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Spatial correlation effects of molecules on the helical structure of cholesteric liquid crystals

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An extended mean field theory that is somewhat different from the Maier-Saupe (MS) type of mean field theory is proposed for cholesteric liquid crystals. This extended mean field theory is based on Lennard-Jones and Devonshire's mean field treatment of isotropic classical liquids. Unlike the MS type of mean field theory, our treatment can include both orientation and spatial correlation effects of molecules. A set of mean field parameters are introduced and the corresponding self-consistent equations are derived. The results show that the spatial correlation of molecules may have non-negligible effects on the helical structure of cholesteric liquid crystals. [S1063-651X(98)01803-0]

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I. INTRODUCTION

The cholesteric liquid crystal is generally regarded as a distorted form of the nematic mesophase and is characterized by a macroscopic twist, i.e., the helical structure [1]. Besides this helical structure there is no long-range order in the spatial distribution of molecules. The existence of a finite pitch is a common feature of all materials found in the cholesteric mesophase. This description of the cholesteric phase as twisted nematics is consistent with experimental observation; it provides at least a very good approximation to physical reality. The helical structure results from the microscopic structure of molecules and the nature of the intermolecular interactions. From the point of view of global symmetry, it has been argued that cholesteric liquid crystals are made up of chiral molecules and chirality is the major cause for the macroscopic twist [2–5]. Based on this assumption, a few potential models were presented for the cholesteric phase and the formation of the helical structure can be explained by the corresponding molecular theory [2–7]. Most of the previous molecular theory of cholesteric liquid crystals is based on Maier-Saupe's (MS) mean field treatment of nematic liquid crystals [8],which has proven to be very successful in the nematic case. Generally speaking, the MS type of mean field theory can be described as follows. First, one begins by writing down a model potential $V(\vec{r}_1,\vec{\Omega}_1,\vec{r}_2,\vec{\Omega}_2)$ that describes the interaction between a pair of molecules, where $\vec{r}_i$ and $\vec{\Omega}_i$ denote the position and orientation vectors of the ith molecule. Second, one assumes that the local molecular arrangement can be described by a distribution function $f(\vec{n}(\vec{r})\cdot\vec{\Omega})$, where $\vec{n}(\vec{r})$,$\vec{\Omega}$ is the local director (direction of the local nematic axis) and the orientation vector of molecules, respectively. It should be noted according to this assumption that the distribution function $f(\vec{n}(\vec{r})\cdot\vec{\Omega})$ will depend only on the relative angle between the local director $\vec{n}(\vec{r})$ and the molecular orientation vector $\vec{\Omega}$, but independent of the spatial coordinates of molecules. Third, for the assumed distribution function, the Helmholtz free energy function F can be calculated in the mean field approximation, which is written as

$$F\{f(\vec{r},\vec{\Omega})\}=F_0+\rho kT\int f(\vec{r}_1,\vec{\Omega}_1)\ln\{4\pi f(\vec{r}_1,\vec{\Omega}_1)\}d\vec{r}_1d\vec{\Omega}_1$$
$$+\frac{1}{2}\rho^2\int f(\vec{r}_1,\vec{\Omega}_1)f(\vec{r}_2,\vec{\Omega}_2)$$
$$\times V(\vec{r}_1,\vec{\Omega}_1,\vec{r}_2,\vec{\Omega}_2)d\vec{r}_1d\vec{\Omega}_1d\vec{r}_2d\vec{\Omega}_2,$$

where ρ is the average number density, F_0 is the ideal-gas free energy, and $\rho f(\vec{r},\vec{\Omega})$ is the one-particle distribution function normalized by $\int\rho f(\vec{r},\vec{\Omega})d\vec{r}d\vec{\Omega}=N$, where N is the total number of particles in the system. By minimizing F with respect to $f(\vec{r},\vec{\Omega})$ under the constraint $\int\rho f(\vec{r},\vec{\Omega})d\vec{r}d\vec{\Omega}=N$, one can obtain the mean field self-consistency equations and the corresponding mean field potential V_{mf}. From this simple introduction, one can see that in this type of mean field theory, only the molecule-molecule orientation correlation is taken into account, and the molecule-molecule spatial correlation is neglected. It has been shown that such a mean field theory is rather successful in predicting certain thermodynamic properties of liquid crystals, e.g., phase diagrams, order parameters, etc., but poor in predicting volume change at transition, latent heats, and maximum supercooling temperature [1]. While the orientation correlation of molecules may be dominant in determining the physical properties of liquid crystals, however, the short-range spatial correlation of molecules may have some effects in some aspects and cannot be neglected completely. But as has been shown, the inclusion of both orientation and spatial correlation effects in the mean field theory is rather difficult. To overcome this shortcoming of the MS type of mean field theory, in the nematic case, some authors have presented an orientation-averaged pair correlation func-

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tion method within the framework of the MS type of mean field theory to take into account the short-range spatial correlation effects [9]. In a previous paper [10], an extended mean field theory that includes both orientation and spatial correlation effects of molecules has been proposed for nematic liquid crystals. The theory is based on Lennard-Jones and Devonshire's mean field treatment of isotropic classical liquids and it is found that the theory is in good agreement with the experimental results. Recently, an extended Landau–de Gennes phenomenon theory of the nematic-isotropic phase transition was developed to include the coupling of the density and the orientation order parameter and it is found that most of the experimental measurements except $(dQ/dT)_{T=NI}$, where T is temperature and Q is the orientation order parameter, can be reproduced reasonably well [11]. All these extensions of the MS mean field theory show that the short-range spatial correlation of molecules may have some significant effects on some physical properties of liquid crystals and should not be neglected. In this paper we will apply the extended mean field theory developed in the previous paper [10] to the case of cholesteric liquid crystals. Our main purpose is to see whether the short-range spatial correlation effects of molecules may have some contribution to the formation of the helical structure, which characterizes cholesteric liquid crystals. This paper will be arranged as follows: In Sec. II, we will briefly review the existing potential model of cholesterics and a simplified model potential is adopted. Then, based on the same approach as in Ref. [10], a set of mean field parameters and the corresponding self-consistency equations are derived according to the adopted model potential. In Sec. III, some numerical results are presented and the basic features of this theory are discussed.

II. MODEL AND THE EXTENDED MEAN FIELD THEORY

It has been powerfully argued that cholesterics are made up of chiral molecules and chirality is the major cause of the helical structure [2–5]. For the uniaxial, hard-rod-like chiral molecule, the pairwise potential $V(\vec{r}_1,\vec{\Omega}_1,\vec{r}_2,\vec{\Omega}_2)$ between two molecules can be decomposed into two parts without losing generality [12]:

$$\begin{aligned} V(x_1,x_2) &\\ &= V_N(r_{12},\vec{\Omega}_1\cdot\vec{r}_{12},\vec{\Omega}_2\cdot\vec{r}_{12},\vec{\Omega}_1\cdot\vec{\Omega}_2)\\ &\quad +(\vec{\Omega}_1\times\vec{\Omega}_2\cdot\vec{r}_{12})V_\chi(r_{12},\vec{\Omega}_1\cdot\vec{r}_{12},\vec{\Omega}_2\cdot\vec{r}_{12},\vec{\Omega}_1\cdot\vec{\Omega}_2) \end{aligned} \tag{1}$$

in which $x_i\equiv(\vec{r}_i,\vec{\Omega}_i)$. The V_N term accounts for the formation of the nematic phase, and the V_χ term manifests what is known as chirality, which vanishes for nonchiral molecules. A completely general form of $V(x_1,x_2)$ is rather difficult to determine, so a more instructive and manageable but less general form is usually assumed, which can be written as

$$\begin{aligned} V(x_1,x_2) &= V_N(r_{12},\vec{\Omega}_1\cdot\vec{\Omega}_2)\\ &\quad +(\vec{\Omega}_1\times\vec{\Omega}_2\cdot\vec{r}_{12})V_\chi(r_{12},\vec{\Omega}_1\cdot\vec{\Omega}_2). \end{aligned} \tag{2}$$

Following the symmetry consideration, one can expand V_N and V_χ in a series of Legendre polynomials:

$$V_N(r_{12},\vec{\Omega}_1\cdot\vec{\Omega}_2)=V_0(r_{12})+\sum_{l=1}^{\infty} V_{2l}(r_{12})P_{2l}(\vec{\Omega}_1\cdot\vec{\Omega}_2), \tag{3}$$

$$V_\chi(r_{12},\vec{\Omega}_1\cdot\vec{\Omega}_2)=\sum_{l=0}^{\infty} V'_{2l+1}(r_{12})P_{2l+1}(\vec{\Omega}_1\cdot\vec{\Omega}_2). \tag{4}$$

In particular, the truncated form

$$\begin{aligned} V(x_1,x_2) &= V_0(r_{12})+V_N(r_{12})P_2(\vec{\Omega}_1\cdot\vec{\Omega}_2)\\ &\quad +V_\chi(r_{12})P_1(\vec{\Omega}_1\cdot\vec{\Omega}_2)(\vec{\Omega}_1\times\vec{\Omega}_2\cdot\vec{r}_{12}) \end{aligned} \tag{5}$$

is rather familiar and most widely adopted. In this paper, we will also adopt this truncated form, considering that it contains most of the physics of cholesteric liquid crystals, and is rather more convenient to be dealt with than the general form. As to the forms of $V_0(r)$, $V_N(r)$, and $V_\chi(r)$, we choose them to be

$$V_0(r)=\epsilon_0\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right], \tag{6}$$

$$V_N(r)=-\epsilon_N\left(\frac{\sigma}{r}\right)^{12}, \tag{7}$$

$$V_\chi(r)=-\epsilon_\chi\frac{1}{r}\left(\frac{\sigma}{r}\right)^{7}. \tag{8}$$

The forms of Eqs. (6) and (8) are the usually adopted forms in the literature (see, for example, Refs. [9], [13], and [14]), and the form of Eq. (7) was suggested by Refs. [10] and [15].

To establish the mean field theory corresponding to the above assumed molecular potential, we will follow the approach of Lennard-Jones and Devonshire (LJD) [16,17]. First, it is necessary to note that due to the form of $V_0(r_{ij})$, there is in general an equilibrium separation between two molecules. Let a denote the averaged equilibrium separation distance between two nearest-neighbor molecules. The LJD approach consists of focusing on one molecule denoted as molecule i, and inscribing its position inside a sphere of radius a (not necessarily located at its center). By considering an isotropic distribution of the nearest-neighbor molecules over this sphere, the resulting approximate effective potential seen by molecule i has a minimum at the center of the sphere, denoted as the equilibrium position (by LJD). Let ρ_i be the distance of molecule i from the center of the sphere, the equilibrium position. The effective potential may be parametrized as a function of ρ_i. This procedure has been done in some detail by Lennard-Jones and Devonshire [16,17]. Following their approach, we have generalized the LJD calculation to molecules with the anisotropic interaction of Eq. (5). The main point of our generalization is to allow molecule i's nearest-neighbor j also to deviate from the respective equilibrium positions, which are isotropic over the sphere, and on account of the symmetry of the interaction it is assumed that the pairwise potential $V(\vec{r}_i,\vec{\Omega}_i,\vec{r}_j,\vec{\Omega}_j)$ can be replaced equivalently by an effective averaged pair potential:

$$
\begin{aligned}
V_{\mathrm{eff}}(\rho_i,\rho_j,\Theta_i,\Theta_j)
&\equiv \frac{1}{(2\pi)^4}\int d\theta_i d\theta_j d\phi_i d\phi_j d\Phi_i d\Phi_j \\
&\quad\times \rho_i^2 \sin\theta_i \rho_j^2 \sin\theta_j V(\vec{r}_i,\vec{\Omega}_i,\vec{r}_j,\vec{\Omega}_j), \qquad (9)
\end{aligned}
$$

where we have denoted $\vec{r}_i \equiv \vec{R}_i + \vec{\rho}_i$. $\vec{R}_i$ is the position vector of the ith molecule's equilibrium position (i.e., the center of the sphere), $\vec{\rho}_i$ is the position vector of the mass center of the ith molecule relative to the center of the sphere. (θ_i,ϕ_i) are the polar and azimuthal angles of $\vec{\rho}_i$, and (Θ_i,Φ_i) are the polar and azimuthal angles of $\vec{\Omega}_i$ relative to the local director $\vec{n}(\vec{R}_i)$. Because the calculation is straightforward but very trivial, we write here only the final form:

$$
\begin{aligned}
V_{\mathrm{eff}}(\rho_i,\rho_j,\Theta_i,\Theta_j)
&= \epsilon_0\left[\left(\frac{\sigma}{a}\right)^{12} l(\rho_i) l(\rho_j) - \left(\frac{\sigma}{a}\right)^{6} m(\rho_i) m(\rho_j)\right] \\
&\quad - \epsilon_N \left(\frac{\sigma}{a}\right)^{12} l(\rho_i) l(\rho_j) P_2(\cos\Theta_i) \\
&\quad \times P_2(\cos\Theta_j) P_2[\vec{n}(\vec{R}_i)\cdot\vec{n}(\vec{R}_j)] \\
&\quad - \epsilon_\chi \left(\frac{\sigma}{a}\right)^{7} n(\rho_i) n(\rho_j) P_2(\cos\Theta_i) P_2(\cos\Theta_j) \\
&\quad \times [\vec{n}(\vec{R}_i)\cdot\vec{n}(\vec{R}_j)][\hat{R}_{ij}\cdot\vec{n}(\vec{R}_i)\times\vec{n}(\vec{R}_j)], \qquad (10)
\end{aligned}
$$

where

$$
\begin{aligned}
l(\rho) &= [1 + 12(\rho/a)^2 + 25.2(\rho/a)^4 \\
&\quad + 12(\rho/a)^6 + (\rho/a)^8][1-(\rho/a)^2]^{-10}, \qquad (11)
\end{aligned}
$$

$$
m(\rho) = [1+(\rho/a)^2][1-(\rho/a)^2]^{-4}, \qquad (12)
$$

$$
n(\rho) = [1+2(\rho/a)^2 + 0.2(\rho/a)^4][1-(\rho/a)^2]^{-5}, \qquad (13)
$$

$$
\cos\Theta_i = \vec{\Omega}_i \cdot \vec{n}(\vec{R}_i), \qquad (14)
$$

$$
\cos\Theta_j = \vec{\Omega}_j \cdot \vec{n}(\vec{R}_j), \qquad (15)
$$

$$
\hat{R}_{ij} = \frac{\vec{R}_{ij}}{|\vec{R}_{ij}|}. \qquad (16)
$$

To obtain Eq. (10) we have used the following relation:

$$
\begin{aligned}
P_n(\cos\theta_{AB}) &= P_n(\cos\theta_A) P_n(\cos\theta_B) \\
&\quad + 2\sum_{m=1}^{n} \frac{(n-m)!}{(n+m)!} P_n^m(\cos\theta_A) \\
&\quad \times P_n^m(\cos\theta_B)\cos m(\phi_A - \phi_B),
\end{aligned}
$$

where $\theta_{AB} = \vec{A}\cdot\vec{B}$ ($\vec{A}$, $\vec{B}$ are unit vectors), (θ_A,ϕ_A) and (θ_B,ϕ_B) are the polar and azimuthal angles of $\vec{A}$ and $\vec{B}$ relative to the same frame of reference. From Eq. (10) one can obtain the mean field potential V_{mf} experienced by molecule i directly by averaging over the coordinates of molecule j:

$$
\begin{aligned}
V_{\mathrm{mf}}(\rho_i,\Theta_i) &= \sum_j{}' \left\{ \epsilon_0\left[\left(\frac{\sigma}{a}\right)^{12}\langle l\rangle l(\rho_i) - \left(\frac{\sigma}{a}\right)^{6}\langle m\rangle m(\rho_i)\right]\right. \\
&\quad - \epsilon_N\left(\frac{\sigma}{a}\right)^{12}\langle l\rangle l(\rho_i) \\
&\quad \times \langle P_2\rangle P_2(\cos\Theta_i) P_2[\vec{n}(\vec{R}_i)\cdot\vec{n}(\vec{R}_j)] \\
&\quad - \epsilon_\chi\left(\frac{\sigma}{a}\right)^{7}\langle n\rangle n(\rho_i)\langle P_2\rangle P_2(\cos\Theta_i) \\
&\quad \left.\times[\vec{n}(\vec{R}_i)\cdot\vec{n}(\vec{R}_j)][\hat{R}_{ij}\cdot\vec{n}(\vec{R}_i)\times\vec{n}(\vec{R}_j)]\right\}, \qquad (17)
\end{aligned}
$$

where $\langle l\rangle \equiv \langle l(\rho_j)\rangle$, $\langle m\rangle \equiv \langle m(\rho_j)\rangle$, $\langle n\rangle \equiv \langle n(\rho_j)\rangle$, $\langle P_2\rangle \equiv \langle P_2[\vec{\Omega}_j\cdot\vec{n}(\vec{R}_j)]\rangle$, and $\langle\ \rangle$ denotes the ensemble averaged values. All these averaged values are assumed to be site independent. The sum $\Sigma_j'\{\ \}$ includes only the nearest-neighbor molecules. To complete the sum $\Sigma_j'\{\ \}$, we can expand $\vec{n}(\vec{R}_j) - \vec{n}(\vec{R}_i)$ into the following series:

$$
\vec{n}(\vec{R}_j) - \vec{n}(\vec{R}_i) = \sum_\alpha R_{ij\alpha}\frac{\partial\vec{n}}{\partial x_\alpha} + \frac{1}{2}\sum_{\beta\gamma} R_{ij\beta}R_{ij\gamma}\frac{\partial^2\vec{n}}{\partial x_\beta \partial x_\gamma} + \cdots,
$$

where $\vec{R} \equiv (x_1,x_2,x_3)$, $\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$. In the case of the isotropic, homogeneous distribution of the nearest-neighbor molecules' equilibrium position over the sphere of molecule i, after some simple calculation, one can obtain the following relations:

$$
\sum_j{}' P_2[\vec{n}(\vec{R}_i)\cdot\vec{n}(\vec{R}_j)] = z_0 - \frac{1}{2} z_0 a^2 \sum_{\alpha\beta}\frac{\partial n_\beta}{\partial x_\alpha}\frac{\partial n_\beta}{\partial x_\alpha} + O(a^3), \qquad (18)
$$

$$
\begin{aligned}
&\sum_j{}' [\vec{n}(\vec{R}_i)\cdot\vec{n}(\vec{R}_j)][\vec{R}_{ij}\cdot\vec{n}(\vec{R}_i)\times\vec{n}(\vec{R}_j)] \\
&\quad = \frac{1}{3} z_0 a^2 \sum_{\alpha\beta\gamma}\epsilon_{\alpha\beta\gamma} n_\alpha \frac{\partial n_\beta}{\partial x_\gamma} + O(a^3) \qquad (19)
\end{aligned}
$$

in which z_0 is the number of the nearest-neighbor molecules (set to twelve). The higher order terms of a^3 are neglected. Using these relations, the sum $\Sigma_j'\{\ \}$ in Eq. (17) can be completed, and then the mean field V_{mf} experienced by molecule i due to its nearest-neighbors can be expressed as

$$
\begin{aligned}
V_{\mathrm{mf}}(\rho,\sigma) &= z_0 g_0(\rho,\sigma) + \frac{1}{2} z_0 a^2 g_2(\rho,\sigma)\sum_{\alpha\beta}\frac{\partial n_\beta}{\partial x_\alpha}\frac{\partial n_\beta}{\partial x_\alpha} \\
&\quad - \frac{1}{3} z_0 a g_3(\rho,\sigma)\sum_{\alpha\beta\gamma}\epsilon_{\alpha\beta\gamma} n_\alpha \frac{\partial n_\beta}{\partial x_\gamma}, \qquad (20)
\end{aligned}
$$

where

$$g_0(\rho,\sigma)=\epsilon_0\left[\left(\frac{\sigma}{a}\right)^{12}\langle l\rangle l(\rho)-\left(\frac{\sigma}{a}\right)^{6}\langle m\rangle m(\rho)\right]-\epsilon_N\left(\frac{\sigma}{a}\right)^{12}\langle l\rangle l(\rho)\langle P_2\rangle P_2(\sigma), \tag{21}$$

$$g_2(\rho,\sigma)=\epsilon_N\left(\frac{\sigma}{a}\right)^{12}\langle l\rangle l(\rho)\langle P_2\rangle P_2(\sigma), \tag{22}$$

$$g_3(\rho,\sigma)=\epsilon_\chi\left(\frac{\sigma}{a}\right)^{7}\langle n\rangle n(\rho)\langle P_2\rangle P_2(\sigma), \tag{23}$$

$$\sigma=\cos\Theta. \tag{24}$$

In Eqs. (20) and (21)–(24) we have removed the subscript i from the expressions. There are four mean field parameters $\langle l\rangle$, $\langle m\rangle$, $\langle n\rangle$, and $\langle P_2\rangle$ in the expression of the mean field potential V_{mf}; they should be determined by the following self-consistency equations:

$$\langle l\rangle=\int_0^{0.5a}d\rho\int_0^1 d\sigma l(\rho)f(\rho,\sigma), \tag{25}$$

$$\langle m\rangle=\int_0^{0.5a}d\rho\int_0^1 d\sigma m(\rho)f(\rho,\sigma), \tag{26}$$

$$\langle n\rangle=\int_0^{0.5a}d\rho\int_0^1 d\sigma n(\rho)f(\rho,\sigma), \tag{27}$$

$$\langle P_2\rangle=\int_0^{0.5a}d\rho\int_0^1 d\sigma P_2(\sigma)f(\rho,\sigma), \tag{28}$$

where

$$f(\rho,\sigma)=\frac{1}{Z}\exp\{-\beta V_{\mathrm{mf}}(\rho,\sigma)\}, \tag{29}$$

$$Z=\int_0^{0.5a}d\rho\int_0^1 d\sigma\exp\{-\beta V_{\mathrm{mf}}(\rho,\sigma)\}. \tag{30}$$

Generally speaking, the structure of the director, i.e., the form of $\vec{n}(\vec{R})$, should be determined by the minimization condition of the total free energy. But in the case of cholesteric liquid crystals, we can proceed with the usual ansatz: $\vec{n}(\vec{R})=(\cos qz, \sin qz, 0)$. Such a representation assumes that the director is uniformly twisted along the z axis with a pitch $p=2\pi/q$. Here q will be treated as a variational parameter and determined by the minimization condition of the total free energy, which gives

$$p=\frac{6\pi a\epsilon_N}{\epsilon_\chi}\frac{\langle g_2(\rho,\sigma)\rangle}{\langle g_3(\rho,\sigma)\rangle}=\frac{6\pi a\epsilon_N}{\epsilon_\chi}\left(\frac{\sigma}{a}\right)^5\frac{\langle l\rangle\langle l(\rho)P_2(\sigma)\rangle}{\langle n\rangle\langle n(\rho)P_2(\sigma)\rangle}. \tag{31}$$

Equations (25)–(28) and (31) constitute a set of complete self-consistency equations. After solving them, one can obtain the values of the mean field parameters and the pitch, and then the free energy and the entropy of the system can be calculated:

$$S=-k\sum_i\langle\ln f(\rho_i,\sigma_i)\rangle, \tag{32}$$

$$F=\frac{1}{2}\sum_i\langle V(\rho_i,\sigma_i)\rangle+kT\sum_i\langle\ln f(\rho_i,\sigma_i)\rangle. \tag{33}$$

III. NUMERICAL RESULTS AND DISCUSSION

In Sec. II, we have established the basic formulas of the extended mean field theory. In order to see whether this type of mean field theory can describe the basic features of cholesteric liquid crystals, we have done some numerical calculations. The numerical procedure will be as follows: For a given set of model parameters ϵ_0, ϵ_N, ϵ_χ, σ/a, and a given temperature T, we first solve the self-consistency equations (25)–(28) and (31) to obtain the values of the mean field parameters $\langle l\rangle$, $\langle m\rangle$, $\langle n\rangle$, $\langle P_2\rangle$, and the pitch p by iteration method, then substitute these quantities into Eq. (32) and Eq. (33) to calculate the entropy S and the free energy F. Due to the fact that there is much uncertainty in the choices of the form of the model potential, including the model parameters, and that our main purpose is only to see what effects the spatial correlation of molecules have on the helical structure, we will not try to make a quantitative comparison between the numerical results of this theory and the experiment data, we will focus on the main features of this theory. We have carried out the numerical calculations for a number of different model parameters and find the main features of this theory may be summed as follows:

(1) For a set of appropriately chosen model parameters, the theory predicts a first order phase transition at a temperature T_C as the temperature varies: when $T<T_C$, the liquids are orientationally ordered and when $T>T_C$, they are orientationally disordered. The basic features of this orientation order-disorder phase transition are similar to the nematic-isotropic phase transition except that a helical structure of the director will form when the system turns into the orientationally ordered phase. The calculated value of the orientation order parameter $\langle P_2\rangle$, as well as the entropy S, will jump at T_C, and the $\langle P_2\rangle$ jump as well as the entropy change ΔS are within a few percent of the corresponding values of the MS mean field theory. Although in these respects this theory is very similar to the MS mean field theory, there are some important differences between them. It is well known that the small magnitude of $(T_C-T^*)/T_C$, where T_C is the nematic-isotropic phase transition and T^* denotes the virtual transition temperature (supercooling temperature), has been a long-standing puzzle in the physics of liquid crystals that cannot be explained by the MS mean field theory [1]. By extending the mean field theory to include the spatial correlation effects of molecules one finds that the magnitude of $(T_C-T^*)/T_C$ becomes in accord with the experimental values [10]. In addition, this theory also yields a value of $\Delta V/V$ and dT_C/dP (P is pressure) which are in accord with the experimental data [10]. Because these features of the theory have been discussed in detail previously [10], we will not pursue them further in this paper. We will focus mainly on the helical structure of the director.

(2) When the liquids turn into the orientationally ordered phase as the temperature decreases to be lower than T_C, a

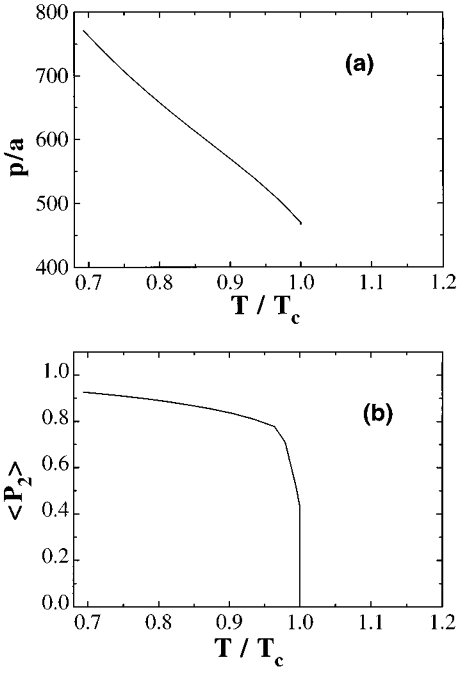

FIG. 1. (a) The temperature dependence of the pitch with the model parameters $\epsilon_N/\epsilon_0=1$, $\epsilon_\chi/\epsilon_0=0.1$, $\sigma/a=1$. (b) The corresponding temperature dependence of the orientation order parameter $\langle P_2\rangle$.

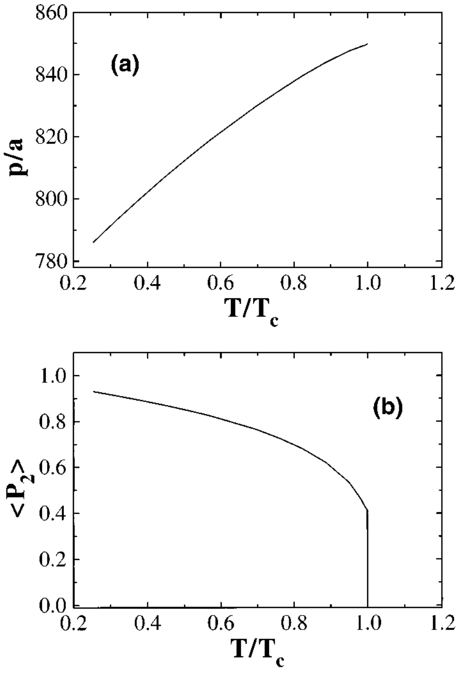

FIG. 2. (a) The temperature dependence of the pitch with the model parameters $\epsilon_N/\epsilon_0=0.2$, $\epsilon_\chi/\epsilon_0=0.005$, $\sigma/a=1.0$. (b) The corresponding temperature dependence of the orientation order parameter $\langle P_2\rangle$.

macroscopic twist of the director, i.e., the helical structure, will form. This is the main difference between the cholesteric phase and the nematic phase. The basic feature of the helical structure is that the pitch invariably depends on the temperature. To give a theoretical explanation of the temperature dependence of the pitch, Keating [18] proposed a microscopic model that assumed the forces opposing the twist are anharmonic so that a macroscopic twist results automatically from the ensemble-averaging process. In his theory, the pitch will decrease with the rising temperature. But experimental results show that there are several types of temperature behaviors of the pitch [18–22]: (i) The pitch increases with decreasing temperature; (ii) the pitch decreases with decreasing temperature; (iii) the pitch increases with decreasing temperature, and at a certain temperature T_d the helicity reverses and the pitch decreases as temperature further decreases. To overcome the shortcomings of Keating's theory, Lin-Liu *et al.* [12] proposed a molecular theory by including higher order terms in the model potential, which is described in Sec. I [see Eq. (5)]. After adding two higher order terms $V_4(r_{12})P_4(\vec{\Omega}_1\cdot\vec{\Omega}_2)$ and $V_3(r_{12})P_3(\vec{\Omega}_1\cdot\vec{\Omega}_2)(\vec{\Omega}_1\times\vec{\Omega}_2\cdot\vec{r}_{12})$ into the model potential (5), the MS type of mean field theory can yield correctly the above mentioned three types of temperature behaviors of the pitch [12]. To see what type of temperature behavior of the pitch will exist in our theory, we have calculated the temperature dependence of the pitch for a number of appropriately chosen model parameters, we find this theory also yields correctly three types of temperature behaviors that are in qualitative agreement with the experimental results, as shown in Figs. 1(a)–3(a). In Fig. 1(a), the pitch increases with decreasing temperature, corresponding to the case (i). In Fig. 2(a), the pitch decreases with decreasing temperature, corresponding to case (ii). In Fig. 3(a), the pitch increases with decreasing temperature; at a certain temperature it reaches a maximum, and then it decreases as temperature further decreases, corresponding to case (iii). For comparison we have also plotted the corresponding temperature dependences of the orientation order parameter $\langle P_2\rangle$ in each

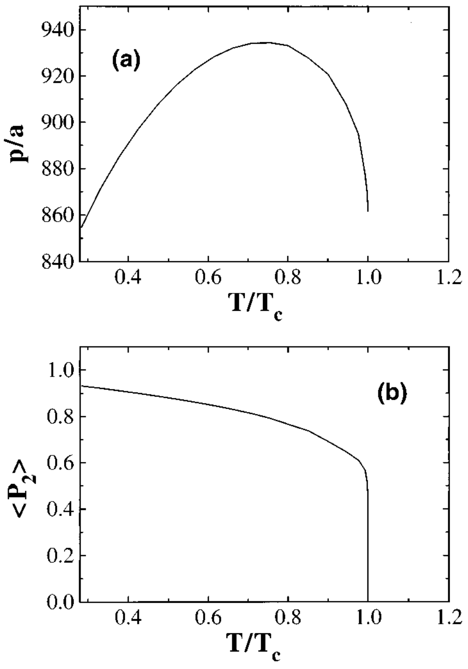

FIG. 3. (a) The temperature dependence of the pitch with the model parameters $\epsilon_N/\epsilon_0=0.8$, $\epsilon_\chi/\epsilon_0=0.04$, $\sigma/a=1.0$. (b) The corresponding temperature dependence of the orientation order parameter $\langle P_2\rangle$.

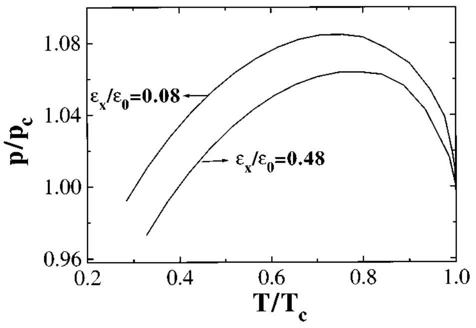

FIG. 4. The temperature dependences of the pitch for the different values of ϵ_χ/ϵ_0 (shown in the figure). The other parameters are fixed to be $\epsilon_N/\epsilon_0=0.8$, $\sigma/a=1$. It is noted that the temperature behavior of the pitch is not sensitive to the change of ϵ_χ/ϵ_0.

case, which are shown in Figs. 1(b)–3(b). It can be seen there is little difference between the $\langle P_2\rangle$-T curves. The numerical results also show that the temperature behavior of the pitch depends mainly on the value of ϵ_N/ϵ_0, and is not sensitive to the change of ϵ_χ/ϵ_0, as is shown in Fig. 4. While the temperature behavior mainly depends on the value of ϵ_N/ϵ_0, the length of the pitch has a far more sensitive dependence on the value of ϵ_χ/ϵ_0 than on ϵ_N/ϵ_0 [see Figs. 4, 5(a), and 6(a)]. The smaller ϵ_χ/ϵ_0 is, the larger p is, and $p \to\infty$ when $\epsilon_\chi/\epsilon_0\to 0$ [this can be seen from Eq. (31)], which corresponds to the nematic case. We have also plotted the dependences of the orientation order parameter P_2 on the value of ϵ_N/ϵ_0 and ϵ_χ/ϵ_0 in Figs. 5(b)–6(b), from which we can see that the order parameter $\langle P_2\rangle$ is sensitive to the change of ϵ_N/ϵ_0, but almost independent of ϵ_χ/ϵ_0.

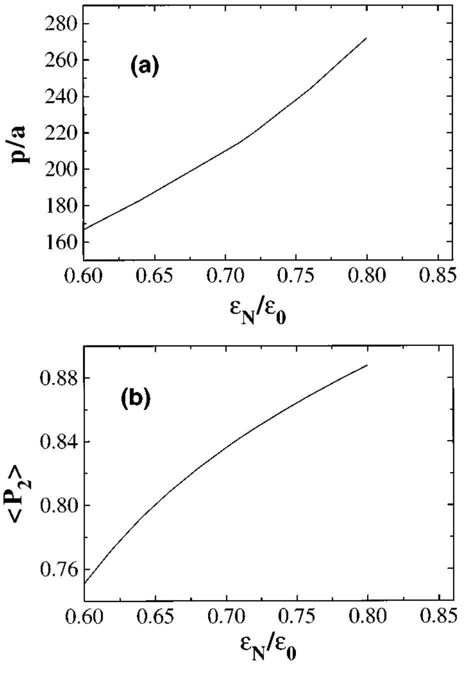

FIG. 5. (a) The dependence of the pitch on the value of ϵ_N/ϵ_0. The other parameters are fixed to be $\epsilon_\chi/\epsilon_0=0.1$, $\sigma/a=1.0$, $T/\epsilon_0=1$. (b) The corresponding dependence of the orientation order parameter $\langle P_2\rangle$ on the value of ϵ_N/ϵ_0.

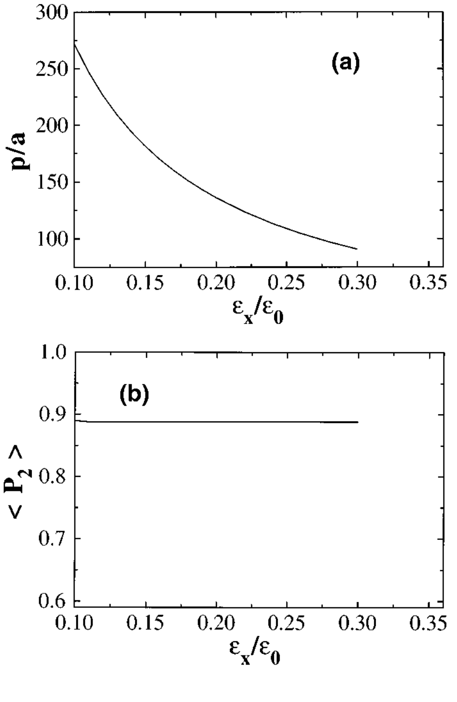

FIG. 6. (a) The dependence of the pitch on the value of ϵ_χ/ϵ_0. The other parameters are fixed to be $\epsilon_N/\epsilon_0=0.8$, $\sigma/a=1.0$, $T/\epsilon_0=1.0$. (b) The corresponding dependence of the orientation order parameter $\langle P_2\rangle$ on the value of ϵ_χ/ϵ_0.

(3) Although the MS type of mean field theory of Ref. [12] yields similar temperature behaviors of the pitch as the present theory, it should be pointed out there are some important differences between the two theories: (i) In the former theory, two higher order terms $V_4(r_{12})P_4(\vec{\Omega}_1\cdot\vec{\Omega}_2)$ and $V_3(r_{12})P_3(\vec{\Omega}_1\cdot\vec{\Omega}_2)(\vec{\Omega}_1\times\vec{\Omega}_2\cdot\vec{r}_{12})$ must be included in the model potential (5), or else a temperature-independent pitch will be obtained. But in the present theory, the two higher order terms need not to be included to get the temperature-dependent pitch. The reason is that in the present theory the spatial correlation effects of molecules are also taken into account. (ii) In the former theory, the temperature behavior of the pitch arises from the temperature dependence of the ratio of $\sigma_4(T)/\sigma_2(T)$, where $\sigma_4(T)\equiv\langle P_4[\vec{\Omega}\cdot\vec{n}(\vec{R})]\rangle$ and $\sigma_2(T)\equiv\langle P_2[\vec{\Omega}\cdot\vec{n}(\vec{R})]\rangle$ are the orientation order parameters. But in the present theory, from Eq. (31), one can see that the temperature dependence of the pitch arises from the temperature dependence of $\langle g_2(\rho,\sigma)\rangle/\langle g_3(\rho,\sigma)\rangle\cong(\sigma/a)^5(\epsilon_N/\epsilon_\chi)\langle l(\rho)\rangle^2/\langle n(\rho)\rangle^2$, which are mainly related to the spatial correlation effects of the molecules [see Eqs. (11)–(13)]. (iii) In the case of the helicity reverse, the pitch remains finite at all temperatures in the present theory, as is shown in Fig. 3(a), but in the former theory, the pitch diverges at a certain temperature T_d, i.e., at $T=T_d$ the cholesteric phase changes into the nematic phase. This divergence of the pitch may be due to the effects of the higher order terms of the interaction. This significant difference between the two types of mean field theory shows that the higher order terms of the interaction may have a great contribution to the temperature dependence of the pitch, especially if one wants to make a quantitative comparison between the results of the theory and the experimental data, the

effects of higher order terms of the interaction must be included, but it may be argued that one must first incorporate the lower order effects that should present such as the spatial correlation effects before assessing the effects due to the higher order terms. The results of this paper show that the spatial correlation of molecules may have a non-negligible contribution to the formation of the helical structure and should be taken into account in the theory. For further improvement of the present theory, the effects of the higher order terms of the interaction, should be included.

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