PHYSICAL REVIEW E VOLUME 58, NUMBER 6 DECEMBER 1998

Extended mean-field molecular theory for the smectic-*C* to smectic-*A* orientational transitions

Liangbin Hu[1] and Ruibao Tao[2,1]
[1]*Department of Physics, Fudan University, Shanghai 200433, People's Republic of China*
[2]*Center for Theoretical Physics, Chinese Center of Advanced Science and Technology (World Laboratory), P.O. Box 8730, Beijing 100080, People's Republic of China*

(Received 9 July 1998)

An extended mean-field molecular theory for the smectic-*C* to smectic-*A* orientational transitions is proposed by extending Lennard-Jones and Devonshire (LJD's) mean-field treatment of isotropic liquids to the case of anisotropic liquid crystals. Unlike the previous mean-field molecular theories for the smectic-*C* to smectic-*A* orientational transitions, this extended mean-field theory can include both orientational and spatial correlation effects of molecules, and both orientational and spatial thermal fluctuations of molecules are taken into account in a self-consistent way. A set of mean-field parameters are introduced and the corresponding self-consistency equations are derived. The numerical results show that this type of mean-field theory can describe the basic features of the smectic-*C* to smectic-*A* orientational transitions. [S1063-651X(98)01212-4]

PACS number(s): 61.30.−v, 64.70.Md

I. INTRODUCTION

Smectic liquid crystals have stratified structures and a variety of molecular arrangements are possible within each stratification [1]. The smectic-*A* phase is the least ordered of all the smectic mesophases. In the smectic-*A* phase the molecules are upright in each layer with their centers irregularly spaced in a liquidlike fashion. The thickness of the layer is the order of the length of the free molecules. The interlayer attractions are weak as compared with the lateral forces between molecules. The main difference between the structures of the smectic-*C* and smectic-*A* mesophases is that the molecular long axis tilts over with respect to the plane normal in the smectic-*C* mesophase. This widely accepted picture of the smectic-*C* mesophase as the tilted form of the smectic-*A* is consistent with most experimental observations, it provides at least a very good approximation to physical reality [1]. For many smectic-*C* mesophases, the tilt angle is temperature dependent; the tilt angle with respect to the plane normal will decrease as the temperature increases, and a transition from the smectic-*C* to smectic-*A* will occur at a certain temperature T_{CA}.

Several molecular theories for the smectic-*C* to smectic-*A* orientational transitions have been proposed based on the microscopic interparticle interactions of molecules [2–5], for example, the electric dipole model of Ref. [2], the steric model of Ref. [3], and the tentative model of Ref. [4]. Though there have been several molecular theories for the smectic-*C* to smectic-*A* orientational transitions, none of them is consistent with all the experimental observations; some controversial issues still remain between different theoretical investigations and also between some theoretical results and experimental observations. For example, the molecular theories of Refs. [2] and [3] both predict a large anisotropy in the orientations of the transverse molecular axes when the tilt angle in the smectic-*C* phase becomes large; the biaxial order parameter Δ in the molecular orientational order is predicted to be on the order of 10^{-1}. This theoretical result contradicts a series of experimental observations that have established that the anisotropy in the orientations of the transverse molecular axes is quite small and the biaxial order parameter Δ is of the order of 10^{-2} instead of 10^{-1} [6–10]. In addition, the molecular theories of Refs. [2–5] all predict that the smectic-*C* to smectic-*A* orientational transition is of second order (the tilt angle of the director will decrease continuously to zero as temperature increasing to the transition point T_{CA}); this also contradicts with experimental observations that have established that both second-order [11–14] and first-order [15] smectic-*C* to smectic-*A* orientational transitions can occur.

These controversial issues show that the smectic-*C* to smectic-*A* orientational transition is far from being completely understood based on the microscopic interparticle interactions between molecules. In this paper, we propose an extended mean-field molecular theory that is somewhat different from the previous mean-filed molecular theories for the smectic-*C* to smectic-*A* orientational transitions. Unlike the previous mean-field molecular theories that based on the Maier-Saupe (MS) type of mean-field approximation [17], this extended mean-field theory is established by extending Lennard-Jones and Devonshire (LJD's) mean-field treatment of isotropic liquids [18,19] to the case of anisotropic liquid crystals. In this extended mean-field theory, both orientational and spatial correlation effects of molecules are taken into account.

It is well known that the MS type of mean-field approximation takes into account the orientation correlation effects of molecules but the short-range spatial correlation effects of molecules are usually neglected. While the orientation correlations of molecules may play the dominant role in determining the basic physical properties of liquid crystals, the short-range spatial correlations of molecules may have some physical effects in some aspects and cannot be neglected completely. To overcome this shortcoming of the MS type of mean-field approximation, in the nematic case, some authors proposed an orientation-averaged spatial correlation theory to take into account the short-range spatial correlation effects of molecules [20]. In the orientation-averaged spatial correlation theory, one assumes that the distribution function of molecules can be decoupled into a product of the orientation distribution function and the spatial distribution function of molecules, which depends only on the orientation coordinates and spatial coordinates of molecules, respectively. In a previous paper [21], an extended mean-field approach that can also include both orientational and spatial correlation effects of molecules is proposed for the nematic liquid crystals. Unlike the orientation-averaged spatial correlation theory, in this extended mean-field theory one need not resort to the decoupling of the distribution functions of molecules as was adopted in the orientation-averaged spatial correlation theory, so the spatial correlation effects of molecules are included in a more self-consistent way in this extended mean-field theory. It is found that the results of this extended mean-field theory are in good agreement with experiment observations [21]. Recently, an extended Landau–de Gennes phenomenon theory of the nematic-isotropic phase transition was also developed to include the coupling of the density and order parameter and it is found that most of the experimental measurements can be reproduced reasonably well [22]. These studies show that the short-range spatial correlations of molecules may have some significant effects on some physical properties of liquid crystals and should be taken into account in some aspects. The extended mean-field approach proposed in Ref. [21] can include both orientation and spatial correlation effects of molecules, but the theoretical formulation established in Ref. [21] is only suitable for the nematic liquid crystals and cannot be applied to the smectic liquid crystals that have layered structures.

In this paper, we will generalize the extended mean-field approach developed in Ref. [21] to the case of the smectic liquid crystals that have layered structures, and we will apply this extended mean-field approach to study the smectic-*C* to smectic-*A* orientational transitions. Our main purpose is to see whether the short-range spatial correlations of molecules may have some effects on the basic features of the smectic-*C* to smectic-*A* orientational transitions. The paper will be organized as follows: In Sec. II, we will first introduce briefly the theoretical model and a simplified pairwise molecular potential will be adopted. Based on the adopted model potential, we will establish the basic formulas of the extended mean-field theory. A set of mean-field parameters are introduced and the corresponding self-consistency equations are derived. In Sec. III, we will apply the basic formulas established in Sec. II to study the smectic-*C* to smectic-*A* orientational transitions.

II. MODEL AND EXTENDED MEAN-FIELD THEORY

In this paper, we assume that liquid crystals are composed of axially symmetric elongated hard-rod-like organic molecules, as is usually assumed in many other molecular theories of liquid crystals [1]. It has been powerfully argued that the most general form of the interparticle interaction potential between a pair of such molecules at positions $\vec{r}_i$ and $\vec{r}_j$ with orientations $\vec{\Omega}_i$ and $\vec{\Omega}_j$ is a function of five variables [23–25]: r_{ij}, $\vec{\Omega}_i\cdot\vec{r}_{ij}$, $\vec{\Omega}_j\cdot\vec{r}_{ij}$, $\vec{\Omega}_i\cdot\vec{\Omega}_j$, and $\vec{\Omega}_i\times\vec{\Omega}_j\cdot\vec{r}_{ij}$. The pseudoscalar $\vec{\Omega}_i\times\vec{\Omega}_j\cdot\vec{r}_{ij}$ offers a selection between two signs, it gives rise to a chiral term. Assuming that the molecules are nonchiral, we need not consider the latter, so we can adopt the following pairwise potential:

$$\begin{aligned}V(\vec{r}_i,\vec{\Omega}_i,\vec{r}_j,\vec{\Omega}_j)=&V_0(r_{ij})+V_1(r_{ij})P_2(\vec{\Omega}_i\cdot\vec{\Omega}_j)\\&+V_2(r_{ij})[P_2(\vec{\Omega}_i\cdot\vec{r}_{ij})+P_2(\vec{\Omega}_j\cdot\vec{r}_{ij})]\\&+V_3(r_{ij})P_2(\vec{\Omega}_i\cdot\vec{r}_{ij})P_2(\vec{\Omega}_j\cdot\vec{r}_{ij}),\end{aligned}\tag{1}$$

where $P_2(x)$ denotes the Legendre polynomial of second order. The higher-order terms such as $P_4(\vec{\Omega}_i\cdot\vec{\Omega}_j)$, $P_4(\vec{\Omega}_i\cdot\vec{r}_{ij})$, $P_4(\vec{\Omega}_j\cdot\vec{r}_{ij})$, etc., have been neglected in Eq. (1). It has been argued such a pairwise potential is suitable for describing the interparticle interactions between a pair of axially symmetric hard-rod-like elongated molecules that do not have permanent dipole moments [23–25].

In order to characterize the structures of the smectic liquid crystals, one must introduce some order parameters. In the smectic liquid crystals, there are two kinds of orders, one is the orientation order of molecules, the other is the position order of molecules due to the layered structure. To characterize the orientation order of molecules, one usually defines the orientation order parameter $\overline{\sigma}$ as $\overline{\sigma}=\langle P_2(\vec{\Omega}\cdot\vec{n})\rangle$, where the unit vector $\vec{\Omega}$ denotes the orientations of the molecular long axis, and the unit vector $\vec{n}$ denotes the director of molecules, i.e., the averaged orientation of the molecular long axis. The symbol $\langle\cdots\rangle$ denotes the statistical averaged values. In the smectic-*A* phase, the director $\vec{n}$ is parallel to the *z*-axis, i.e., the normal of the layer plane. In the smectic-*C* phase, the director $\vec{n}$ tilts over with respect to the normal of the layer plane. In the following, we will denote the tilt angle of the director $\vec{n}$ as $\overline{\theta}$ (its azimuthal angle is taken to be zero).

Strictly speaking, in addition to the orientation order parameter $\overline{\sigma}$, one needs to introduce another orientation order parameter for the smectic-*C* mesophase to characterize the anisotropy in the orientations of the transverse molecular axes, i.e., the biaxial order parameter Δ. But experimental observations have shown that the biaxial order parameter Δ in the smectic-*C* mesophase is rather small (the magnitude of Δ is the order of 10^{-2}); for simplicity, we will neglect the small biaxiality of the smectic-*C* mesophase in this paper. This negligence will not change the basic features of the present theory. The effects of the small biaxiality of the smectic-*C* mesophase will be discussed elsewhere. In order to characterize the stratified structures of the smectic mesophases, one usually defines a position order parameter $\overline{\tau}$ [1]. As usual, we define $\overline{\tau}$ as $\overline{\tau}=\langle\cos(2\pi z/d)\rangle$, where d is the thickness of the layers. Using the two order parameters $\overline{\sigma}$, $\overline{\tau}$ and the tilt angle $\overline{\theta}$ of the director $\vec{n}$ of molecules, the mesophases of the system can be divided into four as follows: (1) $\overline{\sigma}=\overline{\tau}=\overline{\theta}=0$, no order characteristic of the isotropic liquid phase; (2) $\overline{\sigma}\neq 0,\overline{\tau}=\overline{\theta}=0$, orientational order only characteristic of the nematic phase; (3) $\overline{\sigma}\neq 0,\overline{\tau}\neq 0,\overline{\theta}=0$, both orientational and positional order, and the director is normal to the layer plane; this is characteristic of the smectic-*A* phase. (4) $\overline{\sigma}\neq 0,\overline{\tau}\neq 0,\overline{\theta}\neq 0$, both orientational and positional order, and the director tilts over with respect to the normal of the layer plane; this is characteristic of the smectic-*C* phase.

To establish the extended mean-field theory based on the adopted model potential (1), unlike the traditional MS type of mean-field approximation, we will follow the approach of Lennard-Jones and Devonshire [18–19]. In LJD's mean-field treatment of isotropic liquids, they assume that the system consists of *N* particles moving in a volume *V*, which is divided in some regular way into *N* equal cells each of volume v^*, and each particle is confined to one of these cells. Each particle will be moving in the field of the others, which will vary with time, and to obtain the partition function for the individual particle one can replace this field by some suitable average. The simplest assumption one can make is that the average field in which one molecule moves is that due to its immediate neighbors. This procedure has been followed in some detail by LJD [18–19]. Following their approach, we generalize LJD's calculation to the case of the stratified smectic liquid crystals with the anisotropic interparticle interaction potential of Eq. (1). Considering the stratified structures of the smectic-*A* and -*C* mesophases, we assume that each molecule moves in an upright cylindrical cell whose radius is $\frac{1}{2}a$ and length is $\frac{1}{2}d$, where *a* is the averaged separation distance between two intralayer nearest-neighboring molecules and *d* is the averaged separation distances between two interlayer nearest-neighboring molecules (equal to the thickness of the layer). The centers of the upright cylindrical cells that belong to the same layer will sit on the same plane perpendicular to the *z*-axis (i.e., the normal of the layer plane). According to this assumption, each of the molecules have two types of immediate neighbors, namely, that the intralayer and interlayer immediate neighbors. In the following, we will establish a set of local Cartesian coordinate axes at each cell *i* with the origin of the coordinates being the centers of the cells. The position vector $\vec{r}_i$ of the mass center of molecule *i* can be specified by a local position vector $\vec{\xi}_i$: $\vec{r}_i=\vec{R}_i+\vec{\xi}_i$, where $\vec{R}_i$ is the position vector of the center of cell *i* and $\vec{\xi}_i=(x_i,y_i,z_i)$ is the local position vector of the mass center of molecule *i* relative to the center of cell *i*. We further perform a coordinate transformation: $x_i=a\rho_i\sin\alpha_i\cos\beta_i$, $y_i=a\rho_i\sin\alpha_i\sin\beta_i$, $z_i=d\rho_i\cos\alpha_i$, where $0\leqslant\rho_i\leqslant\frac{1}{2}$, $0\leqslant\alpha_i\leqslant\pi$, $0\leqslant\beta_i\leqslant 2\pi$.

Now we can derive the mean field experienced by one molecule denoted as molecule *i* due to its immediate neighbors by generalizing the LJD calculation to two molecules with the anisotropic interaction potential of Eq. (1). The main point of our generalization is to allow molecule *i*'s immediate neighbors (denoted as molecule *j*) also to deviate from their respective equilibrium positions (the centers of the cells), and considering the cylindrical symmetry of the distributions of the mass centers of molecules in the cells, we can assume that the pairwise potential $V(\vec{r}_i,\vec{\Omega}_i,\vec{r}_j,\vec{\Omega}_j)$ can be replaced equivalently by an effectively averaged pairwise potential $V_{\text{eff}}(\rho_i,\alpha_i,\Theta_i,\Phi_i;\rho_j,\alpha_j,\Theta_j,\Phi_j)$, which is independent of the azimuthal angles β_i and β_j:

$$V_{\text{eff}}(\rho_i,\alpha_i,\Theta_i,\Phi_i,\rho_j,\alpha_j,\Theta_j,\Phi_j)=\frac{1}{(2\pi)^2}\int d\beta_i d\beta_j V(\vec{r}_i,\vec{\Omega}_i,\vec{r}_j,\vec{\Omega}_j), \tag{2}$$

where $(\Theta_i,\Phi_i),(\Theta_j,\Phi_j)$ are the polar and azimuthal angles of $\vec{\Omega}_i$ and $\vec{\Omega}_j$ relative to the *z*-axis, respectively, i.e., $\vec{\Omega}=(\sin\Theta\cos\Phi,\sin\Theta\sin\Phi,\cos\Theta)$. This effectively averaged pairwise potential V_{eff} depends on the forms of $V_0(r_{ij})$ $V_1(r_{ij})$, $V_2(r_{ij})$, and $V_3(r_{ij})$ [see Eq. (1)]. The accurate forms of $V_0(r_{ij})$, $V_1(r_{ij})$, $V_2(r_{ij})$, and $V_3(r_{ij})$ are very difficult to determine. In order to simplify the calculations, the Gaussian forms are usually adopted in the literature [25,26]. As usual, we choose them to be the following Gaussian forms:

$$\begin{aligned}V(\vec{r},\vec{\Omega}_i,\vec{r}_j,\vec{\Omega}_j)={}&v_0\exp(-r_{ij}^2/r_0^2)[-\delta-P_2(\vec{\Omega}_i\cdot\vec{\Omega}_j)\\&+\epsilon_1P_2(\vec{\Omega}_i\cdot\vec{r}_{ij})+\epsilon_1P_2(\vec{\Omega}_j\cdot\vec{r}_{ij})]\\&-\epsilon_2P_2(\vec{\Omega}_i\cdot\vec{r}_{ij})P_2(\vec{\Omega}_j\cdot\vec{r}_{ij})].\end{aligned} \tag{3}$$

For the above adopted forms of the pairwise potential, the integral in Eq. (2) cannot be carried out analytically. But we note that the possibility for the mass center of molecule *i* (or *j*) to be sited at the center of the cell *i* (or *j*) is optimum; we can expand the pairwise potential $V(\vec{r}_i,\vec{\Omega}_i,\vec{r}_j,\vec{\Omega}_j)$ into a series of the relative position vectors $\vec{\xi}_i$ and $\vec{\xi}_j$. If molecules *i* and *j* are the intralayer immediate neighbors, by this procedure we get

$$\begin{aligned}V_{\text{eff}}(\rho_i,\alpha_i,\Theta_i,\Phi_i;\rho_j,\alpha_j,\Theta_j,\Phi_i)={}&v_0\delta[l_1(\rho_i^2,\rho_i^4,\rho_j^2,\rho_j^4)-m_1(\rho_i^2,\rho_j^2)q(\cos^2\alpha_i,\cos^2\alpha_j)]+v_0[l_2(\rho_i^2,\rho_i^4,\rho_j^2,\rho_j^4)\\&-m_2(\rho_i^2,\rho_j^2)q(\cos^2\alpha_i,\cos^2\alpha_j)]P_2(\cos\Theta_{ij})+v_0\epsilon_1[l_3(\rho_i^2,\rho_i^4,\rho_j^2,\rho_j^4)\\&-m_3(\rho_i^2,\rho_j^2)q(\cos^2\alpha_i,\cos^2\alpha_j)][P_2(\cos\Theta_i)+P_2(\cos\Theta_j)]\\&-v_0\epsilon_2[l_4(\rho_i^2,\rho_i^4,\rho_j^2,\rho_j^4)-m_4(\rho_i^2,\rho_j^2)q(\cos^2\alpha_i,\cos^2\alpha_j)]P_2(\cos\Theta_i)P_2(\cos\Theta_j),\end{aligned} \tag{4}$$

where $\cos\Theta_{ij}=\vec{\Omega}_i\cdot\vec{\Omega}_j$, $\cos\Theta_i=\vec{\Omega}_i\cdot\vec{z}$, $\cos\Theta_j=\vec{\Omega}_j\cdot\vec{z}$, $\vec{z}$ is the unit vector along the *z* axis. The functions $l_n(\rho_i^2,\rho_i^4,\rho_j^2,\rho_j^4)$ and $q(\cos^2\alpha_i,\cos^2\alpha_j)$ are expressed as follows:

$$q(\cos^2\alpha_i,\cos^2\alpha_j)=\cos^2\alpha_i+\cos^2\alpha_j-3\cos^2\alpha_i\cos^2\alpha_j, \tag{5}$$

$$l_n(\rho_i^2,\rho_i^4,\rho_j^2,\rho_j^4)=a_n+b_n(\rho_i^2+\rho_j^2)+c_n\rho_i^2\rho_j^2+d_n(\rho_i^4+\rho_j^4)\quad(n=1,2,3,4), \tag{6}$$

$$m_n(\rho_i^2,\rho_j^2)=e_n\rho_i^2\rho_j^2\quad(n=1,2,3,4), \tag{7}$$

in which a_n, b_n, c_n, d_n, e_n $(n=1,2,3,4)$ are constant coefficients that depend only on the model parameters but are independent of the orientational and spatial coordinates of molecules. The higher-order terms of ρ^4 have been neglected in Eqs. (4)–(7). If molecule j is the interlayer immediate neighbor of molecule i, the effectively averaged pairwise potential has a form similar to that of Eq. (4) except that the coefficients a_n, b_n, c_n, d_n, e_n, $(n=1,2,3,4)$ are different. After obtaining this effectively averaged pairwise potential V_{eff}, the mean-field potential V_{mf} experienced by molecule i due to all its immediate neighbors are easily obtained by directly averaging over the coordinates of molecule j:

$$\begin{aligned}V_{\text{mf}}(\rho_i,\alpha_i,\Theta_i,\Phi_i)=&\sum_j{}' \langle V_{\text{eff}}(\rho_i,\alpha_i,\Theta_i,\Phi_i;\rho_j,\alpha_j,\Theta_j,\Phi_j)\rangle_j=\sum_j{}' v_0\delta[\langle l_1(\rho_i^2,\rho_i^4,\rho_j^2,\rho_j^4)\rangle_j\\&-\langle m_1(\rho_i^2,\rho_j^2)q(\cos^2\alpha_i,\cos^2\alpha_j)\rangle_j]+v_0[\langle l_2(\rho_i^2,\rho_i^4,\rho_j^2,\rho_j^4)\rangle_j\\&-\langle m_2(\rho_i^2,\rho_j^2)q(\cos^2\alpha_i,\cos^2\alpha_j)\rangle_j]\langle P_2(\cos\Theta_{ij})\rangle_j+v_0\epsilon_1[\langle l_3(\rho_i^2,\rho_i^4,\rho_j^2,\rho_j^4)\rangle_j\\&-\langle m_3(\rho_i^2,\rho_j^2)q(\cos^2\alpha_i,\cos^2\alpha_j)\rangle_j][P_2(\cos\Theta_i)+\langle P_2(\cos\Theta_j)\rangle_j]\\&-v_0\epsilon_2[\langle l_4(\rho_i^2,\rho_i^4,\rho_j^2,\rho_j^4)\rangle_j-\langle m_4(\rho_i^2,\rho_j^2)q(\cos^2\alpha_i,\cos^2\alpha_j)\rangle_j]P_2(\cos\Theta_i)\langle P_2(\cos\Theta_j)\rangle_j,\end{aligned}\tag{8}$$

where the sum $\Sigma_j'\{\cdots\}$ includes only the immediate neighbors, and $\langle\cdots\rangle_j$ means that the quantities related to molecule j are replaced by their statistical averaged values. To carry out the statistical average over the orientation coordinates of molecule j, we assume that the orientation distributions of the molecular long axes (i.e., the orientation vectors $\vec{\Omega}$ of molecules) are rotational symmetrical around their averaged orientations (i.e., the director $\vec{n}$ of molecules); this assumption should be a good approximation considering that the biaxiality of the smectic-C mesophase is rather small. Within this approximation, we have the following relations:

$$\begin{aligned}\langle P_2(\cos\Theta_j)\rangle_j=&\langle P_2(\vec{\Omega}_j\cdot\vec{z})\rangle_j=P_2(\vec{z}\cdot\vec{n})\langle P_2(\vec{\Omega}_j\cdot\vec{n})\rangle_j\\=&P_2(\cos\overline{\theta})\langle P_2(\vec{\Omega}_j\cdot\vec{n})\rangle_j,\end{aligned}\tag{9}$$

$$\begin{aligned}\langle P_2(\cos\Theta_{ij})\rangle_j=&\langle P_2(\vec{\Omega}_i\cdot\vec{\Omega}_j)\rangle_j=P_2(\vec{\Omega}_i\cdot\vec{n})\langle P_2(\vec{\Omega}_j\cdot\vec{n})\rangle_j\\=&[P_2(\cos\overline{\theta})P_2(\vec{\Omega}_i\cdot\vec{z})\\&+\tfrac{3}{4}\sin 2\overline{\theta}\sin 2\Theta_i\cos\Phi_i\\&-\tfrac{3}{8}\sin^2\overline{\theta}\cos 2\Theta_i\cos 2\Phi_i\\&+\tfrac{3}{8}\sin^2\overline{\theta}\cos 2\Phi_i]\langle P_2(\vec{\Omega}_j\cdot\vec{n})\rangle_j.\end{aligned}\tag{10}$$

In obtaining the above relations, we have used the following equation: $P_n(\cos\Theta_{AB})=P_n(\cos\Theta_A)P_n(\cos\Theta_B)+2\Sigma_{m=1}^n\{[(n-m)!]/[(m+n)!]\}P_n^m(\cos\Theta_A)P_n^m(\cos\Theta_B)\cos m(\Phi_{A-\Phi_B})$,where Θ_{AB} is the cross angle between vector $\vec{A}$ and vector $\vec{B}$; (Θ_A,Φ_A) and (Θ_B,Φ_B) are, respectively, the polar and azimuthal angles of vector $\vec{A}$ and vector $\vec{B}$ relative to the same reference axis. This equation is also used in deriving Eq. (4). Using Eqs. (9) and (10), and removing the subscript i and j from the expressions due to translational invariance, the mean-field potential V_{mf} can be expressed as

$$\begin{aligned}V_{\text{mf}}(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})=&v_0\delta g_1(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})\\&+v_0 g_2(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})\\&+v_0\epsilon_1 g_3(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})\\&+v_0\epsilon_2 g_4(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\}),\end{aligned}\tag{11}$$

where $\{\overline{\varsigma_l}\}\equiv\{\overline{\sigma},\overline{\theta},\overline{\cos^2\alpha},\overline{\rho^2},\overline{\rho^4}\}$, in which $\overline{\varsigma_1}\equiv\overline{\sigma}\equiv\langle P_2(\vec{\Omega}_j\cdot\vec{n})\rangle$, $\overline{\varsigma_2}\equiv\overline{\theta}$, $\overline{\varsigma_3}\equiv\overline{\cos^2\alpha_j}\equiv\langle\cos^2\alpha_j\rangle$, $\overline{\varsigma_4}\equiv\overline{\rho_j^2}\equiv\langle\rho_j^2\rangle$, $\overline{\varsigma_5}\equiv\overline{\rho_j^4}\equiv\rho_j^4$. All these statistical averaged values are assumed to be site independent due to translational invariance. The functions $g_0(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})$, $g_1(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})$, $g_2(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})$, and $g_3(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})$ are defined as follows:

$$\begin{aligned}g_1(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})=&l_{11}(\rho^2,\rho^4,\overline{\rho^2},\overline{\rho^4})\\&-m_{22}(\rho^2,\rho^4,\overline{\rho^2},\overline{\rho^4})q(\cos^2\alpha,\overline{\cos^2\alpha}),\end{aligned}\tag{12}$$

$$\begin{aligned}g_2(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})=&[l_{22}(\rho^2,\rho^4,\overline{\rho^2},\overline{\rho^4})-m_{22}(\rho^2,\rho^4,\overline{\rho^2},\overline{\rho^4})\\&\times q(\cos^2\alpha,\overline{\cos^2\alpha})]\\&\times\overline{\sigma}[P_2(\cos\overline{\theta})P_2(\cos\Theta)\\&+\tfrac{3}{4}\sin 2\overline{\theta}\sin 2\Theta\cos\Phi\\&-\tfrac{3}{8}\sin^2\overline{\theta}\cos 2\Theta\cos 2\Phi\\&+\tfrac{3}{8}\sin^2\overline{\theta}\cos 2\Phi],\end{aligned}\tag{13}$$

$$\begin{aligned}g_3(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})=&[l_{33}(\rho^2,\rho^4,\overline{\rho^2},\overline{\rho^4})-m_{33}(\rho^2,\rho^4,\overline{\rho^2},\overline{\rho^4})\\&\times q(\cos^2\alpha,\overline{\cos^2\alpha})][P_2(\cos\Theta)\\&+\overline{\sigma}P_2(\cos\overline{\theta})],\end{aligned}\tag{14}$$

$$\begin{aligned}g_4(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})=&[l_{44}(\rho^2,\rho^4,\overline{\rho^2},\overline{\rho^4})-m_{44}(\rho^2,\rho^4,\overline{\rho^2},\overline{\rho^4})\\&\times q(\cos^2\alpha,\overline{\cos^2\alpha})]\\&\times\overline{\sigma}P_2(\cos\overline{\theta})P_2(\cos\Theta),\end{aligned}\tag{15}$$

in which

$$l_{nn}(\rho^2,\rho^4,\overline{\rho^2},\overline{\rho^4})=\sum_j{}' \; l_n(\rho_i^2,\rho_i^4,\overline{\rho_j^2},\overline{\rho_j^4}), \quad (n=1,2,3,4), \tag{16}$$

$$m_{nn}(\rho^2,\overline{\rho^2})=\sum_j{}' \; m_n(\rho_i^2,\overline{\rho_j^2}), \quad (n=1,2,3,4), \tag{17}$$

where we have removed the subscripts *i* and *j* in the left sides of Eqs. (15) and (16) due to translational invariance. We can see that there are five unknown mean-field parameters $\overline{\sigma},\overline{\theta},\overline{\cos^2\alpha},\overline{\rho^2},\overline{\rho^4}$ in the mean-field potential V_{mf}. The mean-field parameters $\overline{\sigma},\overline{\cos^2\alpha},\overline{\rho^2},\overline{\rho^4}$ should be determined by the following self-consistency equations:

$$\begin{aligned}\overline{\sigma}=\langle P_2(\vec{\Omega}\cdot\vec{n})\rangle=&\int_0^{1/2}\rho^2 d\rho\int_0^{\pi}\sin\alpha d\alpha\int_0^{\pi}\sin\Theta d\Theta\\ &\times\int_0^{2\pi}d\Phi f(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})[P_2\cos\overline{\theta})P_2(\cos\Theta)\\ &+\tfrac{3}{4}\sin 2\overline{\theta}\sin2\Theta\cos\Phi+\tfrac{3}{8}\sin^2\overline{\theta}\cos 2\Phi\\ &-\tfrac{3}{8}\sin^2\overline{\theta}\cos 2\Theta\cos 2\Phi],\end{aligned} \tag{18}$$

$$\begin{aligned}\overline{\cos^2\alpha}=&\int_0^{1/2}\rho^2 d\rho\int_0^{\pi}\sin\alpha d\alpha\int_0^{\pi}\sin\Theta d\Theta\\ &\times\int_0^{2\pi}d\Phi\cos^2\alpha f(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\}),\end{aligned} \tag{19}$$

$$\begin{aligned}\overline{\rho^2}=&\int_0^{1/2}\rho^2 d\rho\int_0^{\pi}\sin\alpha d\alpha\int_0^{\pi}\sin\Theta d\Theta\\ &\times\int_0^{2\pi}d\Phi\rho^2 f(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\}),\end{aligned} \tag{20}$$

$$\begin{aligned}\overline{\rho^4}=&\int_0^{1/2}\rho^2 d\rho\int_0^{\pi}\sin\alpha d\alpha\int_0^{\pi}\sin\Theta d\Theta\\ &\times\int_0^{2\pi}d\Phi\rho^4 f(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\}),\end{aligned} \tag{21}$$

where

$$f(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})=\frac{1}{N}\exp[-\beta V_{\mathrm{mf}}(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\})], \tag{22}$$

$$\begin{aligned}N=&\int_0^{1/2}\rho^2 d\rho\int_0^{\pi}\sin\alpha d\alpha\int_0^{\pi}\sin\Theta d\Theta\\ &\times\int_0^{2\pi}d\Phi\exp[-\beta V_{\mathrm{mf}}(\rho,\alpha,\Theta,\Phi,\{\overline{\varsigma_l}\}].\end{aligned} \tag{23}$$

The tilt angle $\overline{\theta}$ should be determined by the minimization condition of the free energy *F*:

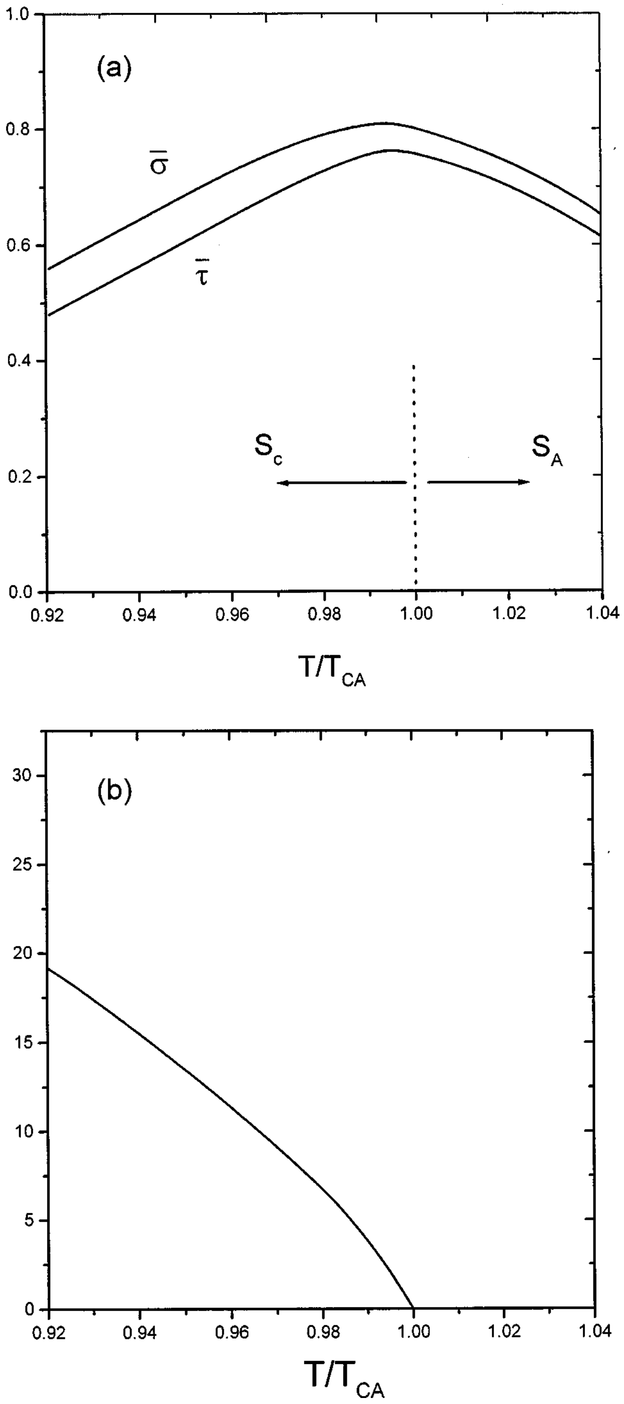

FIG. 1. (a) The temperature dependences of the order parameters $\overline{\sigma}$ and $\overline{\tau}$ for model parameters $d/r_0=2.36$, $a/r_0=0.96$, $\delta=0.64$, $\epsilon_1=0.042$, and $\epsilon_2=0.016$. (v_0 is taken to be unity). (b) The corresponding temperature dependence of the tilt angle $\overline{\theta}$ of the director.

$$\partial F/\partial\overline{\theta}=0, \quad \partial^2 F/\partial\overline{\theta}^2>0, \tag{24}$$

in which the free energy *F* can be calculated through the following relations:

$$F=\frac{1}{2}\sum_i\langle V_{\mathrm{mf}}(\rho_i,\alpha_i,\Theta_i,\Phi_i,\{\overline{\varsigma_l}\})\rangle-TS, \tag{25}$$

$$S=-k\sum_i \langle \ln f(\rho_i,\alpha_i,\Theta_i,\Phi_i,\{\overline{\varsigma_l}\})\rangle. \qquad (26)$$

Equations (18)–(21) and (24) constitute a set of complete simultaneous equations. From these self-consistent equations, we can obtain the values of the unknown mean-field parameters $\{\overline{\varsigma_l}\}$. After these mean-field parameters are obtained, the mean-field potential $V_{\rm mf}$ can be determined, then the order parameters $\overline{\sigma},\overline{\tau}$, the tilt angle $\overline{\theta}$ of the director $\vec{n}$, and the thermodynamic quantities such as the free energy, entropy, specific heat, etc., can be calculated.

III. NUMERICAL RESULTS AND DISCUSSIONS

In Sec. II, we have established the basic formulas of this extended mean-field molecular theory. The main difference between this extended mean-field molecular theory and the MS type of mean-field molecular theories is that both orientational and spatial correlation effects of molecules are taken into account in this extended mean-field theory. This extended mean-field approach is also significantly different from the orientation-averaged spatial correlation function method [20]. In this extended mean-field theory, to take into account the spatial correlation effects of molecules one need not resort to the decoupling of the distribution functions of molecules, so the spatial correlation effects of molecules are included in a more self-consistent way in this extended mean-field theory. In order to see whether this type of mean-field theory can describe the basic features of the smectic-*C* to smectic-*A* orientational transitions, we have done some numerical calculations. Due to the fact that there is much uncertainty in the choices of the model potential, including the model parameters, as well as to the fact that the main purpose of this paper is only to see whether this type of mean-field theory can describe the basic features of the smectic-*C* to smectic-*A* orientational transitions, we will not try to compare the numerical results with the experiment data quantitatively; the detailed comparison between the theoretical results of this extended mean-field theory and the experiment data will be moved too late. In this paper we will focus on the main qualitative features of this extended mean-field theory. We have carried out the numerical calculations for a number of model parameters, and we note that while the main features of this extended mean-field theory are similar to that of the MS type of mean-field theories, this extended mean-field theory does have some new features arising from the spatial correlation effects of molecules.

In Figs. 1 and 2 we have plotted two typical calculated temperature dependences of the tilt angle of the director and the order parameters in the vicinity of the smectic-*C* to smectic-*A* orientational transition point T_{CA}. Like the previous mean-field molecular theories of Refs. [2–5], this extended mean-field theory predicts that a second-order smectic-*C* to smectic-*A* orientational transition may occur as temperature increasing, as is shown in Fig. 1. From Fig. 1, we can see that the tilt angle $\overline{\theta}$ of the director of molecules decreases continuously to zero as temperature increases to the transition point T_{CA}. Correspondingly, the order parameters $\overline{\sigma}$ and $\overline{\tau}$ also vary continuously in the vicinity of the transition point T_{CA}. The calculated temperature dependences of the tilt angle and the order parameters are in qualitative agreement with the experimental results [11–14]. This type of temperature behaviors of the order parameters and the tilt angle are characteristic of a second-order smectic-*C* to smectic-*A* orientational transition. But unlike the mean-field molecular theories of Refs. [2–5], this extended mean-field theory also predicts that the discontinuous (first-order)

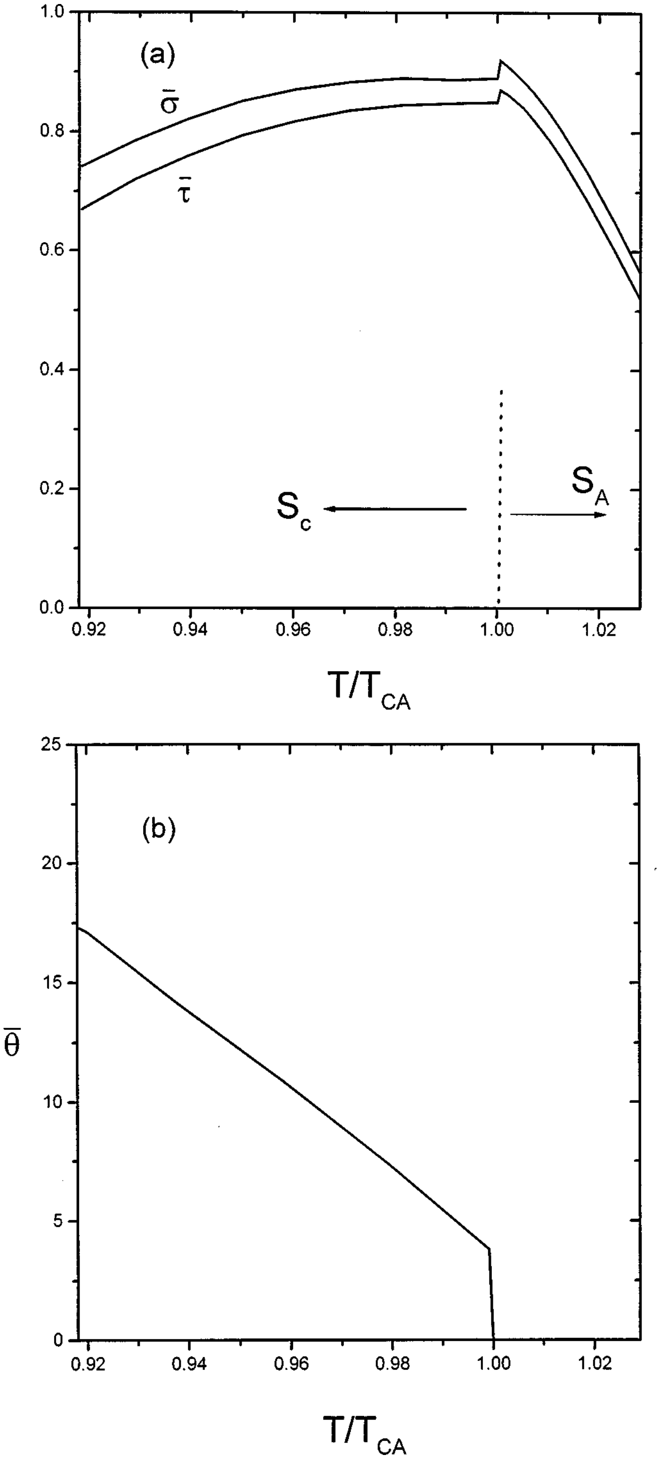

FIG. 2. (a) The temperature dependences of the order parameters $\overline{\sigma}$ and $\overline{\tau}$ for model parameters $d/r_0=2.28$, $a/r_0=0.92$, $\delta=0.60$, $\epsilon_1=0.05$, and $\epsilon_2=0.004$. (v_0 is taken to be unity). (b) The corresponding temperature dependence of the tilt angle $\overline{\theta}$ of the director.

smectic-C to smectic-A orientational transitions may also occur, as is shown in Fig. 2. This is in agreement with experimental observations that have established that both second-order [11–14] and first-order [15] smectic-C to smectic-A orientational transitions may occur. From Fig. 2, we can see that as the temperature increases, the tilt angle of the director of molecules decreases gradually, but it jumps to zero at the transition point T_{CA}. Correspondingly, the order parameters $\overline{\sigma}$ and $\overline{\tau}$ also vary discontinuously at the transition point T_{CA}. This type of temperature behavior of the tilt angle and the order parameters is characteristic of a first-order smectic-C to smectic-A orientational transition. From Figs. 1 and 2, we can see that before the smectic-C to smectic-A orientational transitions occurs, the orientation order parameter $\overline{\sigma}$ increases as temperature increasing in the smectic-C mesophase (i.e., in the temperature range of $T<T_{CA}$), and decreases as temperature increasing in the smectic-A mesophase (i.e., in the temperature range of $T>T_{CA}$); this is also in agreement with experimental observations [16] but in contrast with the results of the mean-field molecular theories of Refs. [2–5] which predicts that the order parameters $\overline{\sigma}$ decreases as temperature increasing in the both temperature ranges of $T<T_{CA}$ and $T>T_{CA}$. These results indicate that the spatial correlations of molecules may have some non-negligible effects on the basic features of the smectic-C to smectic-A orientational transitions and should not be neglected completely.

In conclusion, we have established an extended mean-field molecular theory for the smectic-C to smectic-A orientational transitions. In this extended mean-field theory both orientational and spatial correlation effects of molecules are taken into account, and the spatial thermal fluctuation effects of molecules are included in a self-consistent way. While the orientation correlations effects of molecules may play the dominant role in determining the basic physical properties of liquid crystals, the short-range spatial correlations of molecules may have some effects in some aspects and should not be neglected completely. In these aspects, the extended mean-field approximation method introduced in this paper may be useful considering that it can include both orientational and spatial correlation effects of molecules. Of course, the molecular model adopted in this paper is idealized, for further improvements, a more realistic molecular model may be needed.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation of China under Grant No.19334042, and a grant from the National Education Commission.

---

[1] See, for example, P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974); S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, 1977); *Introduction to Liquid Crystals*, edited by E. B. Priestly, P. J. Wojtowicz, and P. Sheng (Plenum, New York, 1974).
[2] W. L. McMillan, Phys. Rev. A **8**, 1921 (1973).
[3] A. Wulf, Phys. Rev. A **11**, 365 (1975).
[4] A. Wulf, Phys. Rev. A **17**, 2077 (1978).
[5] D. Cabib and L. Benguigui, J. Phys. (Paris) **38**, 419 (1977).
[6] H. Luz, R. C. Hewitt, and S. Meiboom, J. Chem. Phys. **61**, 1758 (1974).
[7] H. Hervet, F. Volino, A. J. Dianoux, and R. E. Lechner, J. Phys. (Paris) **35**, L-151 (1974).
[8] D. Johnson and A. Saupe, Phys. Rev. A **15**, 2079 (1977).
[9] P. J. Bos, J. Pirs, P. Ukleja, J. W. Doane, and M. E. Neubert, Mol. Cryst. Liq. Cryst. **40**, 59 (1979).
[10] J. Seliger, R. Osredhar, V. Zagar, and R. Blinc, Phys. Rev. Lett. **38**, 411 (1977).
[11] M. Meichle and C. W. Garland, Phys. Rev. A **27**, 2624 (1983).
[12] E. K. Hobbie and C. C. Huang, Phys. Rev. A **36**, 5459 (1987).
[13] N. V. S. Rao and V. G. K. M. Pistipati, Mol. Cryst. Liq. Cryst. **104**, 301 (1984).
[14] R. Birgeneau *et al.*, Phys. Rev. A **27**, 1251 (1983).
[15] S. Kumar, Phys. Rev. A **23**, 3207 (1981).
[16] A. J. Leadbetter and P. G. Write, J. Phys. Colloq. **40**, C3-234 (1979).
[17] W. Maier and A. Saupe, Z. Naturforsch. A **14a**, 882 (1959); **15a**, 287 (1960).
[18] J. E. Lennard-Jones, Proc. Phys. Soc. London **43**, 461 (1931).
[19] J. E. Lennard-Jones and A. F. Devonshire, Proc. R. Soc. London **163**, 53 (1937).
[20] V. T. Rajan and C.-W. Woo, Phys. Rev. A **17**, 382 (1978).
[21] R. B. Tao, P. Sheng and Z. F. Lin, Phys. Rev. Lett. **70**, 1271 (1993).
[22] P. K. Mukherjee, T. R. Bose, D. Ghose, and M. Saha, Phys. Rev. E **51**, 4570 (1995).
[23] C. W. Oseen, Trans. Faraday Soc. **29**, 883 (1933).
[24] Y. R. Lin-Liu, Y. M. Shih, and C.-W. Woo, Phys. Rev. A **14**, 445 (1976).
[25] L. Senbetu and C.-W. Woo, Phys. Rev. A **17**, 1529 (1978).
[26] W. L. McMillan, Phys. Rev. A **4**, 1238 (1971); **6**, 936 (1972).