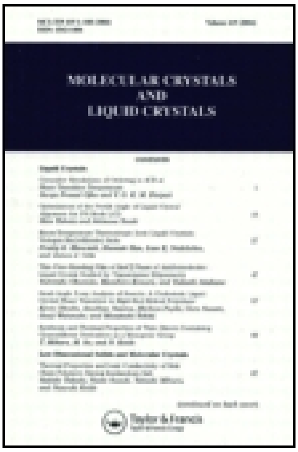

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Barbara Rovšek [a] & Boštjan Žekš [a b]

[a] J. Stefan Institute, Jamova 39, 61111, Ljubljana, Slovenia

[b] Institute of Biophysics, Medical Faculty, Lipičeva 2, 61105, Ljubljana, Slovenia

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THE SmA $\leftrightarrow$ SmC* (SmC) PHASE TRANSITION IN A PLANAR CELL WITH A POLAR SURFACE COUPLING

BARBARA ROVŠEK† and BOŠTJAN ŽEKŠ*†
† J. Stefan Institute, Jamova 39, 61111 Ljubljana, Slovenia
* Institute of Biophysics, Medical Faculty, Lipičeva 2, 61105 Ljubljana, Slovenia

Abstract The phase transition from the SmA to the lower-temperature SmC*or SmC phase in a restricted geometry of a planar cell is studied theoretically, considering a polar coupling of the ferroelectric liquid crystal to the surfaces. The λ-line in a $(2L, T)$ phase diagram, where T is the temperature and $2L$ is the cell thickness, is determined numerically. The critical temperature T_c of the SmA $\leftrightarrow$ SmC* (SmC) phase transition exibits nonmonotonic dependence on the cell thickness $2L$. Two tricritical points are found on the λ-line, which could be candidates for the Lifshitz points.

INTRODUCTION

Much attention has been paid already to investigation of the physical mechanisms of the surface induced ordering and the influence of restricted geometries on thermodynamical properties of ferroelectric liquid crystals (FLC) [1-7]. Recently it has been experimentally shown [7], that the cell thickness - temperature $(2L, T)$ phase diagram of FLC in a planar cell is similar to the field strength - temperature (H, T) phase diagram in an external magnetic field. A theoretical explanation, based on an assumption of the soft quadrupolar surface coupling between the liquid crystal and the bounding plates has been also given in the same paper. The λ-line has been evaluated within the Landau theory and it has been found out, that the quadrupolar boundary conditions stabilize spatially nonmodulated SmC phase below the λ-line in thin cells. The existence of the Lifshitz point, which separates the region of the SmA $\leftrightarrow$ SmC* transition from the SmA $\leftrightarrow$ SmC transition on the λ-line was theoretically confirmed. The SmA $\leftrightarrow$ SmC* transition temperature was found to decrease with decreasing cell thickness $2L$, while the SmA $\leftrightarrow$ SmC transition temperature was thickness independent.

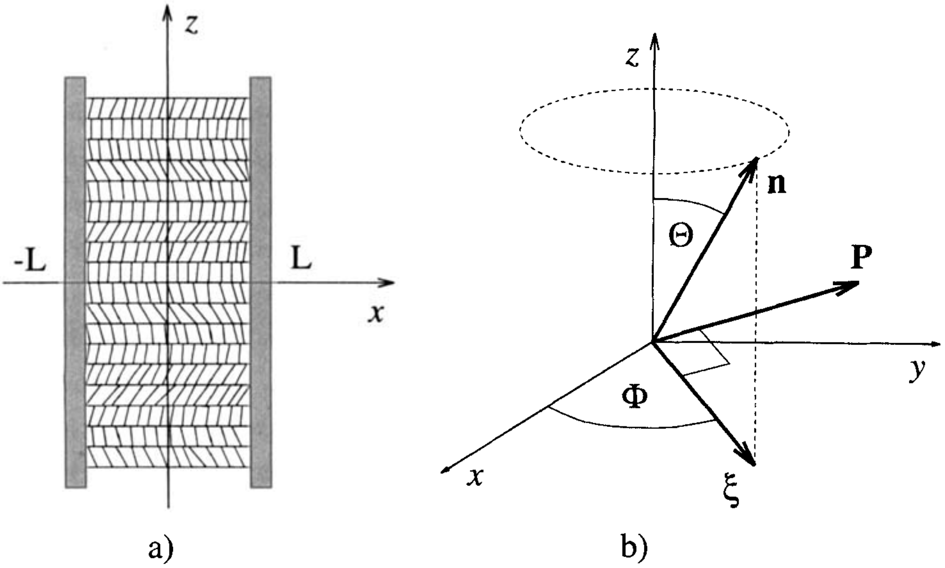
However, it has been reported [2,3,6], that for ferroelectric liquid crystals polar (ferroelectric) surface interactions are especially important. So the final interpretation will have to combine both mechanisms of surface coupling, polar (electrostatical) and quadrupolar (sterical). In order to find a more complete picture of the surface-induced phase transitions we present here some results referring primarily to the study of the soft polar boundary conditions and their influence on the planar-cell structures.

In the following a SmA $\leftrightarrow$ SmC* (SmC) transition line in the $(2L, T)$ phase diagram will be derived within the phenomenological Landau theory of second-order phase transitions.

THE λ-LINE

The question is, how do the planar cell thickness and the polar coupling of the ferroelectric liquid crystal to the surfaces affect the SmA $\leftrightarrow$ SmC* (SmC) transition temperature T_c.

A planar geometry of the ferroelectric liquid crystal sample is shown in Fig.1.a. Smectic planes are perpendicular to the bounding plates, which are separated by a distance $2L$. The helical axis of the modulated SmC* phase is parallel to the z-axis and the bounding plates are perpendicular to the x-axis. We assume the system is



a) b)

Figure 1: a) Ferroelectric liquid crystal in a planar geometry. b) Two dimensional smectic order parameter ξ.

homogeneous along the y direction. As usual the ordering will be described by the two-dimensional tilt vector $\tilde{\boldsymbol{\xi}} = (\tilde{\xi}_1, \tilde{\xi}_2)$, which is the projection of the director $\boldsymbol{n}$ to the plane of the smectic layers (see Fig.1.b).

Assuming that the confining geometry of a sample doesn't alter the order of the phase transition, we shall be able to find the SmA ↔ SmC* (SmC) transition line in the $(2L, T)$ phase diagram as a stability limit of the SmA phase. Since in the case of the second-order transitions the line, which is determined by the stability of the SmA phase is also the line of the phase transition.

Within the classical model the expansion of the nonequilibrium free energy density functional in the order parameter $\tilde{\boldsymbol{\xi}}$ is in one elastic constant approximation written as

$$\begin{aligned}\tilde{f} &= \frac{1}{2}a(\tilde{\xi}_1^2 + \tilde{\xi}_2^2) + \frac{1}{4}b(\tilde{\xi}_1^2 + \tilde{\xi}_2^2)^2 - \Lambda\left(\tilde{\xi}_1\frac{\partial\tilde{\xi}_2}{\partial\tilde{z}} - \tilde{\xi}_2\frac{\partial\tilde{\xi}_1}{\partial\tilde{z}}\right) \\ &+ \frac{1}{2}K_3\left[\left(\frac{\partial\tilde{\xi}_1}{\partial\tilde{x}}\right)^2 + \left(\frac{\partial\tilde{\xi}_2}{\partial\tilde{x}}\right)^2 + \left(\frac{\partial\tilde{\xi}_1}{\partial\tilde{z}}\right)^2 + \left(\frac{\partial\tilde{\xi}_2}{\partial\tilde{z}}\right)^2\right] \\ &- D\delta(\tilde{x} - \tilde{L})\tilde{\xi}_2 + D\delta(\tilde{x} + \tilde{L})\tilde{\xi}_2\,, \qquad (1)\end{aligned}$$

where $a = \alpha(T - T_0)$, T_0 is the SmA ↔ SmC bulk transition temperature in a non-chiral sample and $T_c^{bulk} = T_0 + \Lambda^2/\alpha K_3$ is the SmA ↔ SmC* bulk transition temperature. The wave vector of the helix in the bulk is $\tilde{q}_0 = \Lambda/K_3$. Considering only polar surface interaction we have written the surface free energy density with the last two terms in the most simple polar form.

Polar interactions of the ferroelectric liquid crystal system with the surfaces are of an electrostatical origin and a due to the fact, that two opposite orientations of the permanent polarization at the surfaces are not energetically equivalent. For the most systems the prefered orientation of the permanent polarization at the surfaces is perpendicular to the surfaces: either towards interior or exterior of the cell. Since within the classical model the permanent polarization is always perpendicular to the tilt $\tilde{\boldsymbol{\xi}}$ (see Fig.1.b), we could write the surface interaction terms in (1) as depending on the tilt and not explicitly on the polarization. The coefficient D is a surface coupling constant, which is positive or negative if the prefered orientation of the polarization at the surface is towards interior or exterior of the cell, respectively.

By introducing the dimensionless quantities

$$x = \tilde{q}_0\tilde{x}\,, \qquad z = \tilde{q}_0\tilde{z}\,, \qquad \xi_{1,2} = \tilde{\xi}_{1,2}\sqrt{\frac{K_3 b}{\Lambda^2}}\,, \qquad q = \frac{\tilde{q}}{\tilde{q}_0}\,,$$

$$f = \tilde{f}\frac{K_3^2 b}{\Lambda^4}, \qquad d = D\frac{\sqrt{K_3 b}}{\Lambda^2} \qquad \text{and} \qquad t = \frac{T - T_0}{\Lambda^2/\alpha K_3} \tag{2}$$

the dimensionless free energy density f is written as

$$\begin{aligned} f &= \frac{1}{2}t\left(\xi_1^2+\xi_2^2\right) + \frac{1}{4}\left(\xi_1^2+\xi_2^2\right)^2 - \left(\xi_1\frac{\partial\xi_2}{\partial z} - \xi_2\frac{\partial\xi_1}{\partial z}\right) \\ &+ \frac{1}{2}\left[\left(\frac{\partial\xi_1}{\partial x}\right)^2 + \left(\frac{\partial\xi_2}{\partial x}\right)^2 + \left(\frac{\partial\xi_1}{\partial z}\right)^2 + \left(\frac{\partial\xi_2}{\partial z}\right)^2\right] \\ &- d\delta(x-L)\xi_2 + d\delta(x+L)\xi_2 \,. \end{aligned} \tag{3}$$

The new temperature $t = 0$ corresponds to $T = T_0$ and $t = 1$ corresponds to $T = T_c^{bulk}$.

To find the equilibrium structure of the nonhelicoidal SmA phase we omit the z-dependent terms in functional (3) and by minimization we obtain the Euler-Lagrange equations in the form

$$\begin{aligned} &\xi_1^3 + \xi_1\left(t+\xi_2^2\right) - \frac{\partial^2\xi_1}{\partial x^2} = 0\,, \\ &\xi_2^3 + \xi_2\left(t+\xi_1^2\right) - \frac{\partial^2\xi_2}{\partial x^2} = 0\,, \end{aligned} \tag{4}$$

with the boundary conditions

$$\left.\frac{\partial\xi_1}{\partial x}\right|_{x=\pm L} = 0 \qquad \text{and} \qquad \left.\frac{\partial\xi_2}{\partial x}\right|_{x=\pm L} = d\,. \tag{5}$$

For $t \geq 0$ it can be shown, that the only solution of (4) satisfies $\xi_1(x) \equiv 0$. The corresponding equation for $\xi_2(x)$ simplifies to

$$\xi_2^3 + t\xi_2 - \frac{\partial^2\xi_2}{\partial x^2} = 0\,. \tag{6}$$

The solution describes the ordering of the nonmodulated phase and it suits the situation, where the tilt $\boldsymbol{\xi}$ is parallel to the bounding plates through the whole sample. It can be found numerically and it is shown in Fig.2 for some surface coupling strengths d and given cell thickness $2L = 6$ and temperature $t = 2$. The polar surface interaction in the planar sample of ferroelectric liquid crystal induces non-zero tilt at the cell surfaces at all temperatures $t \geq 0$ ($\sim T \geq T_0$), whereas in the bulk sample the equilibrium value of the tilt is zero at $t \geq 1$. As the temperature t is lowered below zero, the solution for $\xi_2(x)$ continuously transforms in such a way that a non-zero tilt, parallel to the bounding plates, appears not only at the surfaces, but all over the sample. The component ξ_1 remains zero everywhere and as

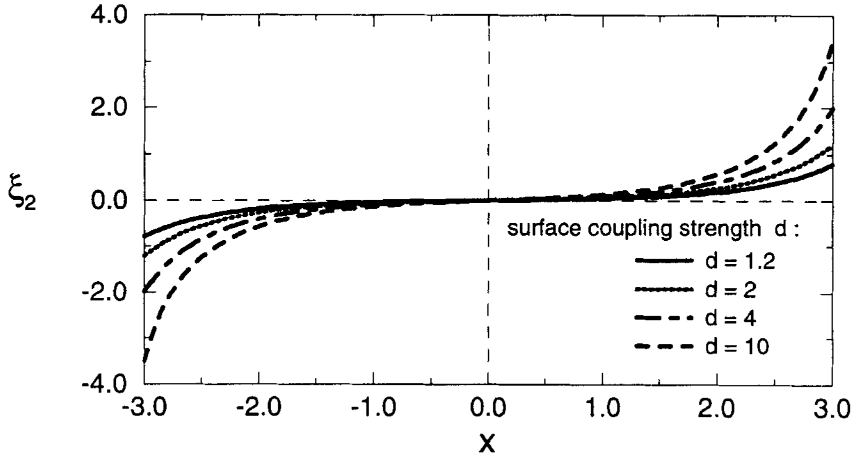


Figure 2: The component $\xi_2(x)$ of the tilt vector, which is parallel to the surfaces, in a higher temperature SmA phase for some surface coupling strengths d. The temperature $t = 2$ and the cell thickness $2L = 6$.

the function $\xi_2(x)$ is still antisymmetrical, the macroscopic polarization of such an ordering remains zero. Numerically obtained solutions $\xi_2(x)$ are for some negative temperatures $t \leq 0$, fixed cell thickness $2L = 6$ and surface coupling strength $d = 4$ presented in Fig.3.

At temperatures $t < 0$ there exist also other types of the spatially nonmodulated solutions for ξ beside the solution with $\xi_1(x) \equiv 0$. But it turns out, that in the

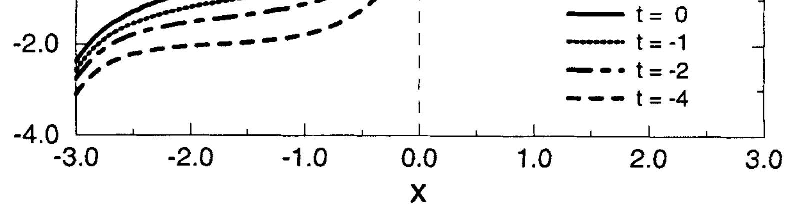


Figure 3: The component $\xi_2(x)$ of the tilt vector in the spatially nonmodulated SmA phase at some negative temperatures $t \leq 0$. The surface coupling strength $d = 4$ and the cell thickness $2L = 6$.

relevant region of the $(2L, t)$ phase diagram the one with the minimum free energy is still the one with the tilt parallel to the confining plates.

In the next step we expand the nonequilibrium free energy density (3) in the fluctuations $\delta\xi_1$ and $\delta\xi_2$ from the equilibrium homogeneous ordering of the SmA phase $\xi_2(x)$. For the stability analysis of the SmA phase only the harmonic part of the free energy has to be considered. We write the components of the tilt as

$$\begin{aligned} \xi_1(x,z) &= \delta\xi_1(x,z)\,, \\ \xi_2(x,z) &= \xi_2(x) + \delta\xi_2(x,z) \end{aligned} \tag{7}$$

and by minimizing the harmonic part of the free energy in fluctuations $\delta\xi_1$ and $\delta\xi_2$ we obtain the following coupled linear differential equations and boundary conditions for $\delta\xi_1$ and $\delta\xi_2$

$$\begin{aligned} \delta\xi_1(t+\xi_2^2) - 2\frac{\partial\delta\xi_2}{\partial z} - \left(\frac{\partial^2\delta\xi_1}{\partial x^2} + \frac{\partial^2\delta\xi_1}{\partial z^2}\right) &= 0\,, \\ \delta\xi_2(t+3\xi_2^2) + 2\frac{\partial\delta\xi_1}{\partial z} - \left(\frac{\partial^2\delta\xi_2}{\partial x^2} + \frac{\partial^2\delta\xi_2}{\partial z^2}\right) &= 0\,, \\ \left.\frac{\partial\delta\xi_{1,2}}{\partial x}\right|_{x=\pm L} &= 0\,. \end{aligned} \tag{8}$$

The solution of (8) has the form of sinusoidal functions

$$\begin{aligned} \delta\xi_1(x,z) &= \Theta_1(x)\cos qz\,, \\ \delta\xi_2(x,z) &= \Theta_2(x)\sin qz\,. \end{aligned} \tag{9}$$

Inserting (9) into eqns. (8) we get equations for Θ_1 and Θ_2,

$$\begin{aligned} \Theta_1\left(t+\xi_2^2+q^2\right) - \frac{\partial^2\Theta_1}{\partial x^2} &= 2q\Theta_2\,, \\ \Theta_2\left(t+3\xi_2^2+q^2\right) - \frac{\partial^2\Theta_2}{\partial x^2} &= 2q\Theta_1\,, \\ \left.\frac{\partial\Theta_{1,2}}{\partial x}\right|_{x=\pm L} &= 0\,. \end{aligned} \tag{10}$$

If we define a linear differential operator $\hat{A}$, which operates on two-dimensional vector $\boldsymbol{\Theta} = (\Theta_1, \Theta_2)$, as

$$\hat{A} = \frac{\partial^2}{\partial x^2} - \left\| \begin{matrix} t+\xi_2^2+q^2 & -2q \\ -2q & t+3\xi_2^2+q^2 \end{matrix} \right\| \tag{11}$$

we can formulate our problem of analysing the stability of the high-temperature SmA phase as an eigen-value problem

$$\hat{A}\boldsymbol{\Theta} = \lambda\boldsymbol{\Theta}\,. \tag{12}$$

We search for a certain non-trivial eigen-vector Θ_0, which corresponds to the eigenvalue $\lambda = 0$. It shows up, that if for a given cell thickness $2L$ and surface coupling strength d, temperature t is larger than some critical temperature t_c, all the eigenvalues λ of the operator $\hat{A}$ are larger than zero for any value of the wave vector q. This means that there is no non-trivial solution Θ of eqn. (10) and that the homogeneous structure of the SmA phase, described by the function $\xi_2(x)$, is stable against any fluctuation at all temperatures $t \geq t_c$. But at temperatures below t_c we can always find pairs (t, q), which correspond to the non-trivial eigen-vectors $\Theta_0(t, q)$. All these different $\Theta_0(t, q)$ are the solutions of Euler-Lagrange equations (10), but the SmA ↔ SmC* (SmC) transition temperature T_c is defined exactly by a pair (t_c, q_c) with maximum t. It corresponds to the highest temperature non-trivial solution for the spatially modulated order parameter $\boldsymbol{\xi}(x, z)$, t_c is the transition temperature and q_c is inversely proportional to the period of the new stable ordering.

Results, obtained numerically, show nonmonotonic dependences of the critical temperature t_c and the critical wave vector q_c on the cell thickness $2L$. The λ-lines on the $(2L, t)$ phase diagram, which are the second-order SmA ↔ SmC*(SmC) transition lines and which denote the temperature of appearance of the first non-trivial spatially modulated solution, are for some surface coupling strengths shown in Fig.4.a. The corresponding critical wave vectors q_c of the modulation of the lower-temperature phase are ploted in Fig.4.b.

For large cell thicknesses the critical temperature t_c asymptotically approaches the bulk transition temperature from below. With decreasing cell thickness the transition temperature is decreased and at some thickness $2L_{min}$ the transition temperature reaches its lowest possible value for given surface coupling strength d. For $2L < 2L_{min}$, t_c becomes larger again and increases continuously towards the transition temperature in the bulk, which is reached in the limit $2L \to 0$. The behaviour of the critical wave vector q_c of the solution on the $t_c(2L)$ transition line is as follows: for large thicknesses of the cell the wave vector equals to the wave vector of the regular helix in the bulk ($q_c = 1$). If the thickness is decreased, q_c is decreased (the period of the modulated solution is continuously enlarged). If the surface interaction is strong enough, two critical points on the $t_c(2L)$ line exist. At the first critical thickness $2L_{c1}$ the critical wave vector becomes zero and stays zero until the second critical cell thickness $2L_{c2}$ is reached, whereupon it begins to enlarge continuosly again. In the limit $2L \to 0$ it equals to the bulk wave vector. In the case when d is less than some d_{crit} , the limiting value of q_c at $2L \to 0$ and $2L \to \infty$ is still the bulk wave vector, but at the thicknesses in between, q_c never reaches zero. For $d < d_{crit}$ there are no critical points on the $t_c(2L)$ line.

On a $(2L, t)$ phase diagram homogeneous SmA phase is stable everywhere above the $t_c(2L)$ transition line. If the critical points exist, then close below transition in the regions, where $2L < 2L_{c2}$ or $2L > 2L_{c1}$, modulated SmC* phase is stable with

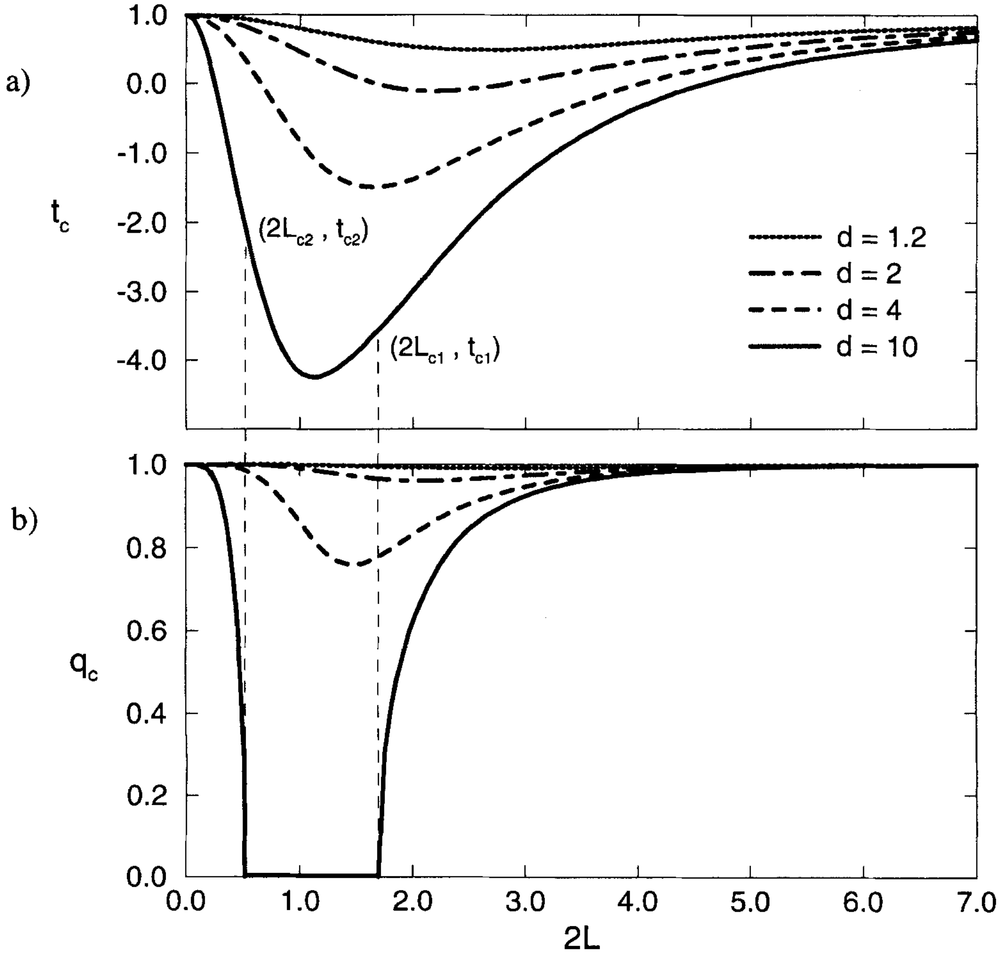


Figure 4: a) The critical temperature t_c of the SmA $\leftrightarrow$ SmC* (SmC) phase transition in dependence on the planar cell thickness $2L$ for some surface coupling strengths d and b) corresponding critical wave vector q_c of the transition.

the period, which depends on a cell thickness, and in the region where $2L_{c2} < 2L < 2L_{c1}$, spatially nonmodulated SmC phase is stable. Two points $(2L_{c1}, t_{c1})$ and $(2L_{c2}, t_{c2})$ are tricritical points where the three smectic phases SmA, SmC and SmC* join. They could both be Lifshitz points, if the SmC* ↔ SmC transition is of the first order in their vicinity, but the proof has not been given yet. If $d < d_{crit}$, tricritical points do not appear on the transition line and in this case the lower temperature phase is always spatially modulated SmC*, no matter how thin the cell is.

At first sight surprising results which reveal that the modulated structure is favoured over the nonmodulated in both thin and thick enough cells, can be easily understood. The polar boundary conditions induce in the SmA phase the twist deformation along the x-axis, which costs the volume elastic free energy, it is therefore unfavourable and will be reduced as much as possible. But then in a very thin cell the orientations of the molecules at the both surfaces will differ the least and the system will gain almost nothing from the surface interaction. The energy that is earned at the first surface, is lost at the other and consequently all the orientations of the average tilt $< \boldsymbol{\xi} >$ in the particular smectic layer are equivalent (since $\boldsymbol{\xi}(x = -L) \cong \boldsymbol{\xi}(x = L) \cong < \boldsymbol{\xi} >$). This corresponds exactly to the situation in the bulk, where there are no surface terms in the free energy density: the SmA ↔ SmC* transition is governed solely by the volume energy terms and occurs at $t_c = 1$, with the critical wave vector $q_c = 1$.

To illustrate the above interpretation a crude estimation of the two critical thicknesses is made within the constant amplitude approximation (CAA). This approach can qualitatively explain the sequence of the stable phases, when the cell thickness is being changed, although the CAA turns out unsuitable for quantitative description of the system close below SmA ↔ SmC* (SmC) transition line. The stability of the spatially nonmodulated ordering of the SmC phase is roughly determined by the comparison of the energy gain due to the surface interaction and the energy losses due to the additional twist along the x-axis and to the absence of the helicoidal modulation along the z-axis. For a simple estimation the case, where the surface energy gain is maximum serves: the tilt at the surfaces is exactly parallel to the bounding plates and changes its phase regularly in between, all together for π. Within the CAA the amplitude of the tilt Θ is constant through the sample and the phase Φ is the only parameter that describes the structure. Therefore the expression for the free energy density (3) simplifies and finally we may write the maximum elastic energy loss in the SmC phase as

$$F_{el} = \frac{1}{2}\Theta^2 \int_{-L}^{L} \left[\left(\frac{\partial \Phi}{\partial x}\right)^2 + \left(\frac{\partial \Phi}{\partial z} - q_0\right)^2 \right] dx = \frac{\Theta^2 \pi^2}{4L} + \Theta^2 q_0^2 L$$

and the maximum surface energy density gain as

$$F_s = 2d\Theta \, .$$

If $F_s > F_{el}$ then the SmC phase is stable, otherwise spatially modulated ordering is prefered. At the critical cell thicknesses $L_\pm$ the relation $F_s = F_{el}$ is satisfied and therefore the phase transition between the two phases occurs. A simple calculus gives us

$$L_\pm = \frac{d}{\Theta q_0^2} \pm \frac{d}{\Theta q_0^2} \sqrt{1 - \frac{\Theta^2 \pi^2}{4d^2}}$$

and relations

$$\begin{array}{lll} \text{if} & 0 < L < L_- & \Longrightarrow \text{SmC unstable,} \\ \text{if} & L_- < L < L_+ & \Longrightarrow \text{SmC stable,} \\ \text{and if} & L_+ < L & \Longrightarrow \text{SmC unstable.} \end{array}$$

This result is of course far from being quantitatively correct, but it shows also another characteristic feature of the polar surface coupling. If d is small enough, there are no critical thicknesses and spatially modulated phase is favoured for all cell thicknesses.

CONCLUSIONS

To complement the picture about the phase transitions between the chiral smectic phases A, C and C* in the restricted geometry of the planar cell, we have discussed the influence of the polar surface interaction to the SmA ↔ SmC* (SmC) transition temperature. When the surface interactions are quadrupolar, the SmA ↔ SmC* (SmC) transition temperature is between T_0 and T_c^{bulk} and decreases monotonically with decreasing cell thickness, whereas the polar surface coupling causes nonmonotonic dependence of the transition temperature on the cell thickness. Correspondingly, for the quadrupolar coupling there is one tricritical point in the $(2L, T)$ phase diagram, where the three phases coexist, while for the polar there is either none or two, depending on the surface coupling strength.

Due to the nonlinearity of the Euler-Lagrange equations (4) a problem of solving them is complex below the SmA ↔ SmC* (SmC) transition line. Therefore an open question remains about the nature of the tricritical points on the $T_c(2L)$ line, which should be clarified in the future. As well as the picture about the other parts of the $(2L, T)$ phase diagram, especially about the surface induced SmC ↔ SmC* phase transition.

It would be also of interest to learn about the influence of the quadrupolar surface interactions, when they are included into the model in combination with the polar interactions and to find out, how does the phase diagram qualitatively change.

REFERENCES

1. M. Glogarova, L. Lejček, J. Pavel, V. Janovec, J. Fousek, Mol. Cryst. Liq. Cryst., 91, 309 (1983).
2. M. Glogarova and J. Pavel, J. Physique, 45, 143 (1984).
3. K. Glogarova, J. Fousek, L. Lejček, J. Pavel, Ferroelectrics, 58, 161 (1984).
4. M. Yamashita, Ferroelectrics, 58, 149 (1984).
5. M.A. Handschy, N.A. Clark, Ferroelectrics, 59, 69 (1984).
6. J. Xue, N.A. Clark, Phys. Rev. Lett., 64, 307 (1990).
7. T. Povše, I. Muševič, B. Žekš and R. Blinc, Liquid Crystals, 14, 1587 (1993).