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Abstract

The period of the layered structure in smectic A and smectic C liquid crystal phases has been calculated numerically by direct minimization of the mean-field free energy which takes into account the interaction between molecules in adjacent smectic layers. The smectic layer spacing is calculated for two systems characterized by conventional and anomalously weak layer contraction in the smectic C phase. It is then compared with the simple estimate based on the average projection of the molecular long axis on the smectic layer normal. For both systems, temperature variation of the average molecular projection is qualitatively similar to that of the calculated layer spacing although certain quantitative deviations exist.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Liquid crystal soft matter materials form a number of smectic phases with orientational and partial translational order of anisotropic molecules. In the smectic C (SmC) phase and other tilted smectic phases the predominant orientation of primary molecular axes, specified by the director $\mathbf{n}$, is tilted with respect to the smectic layer normal $\mathbf{k}$ by an angle Θ. Tilted smectic phases exist also in other soft matter systems including, in particular, mesogenic polymers and SmC elastomers [1–3].

If at least a part of the molecules in the SmC phase are chiral, the phase appears to be ferroelectric. In each smectic layer the polarization is induced by the tilt in the direction perpendicular to the tilt plane. There exist also smectic phases where the direction of the tilt changes strongly from layer to layer [4]. In particular, in the anticlinic smectic C_A^* phase the direction of the tilt and the polarization alternate from layer to layer and, as a result, the phases possess antiferroelectric properties. In the frustration region between ferro- and antiferroelectric phases some smectic materials exhibit the so-called intermediate phases with periodicity of three or four layers. In all these tilted phases the energy associated with the coupling of directors in adjacent layers is much smaller than the energy of the tilt inside one layer. Ferroelectric and antiferroelectric liquid crystals are considered to be very promising materials for applications in new electro-optic devices, and they are already used in camcorders, etc.

When a liquid crystal undergoes a transition from the orthogonal smectic A (SmA) phase to the tilted SmC phase, the layer spacing d usually decreases by a factor of $\cos \Theta$ [5, 6]. This layer shrinkage appears to be a very negative factor in manufacturing and operation of electro-optic devices based on ferro- and antiferroelectric smectic C^* liquid crystals. The layer contraction leads to the development of chevron structures accompanied by the formation of the so-called 'zigzag' defects which seriously degrade the quality of electro-optic devices. Fortunately, different materials show varying degrees of contraction across the SmA–SmC phase transition. Recently it has been found that there exist a number of advantageous smectic C^* materials with different molecular structures [7–10] with anomalously weak layer contraction in the SmC phase. An understanding of why different materials show different degrees of layer contraction at the SmA*–SmC* transition is also extremely interesting from a fundamental research point of view, because it enables one to understand different mechanisms of the tilting transition.

The properties of smectic materials with weak layer contraction were first interpreted by A de Vries using the so-called cone model [11–15]. This model is based on the assumption of a molecular pretilt in the SmA phase, where the tilted molecules are distributed randomly on the cone, and at the SmA–SmC transition the azimuthal directions are ordered, leading to the effective tilt of the director. In this model, the tilt is not accompanied by any layer contraction. Very

recently a detailed molecular theory of the SmA–SmC phase transition has been proposed by the authors [16, 17]. The theory enables us to describe both conventional smectics C and smectics with anomalously weak layer contraction using the same molecular model. At the same time, the results of the theory do not support the original cone model of de Vries as the orientational distribution function in the SmA phase appears to be qualitatively the same in conventional materials and materials with weak layer contraction. In this theory, the anomalously weak layer contraction occurs because the contraction caused by the tilt is compensated by the layer expansion due to the growth of the nematic order parameter. Such a compensation, however, may occur only if two coupling constants in the model interaction potential are close to each other [17] and if the nematic order parameter is far from saturation below the SmA–SmC transition. This explains why the majority of smectic materials are characterized by strong layer contraction. The coupling constants have been calculated numerically for a number of interaction potentials including the Gay–Berne potential, electrostatic coupling of pairs of molecular dipoles and the dipolar induction interaction [17, 18].

The main limitation of the theory presented in [16, 17] is related to the fact that only interactions between molecules within the same smectic layer have been taken into account. This approximation enables one to calculate the tilt angle which is indeed mainly determined by the intralayer interactions. At the same time, the smectic layer spacing is obviously determined by the interlayer interactions. As a result, the layer spacing has been estimated as an average projection of the long molecular axis on the smectic layer normal. As discussed in detail in [17], a correlation between the actual smectic layer period and the projection of the long axis is supported by experiment [19] at least for several smectic C materials. Nevertheless, it would be more consistent to determine the layer spacing by direct minimization of the total free energy of the smectic phase. This can only be done if the interaction between molecules located in different layers is taken into consideration. Moreover, such a minimization can be performed only if the particular form of the intermolecular interaction potential is known.

In this paper, we generalize the molecular theory of the SmC phase taking into account the interaction between molecules in adjacent smectic layers. Tilt angle, nematic order parameter and the layer spacing are determined by minimization of the free energy in the mean-field approximation. The rigorously obtained temperature variation of the layer spacing is then compared with the previously used average projection of molecular long axes on the layer normal.

2. General theory

In the generalized molecular-field approximation, the free energy of the anisotropic fluid can be written in the form

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

$$+ \tfrac{1}{2}\lambda k_{\text{B}} T\rho^2 \int f(\mathbf{r}_1, \mathbf{a}_1)[1 - \Omega(|\mathbf{r}_1 - \mathbf{r}_2| - \boldsymbol{\xi}_{1,2})]$$
$$\times f(\mathbf{r}_2, \mathbf{a}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{a}_1\, d\mathbf{a}_2$$
$$+ k_{\text{B}} T\rho \int f(\mathbf{r}_1, \mathbf{a}_1) \ln[f(\mathbf{r}_1, \mathbf{a}_1)]\, d\mathbf{r}_1\, d\mathbf{a}_1, \tag{1}$$

where ρ is the molecular number density and the one-particle distribution function f depends on the position of the molecular center of mass $\mathbf{r}_i$ and the unit vector $\mathbf{a}_i$ in the direction of the molecular primary axis. The distribution function is normalized as

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

where V is the volume of the system. The first term in equation (1) is the average internal energy where $U_{\text{att}}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_1 - \mathbf{r}_2)$ is the pair attraction interaction potential and the step function $\Omega(|\mathbf{r}_1 - \mathbf{r}_2| - \boldsymbol{\xi}_{1,2})$ describes the steric cutoff: $\Omega(|\mathbf{r}_1 - \mathbf{r}_2| - \boldsymbol{\xi}_{1,2}) = 0$ if the molecular cores intersect and $\Omega(|\mathbf{r}_1 - \mathbf{r}_2| - \boldsymbol{\xi}_{1,2}) = 1$ otherwise. The second term in equation (1) is the so-called packing entropy which describes the excluded-volume effects. Here the particular form of the density-dependent factor $\lambda(\rho) \sim 1$ depends on an approximation [20]. The third term describes the contribution from the ideal-gas-like entropy.

If the SmA–SmC transition is far from the nematic–SmA one, the smectic order in the SmC phase is usually high, and one may use the approximation of perfect smectic order. This approximation can also be used in the SmA phase if the nematic–SmA transition is strongly first order. In the case of perfect smectic ordering with period d, the one-particle distribution function can be expressed as a sum over all smectic layers:

$$f(\mathbf{r}, \mathbf{a}) = d \sum_{n=-\infty}^{\infty} f(\mathbf{a})\delta(z - nd). \tag{3}$$

Then the free energy (1) can be expressed as a sum of the free energies of each layer and the free energy per unit area of a single smectic layer can be written as

$$F_{\text{layer}} = F\frac{d}{V} = \frac{1}{2}\rho_2^2 \int\int f(\mathbf{a}_1) f(\mathbf{a}_2)$$

$$\times \int \sum_{n=-\infty}^{\infty} U_{\text{eff}}(\mathbf{a}_1, \mathbf{a}_2, [\mathbf{r}_\perp + \mathbf{k}nd])\, d\mathbf{r}_\perp\, d\mathbf{a}_1\, d\mathbf{a}_2$$

$$+ k_{\text{B}} T\rho_2 \int f(\mathbf{a}_1) \ln[f(\mathbf{a}_1)]\, d\mathbf{a}_1, \tag{4}$$

where $\rho_2 = \rho d$ is the molecular number density per area of a smectic layer and the effective intermolecular interaction potential is defined as

$$U_{\text{eff}}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}) = U_{\text{att}}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r})\,\Omega(|\mathbf{r}| - \boldsymbol{\xi}_{1,2})$$
$$+ \lambda k_{\text{B}} T[1 - \Omega(|\mathbf{r}| - \boldsymbol{\xi}_{1,2})]. \tag{5}$$

In equation (4) the predominant term corresponds to $n = 0$, i.e. the major contribution comes from intermolecular interactions within the same smectic layer. We assume that the orientational order parameters of the SmC phase are mainly determined by those intralayer interactions. At the same time, the average interlayer spacing is determined by the interactions

between adjacent layers, which correspond to the terms with $n = \pm 1$. Accordingly, we neglect the other terms in the sum over n and notice that, in the non-polar phase, the contributions with $n = 1$ and -1 are equal. Then the layer free energy can be expressed as

$$
\begin{aligned}
F_{\text{layer}} &= \tfrac{1}{2}\rho_2^2 \int \int f(\mathbf{a}_1) f(\mathbf{a}_2) \int U_{\text{eff}}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_\perp) \, \mathrm{d}\mathbf{r}_\perp \, \mathrm{d}\mathbf{a}_1 \, \mathrm{d}\mathbf{a}_2 \\
&+ \rho_2^2 \int \int f(\mathbf{a}_1) f(\mathbf{a}_2) \\
&\times \int U_{\text{eff}}(\mathbf{a}_1, \mathbf{a}_2, [\mathbf{r}_\perp + \mathbf{k}d]) \, \mathrm{d}\mathbf{r}_\perp \, \mathrm{d}\mathbf{a}_1 \, \mathrm{d}\mathbf{a}_2 \\
&+ k_{\text{B}} T \rho_2 \int f(\mathbf{a}_1) \ln[f(\mathbf{a}_1)] \, \mathrm{d}\mathbf{a}_1.
\end{aligned}
\tag{6}
$$

Minimizing the functional (6), we obtain that

$$
f(\mathbf{a}) = \frac{1}{Z} \exp\left[-\frac{U_{MF}(\mathbf{a})}{k_{\text{B}} T} \right],
\tag{7}
$$

where

$$
Z = \int \exp\left[-\frac{U_{MF}(\mathbf{a})}{k_{\text{B}} T} \right] \mathrm{d}\mathbf{a},
\tag{8}
$$

and where the mean-field potential is

$$
\begin{aligned}
U_{MF}(\mathbf{a}) = \rho_2 \int f(\mathbf{a}_2) \int &[U_{\text{eff}}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_\perp) \\
&+ 2U_{\text{eff}}(\mathbf{a}_1, \mathbf{a}_2, [\mathbf{r}_\perp + \mathbf{k}d])] \, \mathrm{d}\mathbf{a}_2.
\end{aligned}
\tag{9}
$$

3. Expansion of the intermolecular potential

Generally, it is convenient to expand the pair interaction potential, integrated over the intermolecular distance $\mathbf{r}_\perp$, in spherical harmonics and to take into account the first few terms [17]. Introducing the polar and azimuthal angles of molecular axes $\gamma_{1,2}$ and $\varphi_{1,2}$, respectively, the expansion of the pair potential is [17]

$$
\begin{aligned}
\rho_2 \int U(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_\perp) \, \mathrm{d}\mathbf{r}_\perp &= \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=0}^{\min(n,l)} C_{ln}^{(m)}(q) \\
&\times P_n^{(m)}(\cos\gamma_1) P_l^{(m)}(\cos\gamma_2) \cos(m\phi),
\end{aligned}
\tag{10}
$$

where $\phi = \varphi_1 - \varphi_2$. The potential should be invariant under the transformation $\mathbf{a} \leftrightarrow -\mathbf{a}$ which excludes the terms with odd n and l from (10). The permutational symmetry, $1 \leftrightarrow 2$, yields that $C_{ln}^{(m)} = C_{nl}^{(m)}$.

Truncating the series and keeping the harmonics with $l, n \leqslant 2$, one obtains

$$
\begin{aligned}
\rho_2 \int U(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_\perp) \, \mathrm{d}\mathbf{r}_\perp &= w_0 + w_1[P_2(\cos\gamma_1) + P_2(\cos\gamma_2)] \\
&+ w_2 P_2(\cos\gamma_1) P_2(\cos\gamma_2) \\
&+ w_3 \sin^2\gamma_1 \sin^2\gamma_2 \cos 2\phi + w_4 \sin 2\gamma_1 \sin 2\gamma_2 \cos\phi
\end{aligned}
\tag{11}
$$

which is similar to the expression used in our recent studies [17, 18]. Note that the constant term is also relevant in the present study since it depends on the layer thickness and thus should be taken into account in the minimization of the

free energy. The constants w_{0-4} are given by the following integrals:

$$
\begin{aligned}
w_0 = \frac{\rho_2}{4\pi} &\int_0^\pi \mathrm{d}\gamma_1 \, \sin\gamma_1 \int_0^\pi \mathrm{d}\gamma_2 \, \sin\gamma_2 \\
&\times \int_0^{2\pi} \mathrm{d}\phi \int U(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_\perp) \, \mathrm{d}\mathbf{r}_\perp,
\end{aligned}
\tag{12}
$$

$$
\begin{aligned}
w_1 = \frac{5\rho_2}{4\pi} &\int_0^\pi \mathrm{d}\gamma_1 \, \sin\gamma_1 P_2(\cos\gamma_1) \int_0^\pi \mathrm{d}\gamma_2 \, \sin\gamma_2 \\
&\times \int_0^{2\pi} \mathrm{d}\phi \int U(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_\perp) \, \mathrm{d}\mathbf{r}_\perp,
\end{aligned}
\tag{13}
$$

$$
\begin{aligned}
w_2 = \frac{25\rho_2}{4\pi} &\int_0^\pi \mathrm{d}\gamma_1 \, \sin\gamma_1 P_2(\cos\gamma_1) \\
&\times \int_0^\pi \mathrm{d}\gamma_2 \sin\gamma_2 P_2(\cos\gamma_2) \\
&\times \int_0^{2\pi} \mathrm{d}\phi \int U(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_\perp) \, \mathrm{d}\mathbf{r}_\perp,
\end{aligned}
\tag{14}
$$

$$
\begin{aligned}
w_3 = \frac{15^2 \rho_2}{2^7 \pi} &\int_0^\pi \mathrm{d}\gamma_1 \, \sin^3\gamma_1 \int_0^\pi \mathrm{d}\gamma_2 \, \sin^3\gamma_2 \\
&\times \int_0^{2\pi} \mathrm{d}\phi \, \cos(2\phi) \int U(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_\perp) \, \mathrm{d}\mathbf{r}_\perp,
\end{aligned}
\tag{15}
$$

$$
\begin{aligned}
w_4 = \frac{15^2 \rho_2}{2^7 \pi} &\int_0^\pi \mathrm{d}\gamma_1 \, \sin\gamma_1 \sin 2\gamma_1 \int_0^\pi \mathrm{d}\gamma_2 \sin\gamma_2 \sin 2\gamma_2 \\
&\times \int_0^{2\pi} \mathrm{d}\phi \, \cos\phi \int U(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_\perp) \, \mathrm{d}\mathbf{r}_\perp.
\end{aligned}
\tag{16}
$$

The corresponding mean-field potential (9) depends on the order parameters which define the ordering tensor $\mathbf{Q}$. In liquid crystal phases with a symmetry plane, the tensor $\mathbf{Q}$ can be written in the following general form:

$$
Q_{ij} = S_k(k_i k_j - \delta_{ij}/3) + \tfrac{1}{2} P_k(c_i c_j - h_i h_j) + \tfrac{1}{2} V(k_i c_j + c_i k_j),
\tag{17}
$$

where

$$
\begin{aligned}
S_k = \langle P_2(\cos\gamma) \rangle, \qquad P_k = \langle \sin^2\gamma \cos 2\varphi \rangle, \\
V = \langle \sin 2\gamma \cos\varphi \rangle.
\end{aligned}
\tag{18}
$$

Then the mean-field potential is

$$
\begin{aligned}
U_{MF}(\gamma, \varphi) = w_0 &+ w_1[S_k + P_2(\cos\gamma)] \\
&+ w_2 S_k P_2(\cos\gamma) + w_3 P_k \sin^2\gamma \cos 2\varphi \\
&+ w_4 V \sin 2\gamma \cos\varphi.
\end{aligned}
\tag{19}
$$

Substituting equations (18) and (19) into equation (6) one obtains the following expression for free energy in terms of the orientational order parameters:

$$
\begin{aligned}
F_{\text{layer}} = -\tfrac{1}{2}\rho_2 &[w_0 + 2w_1 S_k + w_2 S_k^2 + w_3 P_k^2 + w_4 V^2] \\
&- k_{\text{B}} T \rho_2 \ln Z.
\end{aligned}
\tag{20}
$$

In the general case, the smectic period can be found by minimization of the total free energy (20). It is known, however, that in the mean-field approximation the minimum of the free energy with respect to a parameter (which is not an ensemble average) corresponds to that of the average

interaction energy [17, 21], which in the present case is expressed as

$$U(d) = w_0(d) + 2w_1(d)S_k + w_2(d)S_k^2 + w_3(d)P_k^2 + w_4(d)V^2. \quad (21)$$

In the minimization procedure one may take into account only the d-dependent parts of the functions w_{0-4}, which are determined by the interaction between nearest-neighbor smectic layers. The corresponding contributions to the coupling constants w_{0-4} as given by equations (12)–(16) with the total potential $U(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_\perp)$ replaced by $2U_{\mathrm{eff}}(\mathbf{a}_1, \mathbf{a}_2, [\mathbf{r}_\perp + \mathbf{k}d])$.

Clearly, both intermolecular attraction U_{att} and steric repulsion have a strong effect on the equilibrium smectic layer thickness. The attractive forces tend to bring the molecules in neighboring layers closer, i.e. to decrease the layer spacing d. This causes, however, a substantial decrease of the packing entropy. As a result of the balance between these two factors, an equilibrium layer thickness appears to be slightly smaller than the molecular length.

It should be noted that the actual minimization of the free energy with respect to the smectic layer period is only possible if a particular form of the intermolecular interaction potential and the related coefficients $w_i(d)$ are known. In the following section we consider the Gay–Berne interaction potential, which is frequently used in modeling of nematic and smectic liquid crystal phases.

4. Gay–Berne potential

The model Gay–Berne (GB) interaction provides a valuable illustration for the general consideration presented above. The GB potential is a kind of an anisotropic Lennard-Jones potential:

$$U_{\mathrm{GB}}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}) = 4\varepsilon(\mathbf{a}_1, \hat{\mathbf{r}}, \mathbf{a}_2)\{[r/r_0 - \sigma(\mathbf{a}_1, \hat{\mathbf{r}}, \mathbf{a}_2) + 1]^{-12}$$
$$- [r/r_0 - \sigma(\mathbf{a}_1, \hat{\mathbf{r}}, \mathbf{a}_2) + 1]^{-6}\} \quad (22)$$

with the orientationally dependent range

$$\sigma(\mathbf{a}_1, \hat{\mathbf{r}}, \mathbf{a}_2)$$
$$= \left[1 - \frac{\chi}{2}\left(\frac{(\hat{\mathbf{r}} \cdot \mathbf{a}_1 + \hat{\mathbf{r}} \cdot \mathbf{a}_2)^2}{1 + \chi\mathbf{a}_1 \cdot \mathbf{a}_2} + \frac{(\hat{\mathbf{r}} \cdot \mathbf{a}_1 - \hat{\mathbf{r}} \cdot \mathbf{a}_2)^2}{1 - \chi\mathbf{a}_1 \cdot \mathbf{a}_2}\right)\right]^{-1/2} \quad (23)$$

and strength of the interaction

$$\varepsilon(\mathbf{a}_1, \hat{\mathbf{r}}, \mathbf{a}_2) = \varepsilon_0[1 - \chi^2(\mathbf{a}_1 \cdot \mathbf{a}_2)^2]^{-1/2}$$
$$\times \left[1 - \frac{\chi'}{2}\left(\frac{(\hat{\mathbf{r}} \cdot \mathbf{a}_1 + \hat{\mathbf{r}} \cdot \mathbf{a}_2)^2}{1 + \chi'\mathbf{a}_1 \cdot \mathbf{a}_2} + \frac{(\hat{\mathbf{r}} \cdot \mathbf{a}_1 - \hat{\mathbf{r}} \cdot \mathbf{a}_2)^2}{1 - \chi'\mathbf{a}_1 \cdot \mathbf{a}_2}\right)\right]^2. \quad (24)$$

Here r_0 is the width of the molecule and the constants $\chi = (\kappa^2 - 1)/(\kappa^2 + 1)$ and $\chi' = (\kappa'^{1/2} - 1)/(\kappa'^{1/2} + 1)$ are determined by the relative elongation of the molecule κ as well as by the parameter κ', defined as the ratio of the potential well depths for side-to-side and end-to-end molecular orientations, respectively. We assume that the steric cutoff takes place at $\xi_{1,2} = r_0\sigma(\mathbf{a}_1, \hat{\mathbf{r}}, \mathbf{a}_2)$ which determines the size of the rigid molecular core.

Using the GB potential U_{GB} and the corresponding steric cutoff distance $\xi_{1,2}$ the d-dependent contributions to the
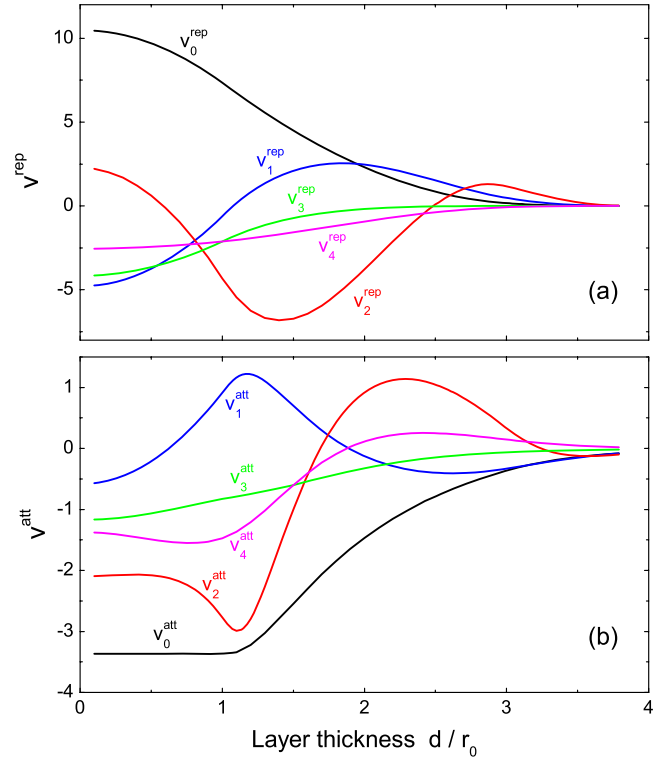

Figure 1. Dimensionless coefficients $v_n(d)$ of the attractive (a) and repulsive (b) interactions calculated for the GB potential with parameters $\kappa = 4$ (molecular elongation) and $\kappa' = 8$.

constants w_{0-4} are given by equations (12)–(16) with the effective potential $U(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r}_\perp)$ taken as

$$2U_{\mathrm{GB}}^{\mathrm{eff}}(\mathbf{a}_1, \mathbf{a}_2, [\mathbf{r}_\perp + \mathbf{k}d])$$
$$= \begin{cases} 2U_{\mathrm{GB}}(\mathbf{a}_1, \mathbf{a}_2, [\mathbf{r}_\perp + \mathbf{k}d]), & \text{when } r > r_0\sigma(\mathbf{a}_1, \hat{\mathbf{r}}, \mathbf{a}_2) \\ 2\lambda k_B T, & \text{when } r \leqslant r_0\sigma(\mathbf{a}_1, \hat{\mathbf{r}}, \mathbf{a}_2). \end{cases}$$

It is convenient to express the coupling constants as the sums of two terms:

$$w_n(d) = 2\rho_2 r_0^2 \varepsilon_0 \left[v_n^{\mathrm{att}}(d) + \frac{\lambda k_B T}{\varepsilon_0}v_n^{\mathrm{rep}}(d)\right], \quad (25)$$

where the dimensionless parameters v are determined only by the molecular geometry.

Typical variation of the coupling constants $v_n(d)$ as functions of the smectic layer spacing d, calculated numerically using the GB potential, are presented in figure 1.

5. Results and discussion

5.1. Smectic A phase

As discussed above, we assume that the temperature variation of the orientational order parameters is determined by the interactions within the same layer. In contrast, the smectic layer thickness is determined by the small d-dependent part of the free energy. In the SmA phase, the order parameters $P_k = V = 0$ and the averaged interaction energy (21) depends only on the nematic order parameter $S = S_k$. In figure 2 the
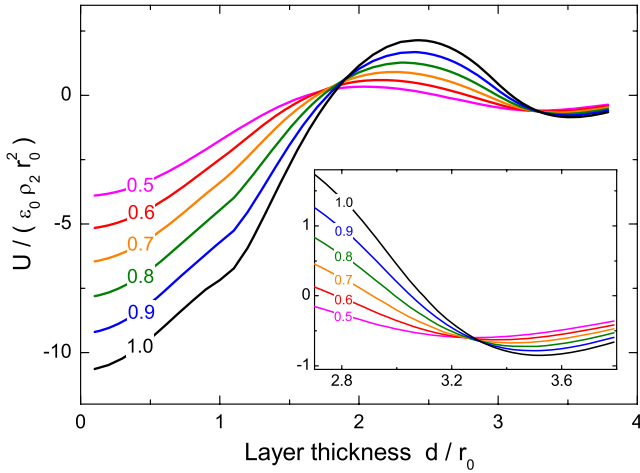
Figure 2. Average interlayer interaction energy U as a function of the smectic layer spacing d for the values of the nematic order parameter S between 0.5 and 1 (indicated in-line). Dimensionless coefficients $v_n(d)$ are as in figure 1, the temperature is $k_BT = 0.4\varepsilon_0$ and $\lambda = 1$. The inset shows shallow minima which correspond to the equilibrium layer thickness.

variation of the average interaction energy $U(d)$ as a function of d is presented for different values of the nematic order parameter S. All the curves possess the global minima at $d = 0$ which corresponds to the general stability of the layered system. At the same time, the shallow minima in the vicinity of $d \approx 4r_0$ correspond to the average layer spacing close to (but slightly higher than) the molecular length $4r_0$. One can readily see that the nematic order stabilizes the smectic order, since both minima are more pronounced for larger values of S. One notes also that the layer spacing d grows slowly with increasing S.

5.2. Smectic C phase

In the SmC phase, the average intermolecular interaction energy depends on all three orientational order parameters S, P and V, which are mainly determined by strong in-layer interactions. The order parameters of the Sm phase and the corresponding layer spacing have been calculated in our previous paper [17] for a number of cases including the systems with conventional and anomalously weak layer contraction. It has been assumed that the smectic layer spacing is approximately equal to the average projection of the molecular long axis on the layer normal. Now it is possible to compare the layer spacing, calculated approximately in [17], with the one obtained by direct minimization of the free energy. The resulting temperature variation of the layer spacing for two limiting cases with conventional and very weak layer contraction is presented in figure 3. One can readily see that the variation of the calculated layer thickness is qualitatively very similar to that of the averaged molecule projection $\langle\cos\gamma\rangle$. At the same time, the calculated layer thickness is slightly lower, and it grows slower in the SmA phase. One notes also that the curvature of the layer spacing curves obtained directly from the free energy is different from the ones calculated
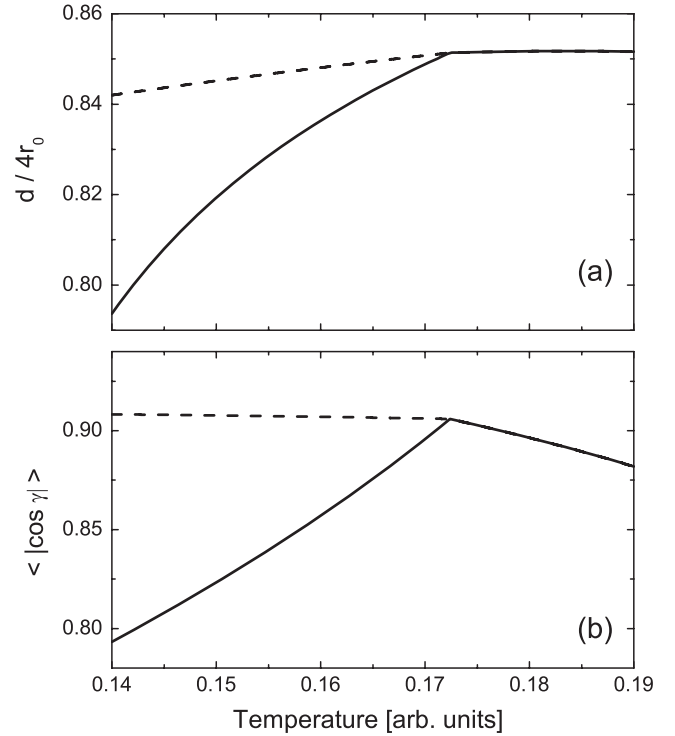

Figure 3. Calculated smectic layer thickness (a) and the averaged projection of the molecular long axis on the layer normal (b) for two transition scenarios: conventional layer contraction (solid) and weak layer contraction (dashed). Order parameters of the SmC phase, presented in figure 4 of [17], have been used. The factor $\lambda = 1$.

using the molecular projection. The former is closer to typical experimental curves.

It is also possible to compare the actual temperature variation of the thickness with that obtained using the extrapolation of the thickness from the SmA phase multiplied by the classical factor of $\cos\Theta$. Representative results are shown in figure 4. One concludes that both the calculated layer thickness and the average molecular projection decrease much slower than they should, according to the classical law. As discussed before [17], this is related to the rapid growth of the nematic order parameter S below the SmA–SmC transition point. One notes also that the calculated layer spacing slightly exceeds the average projection in contrast to the previous case presented in figure 3.

5.3. Conclusions

It has been shown in this paper that the smectic layer period can be determined by minimization of the mean-field free energy which takes into account the interaction between neighboring layers. The smectic period has been calculated numerically for the two systems with conventional and anomalously weak layer contraction in the smectic C phase. The same two systems have been considered in our previous paper [17] where it has been assumed that the smectic layer spacing is approximately equal to the average projection of the molecular long axis on the layer normal. Here it has been shown that the temperature variation of the layer spacing, calculated by minimization of
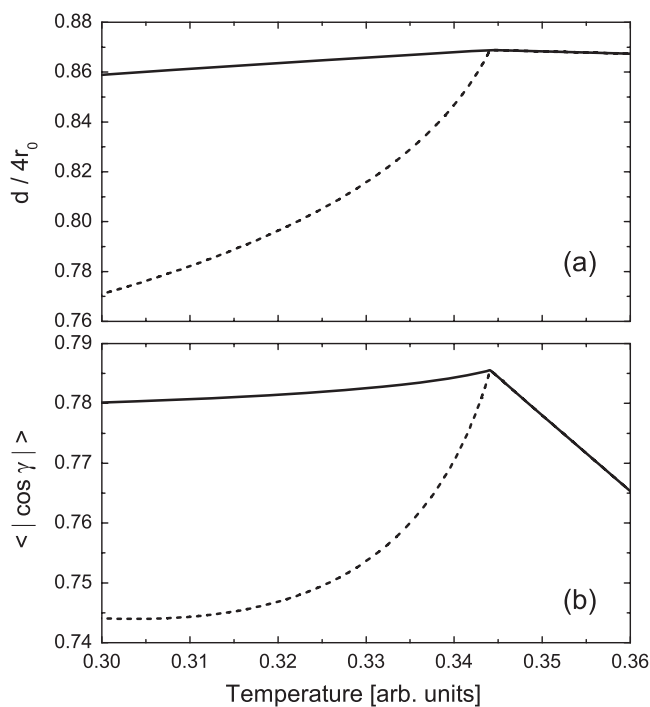
Figure 4. Calculated smectic layer thickness (a) and the averaged projection of the molecular long axis on the layer normal (b) obtained directly for a strong SmA–SmC transition (solid) and those extrapolated from the SmA phase and reduced by the factor of $\cos \Theta$ (dashed). Order parameters of the SmC phase, presented in figure 5 of [17], have been used here.

the free energy, is qualitatively similar to the variation of the average molecular projection. Thus the latter can be used in the first approximation to estimate the degree of layer contraction, and to distinguish between the materials with conventional and anomalously weak layer contraction in the SmC phase. At the same time, there exists some quantitative discrepancy between the calculated and the estimated layer spacing. Thus more quantitatively reliable data can only be obtained by direct minimization of the corresponding free energy. This minimization, however, can only be performed if the particular dependence of the interaction potential on the intermolecular distance is known.

Recently, the theory developed in [16, 17] has been used to model the temperature variation of the spontaneous polarization, tilt and layer spacing observed experimentally for two mixtures [22]. The use of the present model would result in the same curves for polarization and tilt while the curves for the layer spacing will be closer to the experimental ones.

In general, the results of this paper confirm the existence of a correlation between average molecular projection, the orientational order parameter with respect to the layer normal and the smectic layer spacing. The existence of such a correlation has recently been established experimentally for several different smectic materials [19].

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