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Molecular field theory for nematic liquid crystal film with finite layers*

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The nematic liquid crystal film composed of n molecular layers is studied based upon a spatially anisotropic pair potential, which reproduces approximately the elastic free energy density. On condition that the system has perfect nematic order, as in the Lebwohl–Lasher model, the director in the film is isotropic. The effect of the temperature is investigated by means of molecular field theory. Some new results are obtained. Firstly, symmetry breaking takes place when taking account of the temperature, and the state with the director along the normal of the film has the lowest free energy. Secondly, the N–I phase transition temperature increases as an effect of finite sizes instead of decreasing as in the Lebwohl–Lasher model. Thirdly, the nematic order is induced in the layers near the surface in the isotropic phase.

Keywords: spatially anisotropic pair potential, perfect nematic order, effect of temperature, molecular field theory

PACC: 6130, 6470M

1. Introduction

Based upon anisotropic dispersive forces, Maier and Saupe[1,2] constructed a molecular field theory for nematic liquid crystals. Lebwohl and Lasher[3] made a Monte Carlo simulation on the model system consisting of cylindrically symmetric particles confined on the sites of a simple cubic lattice with interacting pair potential

$$V_{ij} = -\varepsilon_{ij} P_2(\hat{\Omega}_i \cdot \hat{\Omega}_j). \tag{1}$$

Here P_2 is the second-order Legendre polynomial, $\hat{\Omega}_i$ and $\hat{\Omega}_j$ are unit vectors along the symmetry axes of molecules i and j respectively. ε_{ij} is equal to ε if the particles i and j are nearest neighbours and is equal to zero otherwise. Based upon the symmetry of molecules and that of liquid crystal phases, a phenomenological description of the pair potential[4,5] can be given.

Recently, Gruhn and Hess[6] proposed an additive pairwise interaction on a simple cubic lattice. It reproduces approximately the elastic free energy density for the lattice, so that the parameters defining the pair potential can be expressed in terms of the elastic constants. Such a type of pair potential is spatially anisotropic; i.e. it depends not only on $\hat{\Omega}_i \cdot \hat{\Omega}_j$, but also on $\hat{\Omega}_i \cdot \hat{r}_{ij}$ and $\hat{\Omega}_j \cdot \hat{r}_{ij}$, where $\hat{r}_{ij}$ is a unit vector pointing from the centre of mass of molecule i to the centre of mass of molecule j. Then, a Monte Carlo simulation on para-azoxyanisole (PAA) in homogeneous nematic phase was made by Romano.[7] In addition, the bulk properties of the liquid crystals, their surfaces and their behaviour in restricted geometries (e.g. polymer-dispersed drops, thin films, mesogens in porous media) are of great interest. Romano has dealt with the above potential model on two-dimensional lattices.[8]

In this paper, we investigate nematic liquid crystal film composed of n molecular layers (n is finite). Firstly, on condition that the system has perfect nematic order, the director of the film is determined. Then, the order parameters are calculated in the molecular field approximation and the nematic–isotropic (N–I) phase transition is studied. Emphasis is put on the comparison between the present result and that of the Lebwohl–Lasher model.

2. Director in the film with perfect nematic order

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Consider $\hat{\Omega}_i$, i.e. the three-components of a unit vector associated with a three-dimensional simple cubic lattice. The pair potential suggested in Ref.[6] takes the form

$$\begin{aligned} V_{ij} =&\varepsilon\Big\{\lambda[P_2(a_i)+P_2(a_j)] \\ &+\mu\left(a_i a_j b_{ij}-\frac{1}{9}\right)+\nu P_2(b_{ij}) \\ &+\rho[P_2(a_i)+P_2(a_j)]P_2(b_{ij})\Big\}, \end{aligned} \tag{2a}$$

$$a_i=\hat{\Omega}_i\cdot\hat{r}_{ij},\quad a_j=\hat{\Omega}_j\cdot\hat{r}_{ij},\quad b_{ij}=\hat{\Omega}_i\cdot\hat{\Omega}_j. \tag{2b}$$

The potential parameters are related to the elastic constants K_i as follows:

$$\lambda=\frac{1}{3}\Lambda(2K_1-3K_2+K_3), \tag{3a}$$

$$\mu=3\Lambda(K_2-K_1), \tag{3b}$$

$$\nu=\frac{1}{3}\Lambda(K_1-3K_2-K_3), \tag{3c}$$

$$\rho=\frac{1}{3}\Lambda(K_1-K_3), \tag{3d}$$

where a factor Λ, with the dimension of length, is introduced. When $\lambda=\mu=\rho$=0 and ν=-1, the pair potential reduces to that given in the Lebwohl–Lasher model. Here and after we also call the pair potential given by Eq.(3) as model I. There is another mapping scheme from the elastic free energy density to the potential parameters (called model II).[9] However, it does not lead to a correct expression of the critical field when dealing with Freedericksz transition[10] and will not be discussed in this paper.

The surfaces of the film are assumed to be normal to the Z axis so as to remove the homogeneity in the Z direction but not in the XY plane. We label the molecular layers parallel to the surfaces by m, with m=1 and $m=n$ denoting the two surface layers. In the hypothesis of perfect nematic order, $\hat{\Omega}$ coincides with the director of the liquid crystal (the statistical average of $\hat{\Omega}$) and the total free energy coincides with the total intermolecular energy. This is equivalent to assuming that the temperature is T=0. In addition, we parametrize the director by the polar angle θ between the director and the surface normal Z:

$$\hat{\Omega}_i=(\sin\theta_i,0,\cos\theta_i), \tag{4}$$

and $\theta_i=\theta_m$, if molecule i is in the mth layer. For molecule i and its four horizontal neighbours in the same layer, the unit vectors $\hat{r}_{ij}$ are given by

$$\begin{aligned} &\hat{r}_{i1}=(-1,0,0),\quad \hat{r}_{i2}=(1,0,0), \\ &\hat{r}_{i3}=(0,-1,0),\quad \hat{r}_{i4}=(0,1,0). \end{aligned} \tag{5a}$$

Its two vertical neighbours in the adjacent layers are

$$\hat{r}_{i5}=(0,0,-1),\quad \hat{r}_{i6}=(0,0,1). \tag{5b}$$

The total interaction energy of one molecule in the mth layer can then be written as

$$\begin{aligned} F(m)=&\sum_{j=1}^{6}V_{ij} \\ =&2\varepsilon\Big\{(\lambda+\rho)(3\sin^2\theta_m-1) \\ &+\mu\left(\sin^2\theta_m-\frac{1}{9}\right)+\nu\Big\} \\ &+2\varepsilon\left(-\frac{1}{9}\mu+\nu-\lambda-\rho\right) \\ &+\varepsilon(1-\delta_{mn})\Big\{\left[\lambda+\frac{3}{2}\rho\cos^2(\theta_m-\theta_{m+1})-\frac{1}{2}\rho\right] \\ &\times\left[\frac{3}{2}(\cos^2\theta_m+\cos^2\theta_{m+1})-1\right] \\ &+\mu\left[\cos\theta_m\cos\theta_{m+1}\cos(\theta_m-\theta_{m+1})-\frac{1}{9}\right] \\ &+\nu\left[\frac{3}{2}\cos^2(\theta_m-\theta_{m+1})-\frac{1}{2}\right]\Big\} \\ &+\varepsilon(1-\delta_{m1})\Big\{\left[\lambda+\frac{3}{2}\rho\cos^2(\theta_m-\theta_{m-1})-\frac{1}{2}\rho\right] \\ &\times\left[\frac{3}{2}(\cos^2\theta_m+\cos^2\theta_{m-1})-1\right] \\ &+\mu\left[\cos\theta_m\cos\theta_{m-1}\cos(\theta_m-\theta_{m-1})-\frac{1}{9}\right] \\ &+\nu\left[\frac{3}{2}\cos^2(\theta_m-\theta_{m-1})-\frac{1}{2}\right]\Big\}. \end{aligned} \tag{6}$$

Here we have two factors $(1-\delta_{m1})$ and $(1-\delta_{mn})$, since the molecules in the first layer have no lower neighbouring molecules and the molecules in the nth layer have no upper neighbouring molecules. The total energy of the sample per unit area of the surface is obtained by summing up the single molecular energies (Eq.6) over all the m layers:

$$F=\frac{\sigma}{2}\sum_{m=1}^{n}F(m), \tag{7}$$

where σ is the molecular density per unit surface.

The total free energy given by Eq.(7) should be minimized with respect to all variables θ_m. It leads to the necessary condition

$$\frac{\partial F}{\partial\theta_m}=0. \tag{8}$$

Substituting Eq.(7) into Eq.(8) yields

$$\begin{aligned}
&\varepsilon(3\lambda+3\rho+\mu)\sin 2\theta_m-(1-\delta_{mn})\varepsilon\\
&\times\left\{\frac{3}{2}\rho\sin 2(\theta_m-\theta_{m+1})\right.\\
&\times\left[\frac{3}{2}(\cos^2\theta_m+\cos^2\theta_{m+1})-1\right]\\
&+\frac{3}{2}\left[\lambda+\frac{3}{2}\rho\cos^2(\theta_m-\theta_{m+1})-\frac{1}{2}\rho\right]\\
&\times\sin 2\theta_m+\mu\cos\theta_{m+1}\sin(2\theta_m-\theta_{m+1})\\
&\left.+\frac{3}{2}\nu\sin 2(\theta_m-\theta_{m+1})\right\}-(1-\delta_{m1})\varepsilon\\
&\times\left\{\frac{3}{2}\rho\sin 2(\theta_m-\theta_{m-1})\right.\\
&\times\left[\frac{3}{2}(\cos^2\theta_m+\cos^2\theta_{m-1})-1\right]\\
&+\frac{3}{2}\left[\lambda+\frac{3}{2}\rho\cos^2(\theta_m-\theta_{m-1})-\frac{1}{2}\rho\right]\\
&\times\sin 2\theta_m+\mu\cos\theta_{m-1}\sin(2\theta_m-\theta_{m-1})\\
&\left.+\frac{3}{2}\nu\sin 2(\theta_m-\theta_{m-1})\right\}=0,\\
&\qquad(m=1,2,\cdots,n).
\end{aligned}\tag{9}$$

One can demonstrate that

$$\theta_{m-1}=\theta_m=\theta_{m+1}=\theta \tag{10}$$

are the solutions of the $n-2$ equations for $m=2,3,\cdots,n-1$. For homogeneousness, the two equations for m=1 and $m=n$ reduce to

$$(3\lambda+3\rho+\mu)\sin 2\theta=0. \tag{11}$$

Substituting Eq.(10) into (7), we find that

$$\begin{aligned}
F=&\sigma\varepsilon\left[(n-2)\left(\frac{2}{3}\mu+3\nu\right)\right.\\
&+(3\lambda+3\rho+\mu)\sin^2\theta\\
&\left.+\left(5\nu+\frac{4}{9}\mu\right)-2(\lambda+\rho)\right].
\end{aligned}\tag{12}$$

Equation (3) gives $3\lambda+3\rho+\mu=0$, and the director in the film is isotropic, i.e. the same result as given in the Lebwohl–Lasher model.

3. Effect of finite temperature

From the viewpoint of molecular statistical theory, at nonzero temperatures the liquid crystal molecules have a distribution of orientations about the director in the nematic phase. The orientational singlet distribution function of molecules $g^{(m)}(\hat{\Omega})$ must be defined for each molecular layer. In the molecular field approximation,[11] the pseudo-potential can be written as

$$\begin{aligned}
V^{(m)}(\hat{\Omega}_i)=&(1-\delta_{m1})\int V(\hat{\Omega}_i,\hat{\Omega}_j)g^{(m-1)}(\hat{\Omega}_j)\mathrm{d}\Omega_j\\
&+\sum_{j=1}^{4}\int V(\hat{\Omega}_i,\hat{\Omega}_j)g^{(m)}(\hat{\Omega}_j)\mathrm{d}\Omega_j\\
&+(1-\delta_{mn})\int V(\hat{\Omega}_i,\hat{\Omega}_j)g^{(m+1)}(\hat{\Omega}_j)\mathrm{d}\Omega_j,
\end{aligned}\tag{13}$$

where the pair potential $V(\hat{\Omega}_i,\hat{\Omega}_j)$ is given by Eq.(2) with $\hat{\Omega}_i=(\sin\Theta_i\cos\Phi_i,\sin\Theta_i\sin\Phi_i,\cos\Theta_i)$ and $\mathrm{d}\Omega_i\equiv\sin\Theta_i\mathrm{d}\Theta_i\mathrm{d}\Phi_i$. The orientational singlet distribution function is then in the form

$$g^{(m)}(\hat{\Omega}_i)=\frac{1}{Z^{(m)}}\exp\left[-\frac{1}{k_{\mathrm{B}}T}V^{(m)}(\hat{\Omega}_i)\right], \tag{14a}$$

$$Z^{(m)}=\int\exp\left[-\frac{1}{k_{\mathrm{B}}T}V^{(m)}(\hat{\Omega}_i)\right]\mathrm{d}\Omega_i. \tag{14b}$$

Iterative method[12,13] is used to solved the set of functional equations. We can define each distribution function $g^{(m)}(\hat{\Omega})$ at $L\times L$ discrete points limited in the domain $0\leq\cos\Theta\leq1$ and $0\leq\Phi\leq2\pi$. For integral calculations, we choose the Gaussian point order

$$h_\Theta(1-1/\sqrt{3}+2k),\quad h_\Theta(1+1/\sqrt{3}+2k),$$

for values of $\cos\Theta$; and

$$h_\Phi(1-1/\sqrt{3}+2k),\quad h_\Phi(1+1/\sqrt{3}+2k),$$

for values of Φ, where $k=0,1,2,\cdots,L/2-1$, $h_\Theta=1/L$ and $h_\Phi=2\pi/L$.

Since $g^{(m)}(\hat{\Omega})$ $(m=1,2,\cdots,n)$ are correlated with each other, in numerical calculations the number of molecular layers n is limited. If the orientational distribution functions are known, one can calculate the tensor order parameters in each layer:[13,14]

$$Q_{\alpha\beta}^{(m)}=\int\left(\frac{3}{2}\Omega_\alpha\Omega_\beta-\frac{1}{2}\delta_{\alpha\beta}\right)g^{(m)}(\hat{\Omega})\mathrm{d}\Omega,$$

$$\alpha,\beta=X,Y,Z. \tag{15}$$

If there are more than one set of solutions for $g^{(m)}(\hat{\Omega})$, the stable one is determined by the minimum of free energy of the film

$$\begin{aligned}
F=&\sigma\left[\frac{1}{2}\sum_{m=1}^{n}\int V^{(m)}(\hat{\Omega})g^{(m)}(\hat{\Omega})\mathrm{d}\Omega\right.\\
&\left.+k_{\mathrm{B}}T\sum_{m=1}^{n}\int g^{(m)}(\hat{\Omega})\ln g^{(m)}(\hat{\Omega})\mathrm{d}\Omega\right].
\end{aligned}\tag{16}$$

Numerical calculation is made for PAA. The potential parameters given by Eq.(3) are chosen as[7]

$$\lambda = 0.79039,\ \mu = -1.0611,\ \nu = -1,\ \rho = -0.43668.$$

In numerical calculation, we introduce the scaled temperature $t(t \equiv kT/\varepsilon)$ and choose L=60.

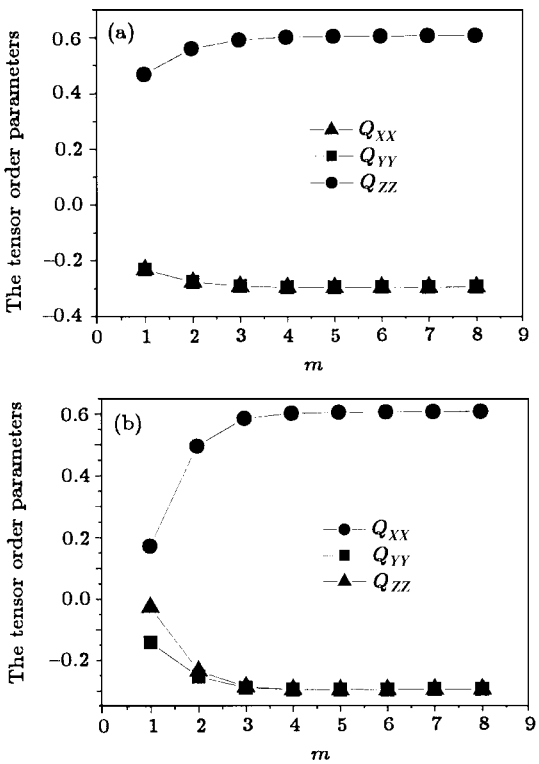


Fig.1. Layer dependence of the tensor order parameters at t=1.5 for model I. (a) The director is along the Z axis, i.e. the director is vertical to the film. (b) The director is along the X axis, i.e. the director lies in the surface plane of the film, in which the biaxial order is induced in the film, i.e. $Q_{YY} \neq Q_{ZZ}$ near the surface.

For illustration, we choose a film composed of n=16 molecular layers. On account of symmetry, only half of the layers need to be considered. Figure 1 shows two sets of the solutions for the tensor order parameters at t=1.5. In one set of the solutions, Q_{ZZ} is the maximum of three non-zero tensor elements $Q_{\alpha\alpha}$ ($\alpha = X, Y, Z$), i.e. the director of the film is along the Z axis. In another set, Q_{XX} has the maximum value and the director is along the X axis. The former has lower free energy and represents the stable state of the nematic film. The latter has higher free energy, since biaxial order is induced in this state, i.e. there are $Q_{yy} \neq Q_{ZZ}$ near the surface of the film. Taking account of the temperature, in the film, symmetry breaking takes place. This effect does not appear in the nematic film represented by the Lebwohl–Lasher model, i.e. the director is spatially isotropic even if at finite temperatures (see Fig.2). In fact, for certain nematics, the director is well established in the free surface of the sample instead of being distributed randomly.[15]

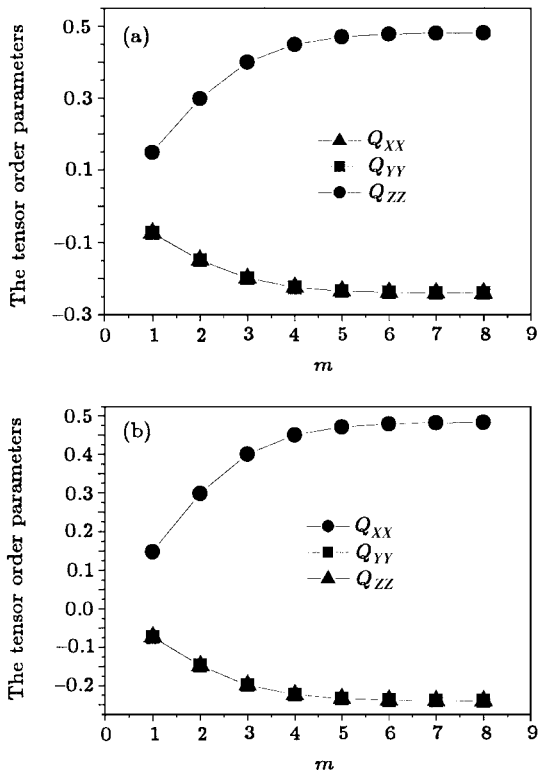


Fig.2. Layer dependence of the tensor order parameters at t=1.3 for the Lebwohl–Lasher model. (a) The director is along the Z axis. (b) The director is along the X axis. The free energy is degenerate in both states and the director is spatially isotropic.

When the temperature is near the N–I phase transition temperature of the bulk system (t_c=1.6327), the solution for the isotropic phase of the film will appear. The N–I phase transition temperature of the film is determined by the free energy at t_c=1.6363 (See Fig.3). We note that, different from the Lebwohl–Lasher model, the N–I phase transition temperature is higher than that of the bulk system (See Table 1). For the Lebwohl–Lasher model, the tensor order parameters are zero constantly for the isotropic phase and so the N–I phase transition temperature decreases due to the effect of finite sizes. But in model I, the tensor order parameters approach zero only in the middle of the film in its isotropic phase, i.e. nematic order is induced in layers near the surface in the isotropic phase (see Fig.4), and instead, the N–I phase transition temperature increases as compared with that of the bulk system. For very thin film (with the number of molecular layers $n < 8$), the N–I transition may change from first order to second order, but it is not definite.

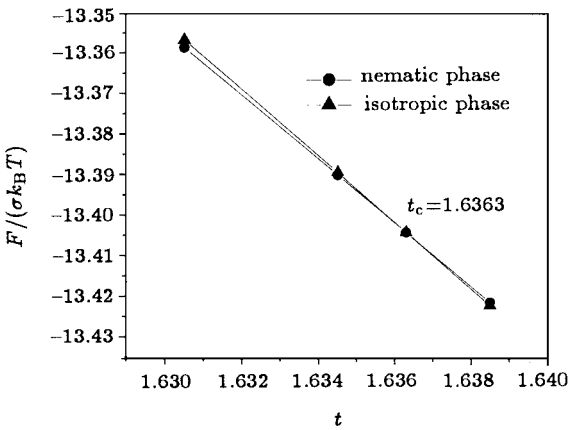


Fig.3. The scaled temperature dependence of the free energy density for nematic film composed of 16 molecular layers. The N–I phase transition temperature is t_c=1.6363.

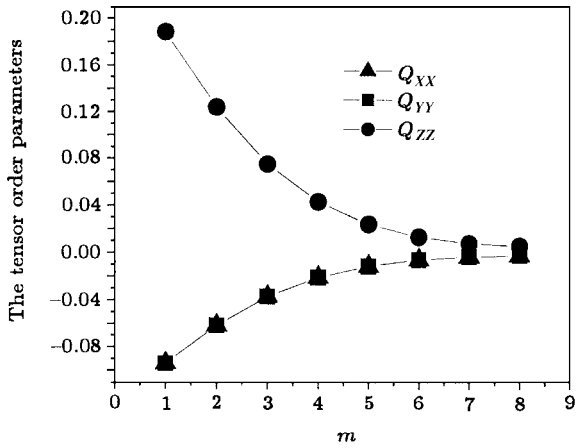


Fig.4. The layer dependence of the tensor order parameters for the isotropic phase at the N–I phase transition temperature t_c=1.6363.

Table 1. The N–I phase transition temperature for nematic film composed of n molecular layers and for the bulk system.

Number of layers	4	8	16	32	Bulk system
Model I	—	1.6422	1.6363	1.6342	1.6327
Lebwohl-Lasher model	1.2331	1.2904	1.3100	1.3167	1.3212

4. Conclusion

For liquid-crystal films composed of finite molecular layers, the spatially isotropic Lebwohl–Lasher model gives the ordinary results. But the spatially anisotropic pair potential gives some surprising new results. Firstly, taking account of the temperature, symmetry breaking takes place, and the state with the director arranged along the normal of the film has the lowest free energy. Secondly, contrary to the Lebwohl–Lasher model, the N–I phase transition increases instead of decreasing due to the effect of finite sizes. Thirdly, in isotropic phase, nematic order is induced in layers near the surface.

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