2 \frac{3}{3} S_2^2 G_2 - 2 \frac{3}{9} S_2^2 G_3 - \frac{1}{3} S_2 G_4 - 8 \frac{35}{35} S_4^2 G_5 - \frac{12}{245} S_2^2 G_6 + \frac{4}{35} S_2 S_4 G_7 \\
\hat{G}_2 &= -\frac{1}{3} S_2^2 G_3 + S_2 G_4 - \frac{4}{49} S_2^2 G_6 - \frac{12}{35} S_2 S_4 G_7 \\
\hat{H}_1 &= S_2^2 H_3 \\
\hat{H}_2 &= -\frac{2}{3} S_2^2 H_3 \\
\hat{H}_3 &= \frac{1}{9} S_2^2 H_3 \\
\hat{H}_4 &= \frac{1}{3} S_2^2 H_4 \\
\hat{H}_5 &= H_1 + \frac{2}{3} S_2^2 H_2 + \frac{1}{9} S_2^2 H_4
\end{align*}

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