Theory of nematic-smectic phase separation in thin twisted liquid crystal cells

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Theory of nematic–smectic phase separation in thin twisted liquid crystal cells

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Recently it has been shown experimentally by the authors that a highly twisted thin nematic cell at low temperatures can separate into a smectic A region in the middle of the cell surrounded by twisted nematic layers at the boundaries. In this case the twist is expelled into the nematic layers and the nematic–smectic A transition temperature is strongly depressed. We present a thermodynamic theory of such a phase transition in a twisted nematic cell, taking into account that the smectic A slab inside the nematic cell can be stable only if the decrease of free energy in the smectic region overcomes the increase in distortion energy of the twist deformation in the nematic layers plus the energy of the nematic–smectic A interface. In such a system the equilibrium thickness of the smectic A slab corresponds to the minimum of the total free energy of the whole cell, which includes all the bulk and surface contributions. Existing experimental data are at least qualitatively explained by the results of the present theory. This opens a unique possibility to study the properties of the nematic–smectic interface which is perpendicular to the smectic layers.

1. Introduction

Over the last decade the properties of liquid crystals in confined geometries have attracted much attention, and a significant amount of largely experimental work has been undertaken in this area. From the practical point of view it may be important to investigate the effect of cell thickness on the parameters of a liquid crystal material in a thin cell. In particular, a significant decrease in the cell thickness may induce a transition into a lower symmetry phase, as happens, for example, in small pores of various geometries [1]. This is generally related to the particularly strong influence of surfaces which may either suppress or promote different types of molecular ordering. For example, in free standing films the free surfaces promote smectic A (SmA) or smectic C phases [2–4], while in small pores the surface usually favours the nematic (N) phase [1]. Recently a N–SmA phase separation has been observed experimentally [5] in a slowly cooled thin twisted nematic cell. Surprisingly, with decreasing temperature the twisted nematic cell does not form a kind of twist grain boundary phase (at least for the material studied)

but instead separates into smectic A and nematic regions. In this case the twist of the director is expelled from the central smectic A layer into the boundary nematic regions. The director profile across the cell (and thus the distribution of the twist) has been studied using the half-leaky guided mode technique [6, 7]. It has been found that the twist angle is constant inside the smectic A layer, which is located approximately in the middle of the cell. The twist is concentrated in nematic regions where the azimuthal angle $\phi(z)$ depends linearly on z (where the z axis is normal to the surfaces). For larger values of the cell thickness there exist several smectic A layers separated by twisted nematic regions (see figure 2 of ref. [6]). It should be noted that these experimental results open the unique possibility to study the flat N–SmA interface. There exists a possibility also to study the N–SmA phase transition in very thin layers with the thickness being controlled by temperature.

One notes also that the thin smectic layer, suspended in the twisted nematic, is confined by two N–SmA interfaces which are *perpendicular* to the smectic layers. Thus one may expect that the properties of such a smectic layer should be different from those of free-standing smectic films in which the layers

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are *parallel* to the surfaces. The dependence of the N–SmA phase transition on the cell thickness in twisted cells may also be qualitatively different from that observed in thin homogeneous liquid crystal cells [8, 9].

Phase transitions in twisted liquid crystal cells are also interesting from an applications point of view because twisted nematic cells are the key elements of the fast and most widespread electro-optic display devices. At present the properties of such nematic cells are well understood but little is known about the behaviour of such systems below the N–Sm phase transition. The formation of a smectic layer inside the twisted nematic cell has been described briefly theoretically in ref. [6]. In this paper we present a more general thermodynamic theory of the N–SmA phase separation in twisted cells which takes into consideration system having both second and first order N–SmA phase transitions in the bulk. The theory takes into account that the formation of a thin smectic layer inside the twisted nematic cell (on decreasing temperature) is possible only if the decrease of free energy inside the layer overcomes the increase in distortion free energy in the narrowing nematic regions. The increase of the distortion energy density in the nematic layers is determined by the increasing twist deformation. The equilibrium thickness of the 'floating' smectic A layer corresponds to the minimum of the total free energy of the cell, which includes the extra free energy of the smectic layer, the distortion free energy of the nematic regions and the free energy of the N–SmA interface. The latter energy is positive and accounts for a depression of the N–SmA transition temperature in twisted thin cells.

The paper is arranged as follows. In §2.1 the wave number of the twist deformation in nematic layers is expressed in terms of the nematic layer thickness, the twist elastic constant and the anchoring energy at the nematic–substrate interface. In §2.2 the N–SmA phase transition in a thin layer is considered, using a simple model which enables one to take into account the energy of the nematic–smectic interface. In §2.3 the total free energy of the twisted nematic cell with a smectic A slab inside is considered in detail. The transition temperature and the critical smectic A slab thickness at the transition are then determined separately for the cases when the N–SmA transition in the bulk is either second (§2.4) or first (§2.5) order in nature. The temperature dependence of the smectic slab thickness below the transition is also presented. Finally in §3 we present our conclusions.

2. The nematic–smectic A transition in a highly twisted cell
2.1. *Wave number of the twisted cell*

Let us consider a twisted cell composed of a central smectic A layer of thickness d_A and two surface nematic layers of total thickness d_N. Here $d_A + d_N = d$ where d is the thickness of the cell. The twist of the director in such a cell is determined by the experimentally controlled angle ϕ_{12} between the two easy axes at the two outer surfaces. In such a cell there exists only twist orientational deformation and the distortion free energy density in the bulk can be expressed as $F_d = K_{22}(\mathbf{n} \cdot \text{curl } \mathbf{n})^2$. The total distortion free energy of a nematic layer also includes the anchoring energy of the director at the two surfaces. Here we assume for simplicity that the azimuthal anchoring energy at the nematic–substrate interface is described by a simple Rapini-type expression: $W_S(\phi) = W_S \cos^2(\phi - \phi_0)$, where $\phi - \phi_0 = \delta\phi$ is a deviation of the director twist angle at the surface from the direction of the easy axis. Secondly, we assume that the anchoring at the N–SmA interface is much stronger than that at the nematic–substrate. This assumption is in fact confirmed experimentally. Indeed, if the anchoring energy at the N–SmA interface is finite, the director would deviate from its equilibrium position due to the action of the torque from the bulk which is determined by the twist deformation. Moreover, the deviations of the azimuthal angles at the top and bottom interfaces, $\delta\phi_1$ and $\delta\phi_2$, would possess opposite signs and therefore there should be a noticeable angle $\delta\phi = \delta\phi_1 + \delta\phi_2$ between the directors at the two surfaces of the central smectic A layer. This conclusion is in contradiction with experiment because the twist angle $\phi(z)$ is the same at the top and bottom surfaces of all smectic A layers which have been observed in our experiment [6].

Now the total distortion free energy of the two nematic layers can be written as

$$F_{dN} = \int_0^{d_{N1}} dz\, K_{22}(\mathbf{n} \cdot \text{curl } \mathbf{n})^2 + \int_{d-d_{N2}}^{d} dz\, K_{22}(\mathbf{n} \cdot \text{curl} \mathbf{n})^2$$
$$+ W_S \cos^2\left(\phi_1 - \phi_1^0\right) + W_S \cos^2\left(\phi_2 - \phi_2^0\right) \qquad (1)$$

where $\phi_1 = \phi(z=0)$ and $\phi_2 = \phi(z=d)$ are the actual azimuthal angles of the director at the two surfaces of the cell (i.e. at $z=0$ and $z=d$, respectively), and the angles ϕ_1^0 and ϕ_2^0 specify the orientation of the two easy axes.

Everywhere in the bulk of the nematic regions the minimum of the distortion free energy corresponds to the constant gradient of the azimuthal angle $d\phi/dz = q$ where q is the wave vector of the helical structure. The

wave vector q can be expressed as

$$q = \frac{\Delta\phi_{12}^0 - \delta\phi_1 - \delta\phi_2}{d_N} \qquad (2)$$

where $\Delta\phi_{12}^0 = \phi_1^0 - \phi_2^0$.

Assuming that the two surfaces of the twisted cell are equivalent (i.e. they have been treated in the same way) one obtains $\delta\phi_1 = \delta\phi_2 = \delta\phi$.

The deviation $\delta\phi$ can be determined from the boundary condition at the surface:

$$K_{22}\frac{d\phi}{dz} = K_{22}q = W_S \sin 2\delta\phi. \qquad (3)$$

Experimentally the deviation $\delta\phi$ is rather small, $\delta\phi < 10°$ [6] and therefore the $\sin 2\delta\phi$ term in equation (3) can be approximated by $2\delta\phi$. Using this approximation one obtains from equation (2) and (3) the explicit expressions for the deviation $\delta\phi$ and the wave number q:

$$\delta\phi = \frac{\Delta\phi_{12}^0}{2\left(1 + \frac{W_S d_N}{K_{22}}\right)}. \qquad (4)$$

$$q = \frac{\Delta\phi_{12}^0}{d_N\left(1 + \frac{K_{22}}{W_S d_N}\right)}. \qquad (5)$$

Taking into account also that $\delta\phi \ll \Delta\phi_{12}^0$ (experimentally $\Delta\phi_{12}^0 \sim \pi/2$ [6]) one obtains a simplified estimate for the wave number q

$$q \approx \frac{\Delta\phi_{12}^0}{d_N}. \qquad (6)$$

One can also see from equation (5) that the estimate (6) is valid when the dimensionless parameter $\Delta = K_{22}/W_S d \ll 1$. Indeed, the characteristic length $l_w = K_{22}/W_S$, which is composed of the elastic constant and the surface anchoring strength, is usually much smaller than a typical cell thickness d. The parameter Δ can be estimated using the director twist angle profile presented in figure 1 of ref. [6]. One notes that the actual difference between the azimuthal angles of the director at the two interfaces $\phi_1 - \phi_2$ is approximately $53.5°$. Using the equation $\phi_1 - \phi_2 = \phi_{12} - 2\delta\phi$ and substituting $\phi_{12} = 85°$, one obtains $\delta\phi \sim 16°$. Substituting these data into equation (4) and taking into account that in figure 1 of ref. [6] $d_N/d \approx 0.53$, one obtains an estimate of $\Delta \sim 0.3$. Thus the parameter Δ is not too small to be completely neglected. On the other hand, this means that the azimuthal anchoring of the director in the twisted cell is not very strong and one expects substantial deviations of the director from the easy
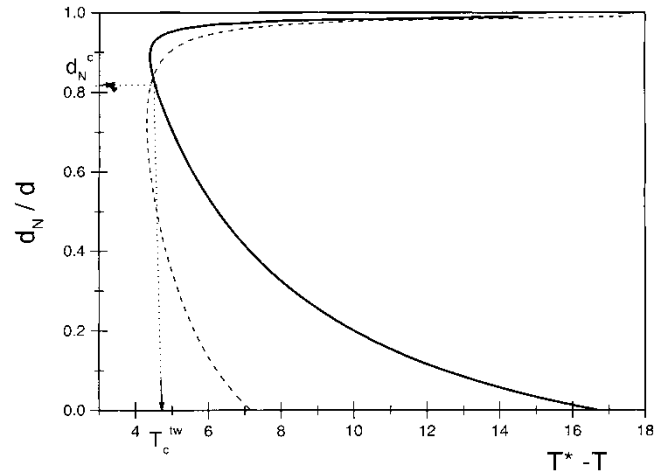
Figure 1. Temperature variation of the total thickness of the two twisted nematic layers in the phase separated twisted cell in the case of a second order N–SmA transition in the bulk (solid curve). Stable solutions correspond to the lower branch of the curve. The dashed line is a boundary of the region of global stability of the phase separated cell. Everywhere to the right of the dashed curve the twisted cell, with an untwisted smectic A region inside, possesses a lower free energy then the twisted nematic cell. The transition temperature T_c^{tw} and critical thickness of the nematic layer are shown by arrows.

axes at the surfaces. Such deviations have indeed been observed experimentally [6].

2.2. *Nematic–smectic A transition in a thin layer*

Let us consider a thin slab of smectic A 'floating' in the twisted nematic with the smectic layers being perpendicular to the nematic–smectic interface. It is reasonable to assume that the amplitude of the smectic density wave vanishes continuously at the N–SmA interface which does not favour smectic ordering. Then the free energy of the smectic A slab (per unit area of the interface) can be expanded in powers of the smectic order parameter ψ in the standard way:

$$\begin{aligned} F_A = F_N + \int_0^{d_A} dz &\left[\frac{1}{2}\alpha(T - T^*)\psi^2 \right. \\ &\left. + \frac{1}{4}b\psi^4 + \frac{1}{6}c\psi^6 + g\left(\frac{d\psi}{dz}\right)^2 \right] \end{aligned} \qquad (7)$$

with the boundary conditions at the two N–A interfaces $\psi(z=0) = \psi(z=d_A) = 0$ where d_A is the thickness of the smectic A slab. The N–SmA transition in the bulk is second order if the coefficient b in equation (7) is positive. In this case the bulk N–SmA transition temperature is equal to T^*.

In a smectic A slab of macroscopic thickness the order parameter ψ is approximately constant in the

middle of the slab and vanishes near $z = 0$ and $z = d$. The thickness of the boundary layer, where the order parameter ψ is strongly positionally dependent, is determined by the coherence length $\xi_c = \left[g / \alpha (T^* - T) \right]^{1/2}$ which diverges as $T \to T^*$. In the case of a second order N–SmA transition, the minimum of the free energy (7) corresponds approximately to the following order parameter profiles near the interfaces [5]:

$$\psi(z) \approx \psi_0 \tanh(z / \xi_c) \qquad (8)$$

for $z \ll d_A$ and

$$\psi(z) \approx \psi_0 \tanh[(d - z) / \xi_c] \qquad (9)$$

for $|d_A - z| \ll d$, where it has been assumed that $d_A \gg \xi$ and where ψ_0 is the smectic order parameter in the central part of the slab.

On the other hand, if the thickness of the smectic slab is much larger than that of the boundary layer, the total free energy of the slab F_A can always be represented as a sum of bulk and surface terms:

$$F_A = F_A^b + \sigma_{NA}. \qquad (10)$$

Here the bulk free energy F_A^b can be expanded in powers of the homogeneous smectic order parameter ψ_0 (according to equation (7) but without gradient terms). In the general case, the structure of the surface free energy σ_{NA} is not known. However, close to the transition point it is possible also to expand it in powers of the order parameter ψ_0 and to retain the first quadratic term, $\sigma_{NA} \approx \sigma_{NA}^0 \psi_0^2$. The free energy of the N–SmA interface can be estimated with the help of equation (7). In the case when $d_A \gg \xi$, the surface free energy is determined by extra positive energy associated with the gradients of the order parameter close to the interface. Thus the surface energy can be estimated as

$$\sigma_{NA} \sim 2 \int_0^\xi dz \, g \left(\frac{d\psi}{dz} \right)^2. \qquad (11)$$

In the surface regions the average order parameter gradient can be estimated as $d\psi / dz \approx \psi_0 / \xi_c$. Substituting this estimate into equation (11) one obtains

$$\sigma_{NA} \sim \frac{2 \psi_0^2 g}{\xi}. \qquad (12)$$

In the vicinity of $T = T^*$ the coherence length ξ and the surface free energy σ_{NA} are strongly temperature dependent. For example, for the liquid crystal material 8CB at temperatures close to the transition point, the parallel correlation length $\xi \approx t^{-n_\parallel}$ where $t = (T - T^*)/T^*$ and $n_\parallel = 0.67$ [10]. At the same time, experimental data indicate [6] that in the highly twisted cell the smectic A region is formed at temperatures well below the bulk N–SmA transition temperature. Thus in that region the

coherence length ξ is small and the surface free energy is weakly temperature dependent.

Now the total free energy of the smectic A slab, as shown in equation (10), can be written approximately as

$$F / d_A \approx \frac{1}{2} \alpha (T - T^*) \psi_0^2 + \frac{1}{4} b \psi_0^4 + \frac{1}{6} c \psi_0^6 + \frac{\sigma_{NA}^0}{d_A} \psi_0^2 \qquad (13)$$

where $\sigma_{NA}^0 \sim 2 g / \xi_c$.

One can see readily from equation (13) that in the slab of thickness d_A the nematic phase is becoming unstable at a temperature $\tilde{T}^*$ which is related to the bulk instability temperature T^* by the following equation:

$$\frac{1}{2} \alpha (\tilde{T}^* - T^*) + \frac{\sigma_{NA}^0}{d_A} = 0. \qquad (14)$$

In the case of a second order N–SmA transition the bulk transition temperature $T_{NA}^b = T^*$. Then the N–SmA transition in a thin slab of thickness d_A occurs at

$$\tilde{T}_{NA} = T_{NA}^b - \frac{2 \sigma_{NA}^0}{d_A \alpha} \qquad (15)$$

One notes that the shift of the transition temperature is inversely proportional to the slab thickness d_A, as expected, and is directly proportional to the positive energy of the N–SmA interface. If the N–SmA transition is first order, the transition temperature T_{NA} is related linearly to T^* and therefore the relation (15) remains valid.

It should be noted that equation (15) expresses the N–SmA transition temperature in terms of the smectic slab thickness d_A which thus far is not known. In a twisted nematic cell the smectic A region of some thickness d_A appears self-consistently at a transition temperature $\tilde{T}_{NA}$ which is related to d_A by equation (15). At the same time, the critical thickness of the smectic slab at the transition point corresponds to the minimum of the *total* free energy of the cell that also includes the distortion energy of the nematic layers. This free energy is considered in the following section.

2.3. *Critical thickness of the smectic A region*

The equilibrium thickness of the smectic A slab inside the twisted nematic cell is generally determined by minimization of the *total* free energy of the whole cell. It is convenient to calculate this free energy with respect to that of the background untwisted nematic state in the cell. Then the total free energy includes the distortion free energy of the nematic regions, the energy of the N–SmA interface and the difference between the free energy densities of the nematic and smectic A phases inside the smectic A region. One notes that the growth of the smectic A region has a two-fold effect.

On one hand, the free energy of the smectic region is decreasing because at temperatures below T_{NA}^b the free energy density of the smectic A state is lower that that of the nematic state. On the other hand, the distortion free energy of the nematic regions is increasing due to the growing twist deformation. Thus the equilibrium thickness of the smectic slab is determined by a balance between the positive distortion energy of the nematic layers and the negative free energy of the smectic A region.

The total free energy of the twisted nematic cell with the smectic A region inside can be written as

$$\Delta F_{N+A} = F_{N+A} - F_N^0 = d_A \left[\frac{1}{2}\alpha(T-T^*)\psi^2 + \frac{1}{4}b\psi^4 + \frac{1}{6}c\psi^6 \right]$$
$$+ 2\sigma_{NA} + \frac{1}{2}d_N K q^2 - 2W_S \cos^2 \delta_\phi \qquad (16)$$

where F_N^0 is the free energy density of the homogeneous (untwisted) nematic phase, the angle $\delta\phi$ specifies a deviation of the director from the easy axis at the surfaces of the cell, d_A. is the thickness of the smectic A slab and $d_N = d - d_A$ is the total thickness of the two nematic layers at the boundaries. In equation (16) the wave number q is given by equation (5), the angle $\delta\phi$ is given by equation (4) and an estimate for the energy of the N–SmA interface σ_{NA} is presented in the previous section. As discussed in section 2.1, the deviation $\delta\phi \ll 1$ and therefore the surface anchoring energy $W_s \cos^2 \delta\phi$ in equation (16) can be expanded in powers of $\delta\phi$, i.e. $W_s \cos^2 \delta\phi \approx W_S \left[1 - (\delta\phi)^2 \right]$.

Introducing the dimensionless variable $y = d_N/d$ and substituting equations (4) and (5) into (16), the free energy (11) can be rewritten as

$$\Delta F_{N+A}/d = (1-y)\left[\frac{1}{2}\alpha(T-T^*)\psi_0^2 + \frac{1}{4}b\psi_0^4 + \frac{1}{6}\psi_0^6 \right]$$
$$+ G\psi_0^2 + \frac{\tilde{K}}{\Delta+y} - \tilde{W} \qquad (17)$$

where

$$\tilde{K} = \frac{K_{22}\phi_{12}^2}{2d^2} \qquad (18)$$

$$\Delta = \frac{K_{22}}{W_S d} \qquad (19)$$

and $G = \sigma_{NA}^0/d$.

The free energy ΔF_{N+A} is to be compared with the distortion free energy of the homogeneously twisted nematic cell F_N^{tw} which is expressed as

$$F_N^{tw}/d = \frac{\tilde{K}}{\Delta+1}. \qquad (20)$$

The N–SmA transition in the twisted cell occurs when $\Delta F_{N+A} = F_N^{tw}$. This condition can be rewritten as

$$\frac{\Delta F_{N+A}}{d} - \frac{F_N^{tw}}{d} =$$
$$(1-y)\left[\frac{1}{2}\alpha(T-T^*)\psi_0^2 + \frac{1}{4}b\psi_0^4 + \frac{1}{6}\psi_0^6 \right]$$
$$+ G\psi_0^2 + \frac{\tilde{K}(1-y)}{(\Delta+y)(\Delta+1)} = 0. \qquad (21)$$

In equation (21) the first term is always negative below the bulk N–SmA transition temperature because locally the liquid crystal material prefers to be in the smectic A phase. This contribution decreases with decreasing dimensionless thickness of the nematic region y. This tendency, is counterbalanced however, by the two other terms in equation (21) which are positive. The second (surface) term does not explicitly depend on y and the third (elastic) contribution increases with decreasing y.

The smectic order parameter ψ_0 and the equilibrium thickness of the nematic layer y can be determined by minimization of the free energy (17). One obtains

$$\frac{\partial \Delta F_{N+A}}{\partial y} = -\frac{1}{2}\alpha(T-T^*)\psi_0^2$$
$$- \frac{1}{4}b\psi_0^4 - \frac{1}{6}\psi_0^6 - \frac{\tilde{K}}{(\Delta+y)^2} = 0 \qquad (22)$$

and

$$\frac{\partial \Delta F_{N+A}}{\partial \psi_0} = (1-y)\left[\alpha(T-T^*)\psi_0 + b\psi_0^3 + \psi_0^5 \right]$$
$$+ 2G\psi_0 = 0. \qquad (23)$$

2.4. *Materials with a second order N–SmA transition in the bulk*

Now let us consider the case of a second order N–SmA phase transition in the bulk. In this case $b > 0$ and one can neglect the sixth-order term in ψ in equations (22) and (23). In this case the order parameter ψ_0 is expressed as

$$\psi_0^2 = \frac{\alpha}{b}\left[\tilde{T}(y) - T \right] \qquad (24)$$

where

$$\tilde{T}(y) = T^* - \frac{2G}{\alpha(1-y)}. \qquad (25)$$

The dimensionless thickness y of the two nematic layers is given by equation (22), which can be rewritten as

$$\frac{1}{2}\alpha(T^*-T)\psi_0^2 - \frac{1}{4}b\psi_0^4 = \frac{\tilde{K}_{22}}{(\Delta+y)^2}. \qquad (26)$$

Substituting equation (25) into (26) one obtains the final

equation for y

$$\frac{\kappa}{(\Delta + y)^2} = (T^* - T)^2 - \frac{G^2}{(1-y)^2} \qquad (27)$$

where $\kappa = 4b\tilde{K}/\alpha^2$, and $G = 2\sigma_{NA}/\alpha d$.

The solution of equation (27) for $\Delta = 0.3$ (see §2.1), $\kappa = 25$ and $G^2 = 0.02$ is shown in figure 1. One notes that for each temperature T there exist two solutions for $y = d_N/d$, and above the global instability temperature $T = T^{**}$ there exists no solution at all. The upper branch of the curve in figure 2 (i.e. for y close to 1) corresponds to unstable solutions. It is interesting to note that at temperatures slightly below T^{**} the thickness of the smectic slab $d_A = d(1-y)$ is very strongly temperature dependent. In this region the temperature variation of d_A is qualitatively similar to the one observed experimentally [6]. Indeed, it has been found [6] that the thickness of the smectic A slab increases by approximately a factor of two within a narrow temperature interval of less a two degrees. One finds the same type of temperature variation in figure 1 directly below T^{**}. It should be noted also that the part of the curve in figure 1 that corresponds to very low thickness of the nematic layer (i.e. for $y \approx 0$), should not be taken too seriously. In particular, the solution $y = 0$ corresponds to a limiting case when the nematic layers at the boundaries vanish completely. In this case the cell is filled with a homogeneous untwisted smectic A phase and the initial twist disappears. This means that the
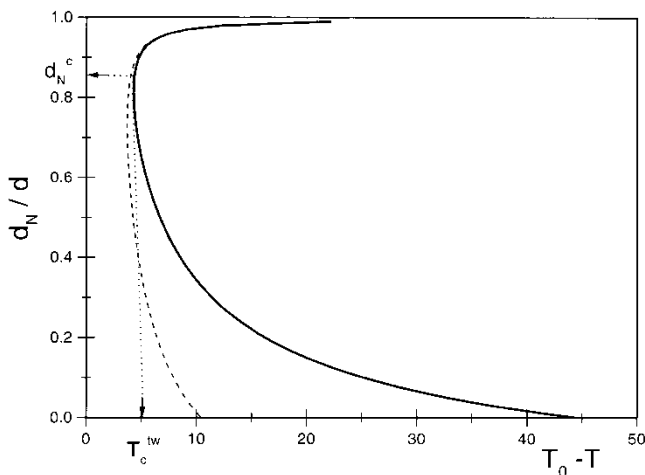

Figure 2.   Temperature variation of the thickness of two twisted nematic layers in the phase separated cell in the case of a first order N–SmA transition in the bulk (solid curve). The dashed line is a boundary of the region of global stability of the phase separated twisted cell, with an untwisted smectic A region inside. The transition temperature T_c^{tw} and the critical thickness of the nematic layer occur at the turning point of the solid curve and are shown by arrows.

deviation of the director from the easy axis at the surface $\delta\phi$ is equal to half the initial twist angle $\phi_{12} \sim \pi/2$. Such deviations of the director from the easy axis are too strong and the corresponding anchoring energy cannot be described by a simple Rapini-like form used in the present model. One may assume that in this case the non-linear effects must be very strong and the elastic energy, concentrated at the surfaces, will be too large. As a result the cell may undergo a transition into some other phase. In our experiments we have never observed $y < 0.4$. When the temperature is further decreased, the system is found to undergo a transition into another state with unknown structure.

In general the temperature variation of y resembles that of the order parameter for a typical first order phase transition. The variation of the thickness of the nematic region, presented in figure 1, enables one to conclude that the N–SmA transition in a highly twisted cell is effectively first order in nature, although the N–SmA transition in the bulk may be second order. At the transition the twisted nematic cell spontaneously separates into a smectic slab (or several slabs) of finite thickness surrounded by twisted nematic layers. Such a transition occurs well below the bulk N–SmA transition temperature and therefore the smectic ordering inside the smectic A slab is already sufficiently high. As discussed above, at the transition the total free energy of the twisted cell with a smectic A region inside is equal to the distortion free energy of the homogeneously twisted nematic cell. This condition is represented by equation (21) which determines the N–SmA transition temperature in the twisted cell T_c^{tw}.

Substituting equation (24) into (21) and neglecting the sixth order term one obtains the following equation for the transition temperature T_c^{tw}:

$$\frac{\tilde{K}}{(\Delta + 1)(\Delta + y_c)} = \frac{\alpha^2 \left(T^* - T_c^{tw} - \frac{G}{1-y_c}\right)^2}{4b} \qquad (28)$$

which yields

$$T^* - T_c^{tw} = \left[\frac{\kappa}{(\Delta + 1)(\Delta + y_c)}\right]^{\frac{1}{2}} + \frac{G}{1-y_c}. \qquad (29)$$

Here y_c is the dimensionless thickness of the nematic layers at the transition temperature T_c^{tw}. One notes that equation (29) establishes a relationship between the transition temperature and the thickness of the nematic layers at the transition. At the same time the temperature variation of the dimensionless thickness y is given by equation (27). Thus the transition temperature T_c^{tw} and the critical thickness y_c can be found by solving the system of equations (27) and (29).

The condition $F_{N+A}(T, y) < F_N^{tw}(T)$ determines the area in the T–$(-y)$ phase diagram where the free energy

of the twisted cell with a smectic A slab is lower than that of the homogeneously twisted nematic cell.

The boundary between the two regions, which corresponds to $F_{N+A}(T, y) = F_N^{tw}(T)$, is shown in figure 2 as a dashed curve. This curve has been plotted with the same parameters Δ, κ and G as the solid curve which presents the temperature variation of the equilibrium thickness of the nematic layer. Everywhere to the right of the dashed curve, the cell with the smectic A region is stable with respect to the homogeneously twisted cell. The transition temperature T_c^{tw} and the critical thickness y_c correspond to the coordinates of the intersection point of the dashed and solid curves. The values of T_c^{tw} and y_c are shown by arrows in figure 1, from which one can also see that stable solutions of $y(T)$ are represented by the lower branch of the solid curve for $T < T_c^{tw}$. The corresponding solutions in the interval between the transition temperature T_c^{tw} and the instability temperature T^{**} (turning point on the solid curve) are metastable.

2.5. *Materials with the first order N–SmA transition in the bulk*

In the previous section we considered the case when the N–SmA transition in the bulk is second order. If the transition is weakly first order, the discontinuity of the smectic order parameter at the transition point is small and the equations presented above remain to be qualitatively valid. However, if the transition in the bulk is strongly first order, the temperature variation of the smectic order parameter is completely different and the consideration presented above has to be modified. One notes that, in the case of a strong first order phase transition, the temperature variation of the order parameter is generally rather weak. Taking into account also that the N–SmA transition in the twisted cell occurs at temperatures well below the bulk transition temperature, one may neglect the variation of the smectic order parameter and assume that $\psi = const$ in some temperature interval around $T = T_c^{tw}$. In this approximation equation (22) for the equilibrium dimensionless thickness of the nematic layer can be rewritten as

$$\frac{\tilde{\kappa}}{(\Delta + y)^2} = T_0 - T - \frac{G}{1 - y} \qquad (30)$$

where $\tilde{\kappa} = 2\tilde{K}/\alpha\psi_0^2$ and $T_0 = T^* + (b/2\alpha)\psi_0^2 + (c/3\alpha)\psi_0^4$. The solution of equation (30) for $\Delta = 0.3$, $G = 0.2$ and $\tilde{\kappa} = 4$ is presented in figure 2 (solid curve). One notes that the temperature variation of the dimensionless thickness of the nematic layer y is qualitatively similar to the one obtained for the case of a second order N–SmA transition in the bulk. The transition point in

the twisted cell is determined by the general equation (21) which can now be written as

$$T_0 - T = \frac{\kappa}{(\Delta + 1)(\Delta + y)} + \frac{G}{1 - y}. \qquad (31)$$

Similar to the case of the second order transition in the bulk, the dashed curve determines the region on the T–$(-y)$ phase diagram (to the right from the curve) where the free energy of the cell with a smectic slab inside is lower than that of the homogeneously twisted cell at the same temperature. One notes that, in the case of a first order transition in the bulk, the whole branch of stable solutions $y(T)$ (i.e. the lower branch of the solid curve in figure 2) is located in the region in which the nematic slab inside the twisted cell is globally stable. Thus the actual transition in the twisted nematic cell occurs at a temperature T_c^{tw} which coincides with the global instability temperature specified by the turning point on the solid curve of solutions $y(T)$. This transition temperature, together with the critical thickness of the nematic layer at the transition point, is indicated by an arrow in figure 2.

3. Discussion

In this paper we have considered the N–SmA phase transition in a twisted thin nematic cell. It has been shown that on decreasing temperature such a cell may separate into a smectic A region in the middle and two nematic layers at the boundaries. The twist of the director is expelled into the nematic regions. The thickness of the smectic A slab is temperature dependent and is determined by a delicate balance between the negative free energy of the smectic region and the positive distortion energy of the nematic layers plus the energy of the N–SmA interface. The equilibrium thickness is then determined by a minimization of the total free energy of the whole cell, and the global stability of the smectic A slab is determined by a condition that this total free energy of the cell is less than that of the homogeneously twisted cell at the same temperature. It is interesting to note that the N–SmA transition in such a cell is always first order, although the corresponding transition in the bulk may be second order. At the transition point a smectic A slab of *finite* thickness is spontaneously formed. This is related to the fact that the smectic A free energy density must be sufficiently low (with respect to that of the nematic phase) to overcome the positive energy of the N–SmA interface and the positive increase of the distortion energy in the nematic layers. As a result, the N–SmA transition temperature is depressed with respect to its value in the bulk. In such a system the temperature variation of the thickness of the smectic A slab (see figures 1 and 2) is similar to that of the order parameter

at a typical first order phase transition. In fact, the smectic slab thickness here plays the role of an additional order parameter of the smectic A region which possesses a variable size. Then both smectic order parameters and the slab thickness are determined by a minimization of the same total free energy of the cell.

It has been found experimentally [6] that in some cases several smectic A slabs are formed in the twisted nematic cell. Such smectic slabs are separated by twisted nematic layers. This may be explained by a nucleation process. One may assume that several smectic regions are formed spontaneously and begin to grow in different parts of the twisted nematic cell. Such smectic regions cannot coalesce easily because they are separated by a high potential barrier determined by a positive distortion energy of the twisted nematic gap. If two smectic slabs approach each other, a decrease of the nematic layer thickness results in a strong repulsion between smectic slabs because the twist is confined within the nematic layer.

It should be noted that the formation of thin smectic A slabs inside a twisted nematic cell allows the unique opportunity to study the N–SmA phase transition and the N–Sm interface in very thin (less then $1000 \overset{\circ}{A}$) flat films. The thickness of the film can be controlled both by temperature and by the initial twist in the nematic cell. Smectic A layers in the twisted nematic cell are formed at temperatures below the bulk N–SmA transition temperature, and thus the nematic is under cooled. In this temperature range one may expect that smectic fluctuations will play an important role. Thus the N–SmA phase transition in highly twisted cells deserves further experimental investigation using other techniques, including high resolution calorimetry and X-ray scattering. One notes, however, that N–Sm phase separation in a twisted cell can be expected only if the surfaces promote the nematic phase. Slightly different surfaces may promote smectic A ordering, and in this case the whole cell may undergo a transition into the smectic phase with the simultaneous formation of a complex defect structure to accommodate the twist [11].

References

[1] CRAWFORD, G. P., and ZUMER, S. (editors), 1996, *Liquid Crystals in Complex Geometries* (London: Taylor and Francis).

[2] STOEBE, T., MACH, P., and HUANG, C. C., 1994, *Phys. Rev. Lett.*, **73,** 1384.

[3] DEMIKHOV, E. I., DOLGANOV, V. K., and MELETOV, K. P., 1995, *Phys. Rev. E*, **52,** 539.

[4] KRAUS, I., PIERANSKI, P., DEMIKHOV, E., STEGE-MEYER, H., and GOODBY, J., 1993, *Phys. Rev. E*, **48,** 1916; Kraus, I., Pieranski, P., Demikhov, E., Stegemeyer, H., Goodby, J., Slaney A., and Osipv, M. A, 1993, *Ber. Bunsenges. phys. Chem.*, **97,** 1376.

[5] OSIPOV, M. A., SAMBLES, J. R., and YANG, F., 1996, *Liq. Cryst.*, **21,** 727.

[6] LIZHEN, R., SAMBLES, J. R., and OSIPOV, M. A., 2001, *Phys. Rev. Lett.*, **86,** 4548.

[7] YANG, F., and SAMBLES, J. R., 1993, *J. opt. Soc. Am.*, **B10,** 858.

[8] PIKIN, S. A., and YOSHINO, K., 1981, *Jpn. J. appl. Phys.*, **20,** L577.

[9] KONDO, K., TAKEZOE, H., FUKUDA, A., and KUZE, E., 1982, *Jpn. J. appl. Phys.*, **21,** 224; Yang Y. B., Bang T., Mochizuki A., and Kobayashi S., 1991, *Ferroelectrics*, **121,** 113.

[10] LITSTER, J. D., ALS-NIELSEN, J., BIRGENAU, R. J., DANA, S. S., DAVIDOV, D., GARCIA-GOLDING, F., KAPLAN, M., SAFINYA, C. R., and SCHAETING, R., 1979, *J. Phys. C: solid State*, **3,** 339.

[11] RICHARDSON, R., private communication.