Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Mirantsev, L. V.(1996) 'Layer-thinning transitions in free-standing smectic A films', Liquid Crystals, 20: 4, 417 — 422
To link to this Article: DOI: 10.1080/02678299608032055
URL: http://dx.doi.org/10.1080/02678299608032055

LIQUID CRYSTALS, 1996, VOL. 20, NO. 4, 417–422

Layer-thinning transitions in free-standing smectic A films

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(Received 28 July 1995; accepted 23 October 1995)

In the present paper a discrete mean-field model for thin smectic A liquid crystal films with two boundary surfaces is offered. The model accounts for the recently observed phenomenon of layer-thinning transitions in free-standing smectic A films upon heating. In particular, the model predicts the observed multiple layer jumps, as well as, for films thinner than 13 layers, the observed power law dependence of the layer-thinning transition temperatures on film thickness.

1. Introduction

It is known that interactions between boundary surfaces and both the liquid and liquid crystal (LC) molecules result in the appearance of surface layers with properties strongly different from those of the bulk phase of a liquid. For example, the liquid–solid substrate interface not only enhances the orientational ordering in nematics, but also induces orientational ordering in the isotropic phase of liquids having a nematic phase [1–6] and imposes some orientational order on non-mesomorphic liquids [7]. Furthermore, the free surfaces of liquids and liquid crystals [8–11] and the liquid–solid substrate interfaces [1, 12, 13] have an effect on the positional molecular order in liquids that leads to the appearance of interfacial layered smectic A (S_A) structures.

Thin LC layers with two boundary surfaces, such as free-standing LC films, are particularly interesting. In these films the effect of finite size combines with the surface effects. In particular, the overlap of two interfacial layers can take place, resulting in the appearance of extra phenomena. For example, Rosenblatt and Amer [14] reported an anomalously high temperature of existence of the S_A phase in a free-standing film of 8OCB and Heinekamp *et al.* [15] observed the smectic C* phase (S_C^*) in a free-standing film of DOBAMBC at a temperature significantly higher than that of the S_C^*–S_A transition in the bulk.

Recently Stoebe *et al.* [16] observed a new extraordinary phenomenon in smectic A free-standing films of members of a homologous series of partially perfluorinated 5-*n*-alkyl-2-[4-*n*-(perfluoroalkylmethyleneoxy)-phenyl]pyrimidines. It was found that the above the bulk smectic A–isotropic transition point these films undergo layer-thinning transitions with increasing temperature. For example, the initially 25 layer film of one of the above mentioned compounds, namely H10F5MOPP, thinned to 15, 11, 9, 8, 7, 6, 5, 4, 3 and 2 layers before it finally ruptured at a temperature about 25 K higher than that of the bulk S_A–I transition. It was also revealed that the temperature of these layer transitions are related to the film thickness by means of the following simple power law:

$$h(t) \sim t^{-\beta}, \qquad (1)$$

where h is the film thickness (in units of layers), $t(N) = [T_c(N) - T_0]/T_0$, $T_c(N)$ is the maximum temperature at which an N-layer S_A film exists, T_0 is the bulk S_A–I transition temperature and $\beta \approx 0{\cdot}74$.

A qualitative and, as will be seen later, reasonable explanation of the above mentioned phenomenon was offered by the authors of [16]. They assumed that the free-standing S_A film thins as its interior layers undergo the S_A–I transition at the temperature $T_c(N)$ and the interaction between the free surfaces squeezes the isotropic phase into the surrounding reservoir of sample. However, this qualitative speculation cannot account for either the observed multiple layer jumps in the sequence of the layer-thinning transitions or the simple power law (1).

In the present paper we propose a simple macroscopic mean-field model for thin smectic LC films with two boundary surfaces. According to this model, the film is considered to consist of N discrete layers with thickness of the molecular length l. The molecules within each layer are assumed to interact only with molecules of the same layer and those of two neighbouring layers. The interaction between LC molecules and the boundary surface is simulated by the short range orienting field. By analogy with McMillan theory [17] for the bulk S_A phase in a homogeneous LC sample, the local orientational and smectic order parameters for each layer are defined. These parameters are determined by self-consistent equations. The solution of these equations allows us to obtain the local orientational and smectic order parameter profiles and the distribution of the free energy over the film layers. Investigation of this model shows that below a critical temperature $T_c(N)$, $(T_c(N) > T_0)$, the S_A phase occurs in the film. In this phase, the local order parameters are different from zero in each film layer and the free energy profile is a monotonic function of the distance from the boundary surface. As a result, all layers of one half of the film are subjected to forces directed towards the first boundary surface and the forces acting on the layers of the other half of the film are directed towards the second surface.

When the critical temperature $T_c(N)$ is reached, the N-layer S_A film becomes absolutely unstable to the occurrence of a composite smectic A film structure (QS_A) in which the interfacial order parameters are different from zero but decay very rapidly to nearly zero with distance from the boundary surface. The monotonic character of the free energy profile appears to be distorted and, as a result, the forces acting on 2–3 interfacial layers are directed towards the boundary surface and the interior layers are subjected to the forces directed in the opposite direction. One can imagine that the interfacial layers seek to squeeze out the interior layers, thinning the film to a stable N' $(N' < N)$ layer smectic A film. The free energy of the N' layer smectic A film must not exceed that of the composite, melted, interior layer structure of the N layer film. Choosing a suitable value of a parameter determining the 'strength' of the bulk S_A–I phase transition, we obtained the sequence of the layer-thinning transitions $(25 \rightarrow 13 \rightarrow 11 \rightarrow 10 \rightarrow 9 \rightarrow 8 \rightarrow ..)$ very similar to the experimentally observed sequence. In addition, for $N \leqslant 13$, the relation between $T_c(N)$ and N similar to experimental equation (1) is found.

2. Basic equations of the model

As said above, we consider an LC film with two boundary surfaces which is assumed to consist of N discrete layers with thickness of the order of the molecular length l. The film is also assumed to be homeotropically oriented, i.e. the director **n** is aligned along the normal **v** to the boundary surfaces. The intermolecular interaction is simulated by the McMillan model pair potential [17]

$$V_{12}(r_{12}, \vartheta_{12}) = -(V_0/n_0 r_0^3 \pi^{3/2})(3/2\cos^2\vartheta_{12} - 1/2) \times \exp(-r_{12}^2/r_0^2), \qquad (2)$$

where V_0 is the interaction constant, ϑ_{12} is the angle between molecular long axes, r_{12} is the distance between molecular centres, r_0 is the characteristic distance for the intermolecular interaction and n_0 is the density of molecules. Since in the framework of McMillan theory, r_0 is assumed to be much smaller than l $(r_0 \ll l)$, this interaction must decay to nearly zero at a distance of the order of the molecular length l and the molecules within each layer can interact only with the molecules of the same layer and those of two neighbouring ones. The interaction between the boundary surfaces and the mesogenic molecules is assumed to be short range and can be simulated by certain orienting fields which act directly only on the molecules within the first and last film layers. Typically, the energies of such interactions are written as [18, 19]

$$\begin{aligned} W_1(\vartheta_1) &= -W_0(3/2\cos^2\vartheta_1 - 1/2), \\ W_N(\vartheta_N) &= -W_0(3/2\cos^2\vartheta_N - 1/2), \end{aligned} \qquad (3)$$

where $\vartheta_1(\vartheta_N)$ is the angle between the long axes of the molecules within the first (last) layer and the normal **v** to the boundary surfaces of the film and W_0 is the interaction constant.

By analogy with McMillan theory [17], we can expand the pair potential (equation 2) in a Fourier series with characteristic period l along the z-axis parallel to **v** and keep the first two terms of this expansion. Then, in a mean-field approximation, the single-particle pseudo-potential $V_i(z_i, \vartheta_i)$ for the molecules within the ith film layer can be written as

$$\begin{aligned} V_1(z_1, \vartheta_1) = &-(V_0/3)(3/2\cos^2\vartheta_1 - 1/2) \\ &\times [q_1 + q_2 + 3W_0/V + \alpha\cos(2\pi z_1/l) \\ &\times (\sigma_1 + \sigma_2)], \end{aligned} \qquad (4)$$

$$\begin{aligned} V_{2 \leqslant i \leqslant N-1}(z_i, \vartheta_i) = &-(V_0/3)(3/2\cos^2\vartheta_i - 1/2) \\ &\times \left[\sum_{j=i-1}^{i+1} q_j + \alpha\cos(2\pi z_i/l) \sum_{j=i-1}^{i+1} \sigma_j\right], \end{aligned} \qquad (5)$$

$$\begin{aligned} V_N(z_N, \vartheta_N) = &-(V_0/3)(3/2\cos^2\vartheta_N - 1/2) \\ &\times [q_{N-1} + q_N + 3W_0/V_0 + \alpha\cos(2\pi z_N/l) \\ &\times (\sigma_{N-1} + \sigma_n)], \end{aligned} \qquad (6)$$

where

$$\alpha = 2\exp[-(\pi r_0/l)^2], \qquad (7)$$

q_i and σ_i are the 'local' orientational and smectic order parameters, respectively, for the ith layer which are determined by self-consistent equations

$$q_i = \langle 3/2\cos^2\vartheta_i - 1/2 \rangle_i, \qquad (8)$$

$$\sigma_i = \langle (3/2\cos^2\vartheta_i - 1/2)\cos(2\pi z_i/l) \rangle_i, \qquad (9)$$

$$\langle G(z_i,\vartheta_i)\rangle_i = \int_{(i-1)l}^{il} dz_i \int_{-1}^{+1} G(z_i,\vartheta_i) f_i(z_i,\vartheta_i) d\cos\vartheta_i \Big/ \int_{(i-1)l}^{il} dz_i \int_{-1}^{+1} f_i(z_i,\vartheta_i) d\cos\vartheta_i, \qquad (10)$$

where $f_i(z_i, \vartheta_i)$ is the single-particle distribution function for the ith layer given by

$$f_i(z_i,\vartheta_i) = A_i^{-1} \exp[-V_i(z_i,\vartheta_i)/K_B T], \qquad (11)$$

where A_i is the normalization constant for the ith layer, T is the absolute temperature of the system and K_B is the Boltzmann constant. It should be added that in the derivation of equations (4)–(6), we assumed that the system under consideration has an axial symmetry and the average number of molecules within each layer is constant. The free energies of the discrete film layers are determined by the following equations:

$$F_1 = N_i V_0 \left[q_1(q_1+q_2)/6 + \alpha\sigma_1(\sigma_1+\sigma_2)/6 - (K_B T/V_0) \ln\left((1/2l) \int_0^l dz_1 \times \int_{-1}^{+1} f_1(z_1,\vartheta_1) d\cos\vartheta_1 \right) \right], \qquad (12)$$

$$F_{2\leqslant i \leqslant N-1} = N_i V_0 \left[q_i \sum_{j=i-1}^{i+1} q_j/6 + \alpha\sigma_i \sum_{j=i-1}^{i+1} \sigma_j/6 - (K_B T/V_0) \ln\left((1/2l) \int_{(i-1)l}^{il} dz_i \times \int_{-1}^{+1} f_i(z_i,\vartheta_i) d\cos\vartheta_i \right) \right], \qquad (13)$$

$$F_N = N_i V_0 \left[q_N(q_{N-1}+q_N)/6 + \alpha\sigma_N(\sigma_{N-1}+\sigma_N)/6 - (K_B T/V_0) \ln\left((1/2l) \int_{(N-1)l}^{Nl} dz_N \times \int_{-1}^{+1} f_N(z_N,\vartheta_N) d\cos\vartheta_N \right) \right], \qquad (14)$$

where N_i is the number of molecules within a single layer. The total free energy F of the N layer film is equal to

$$F = \sum_{i=1}^{N} F_i. \qquad (15)$$

3. The results of numerical calculation and comparison with experiment

The numerical solution of equations (8, 9) allows a determination of the local order parameters q_i and σ_i at given values of the number of film layers N, temperature T, and parameters α and W_0/V_0, and equations (12–15) give the total free energy F of the film and its distribution over the film layers. Since our purpose is to account for the experimentally observed phenomenon of layer-thinning transitions in free-standing smectic A films upon heating, we must choose the values of the parameters N, α and W_0/V_0 most appropriate to the experimental conditions. According to [16] the initial film thickness was equal to 25 layers. Therefore we set the initial number of film layers equal to $N_0 = 25$. Further, in [16], a free-standing LC film exhibiting a bulk S_A–I phase transition was investigated. According to McMillan theory [17], the S_A–I transition occurs for $\alpha > 0{\cdot}98$. Hence, in our numerical calculations we will use $\alpha \geqslant 1$ $(1, 1{\cdot}05, 1{\cdot}1, 1{\cdot}2)$. As for the value of the ratio W_0/V_0, in its choice we can be guided by the fact that the free-standing S_A films experimentally investigated were stable above the bulk S_A–I transition temperature. Consequently, it is reasonable to assume that the LC molecules-boundary surface interaction constant W_0 must be greater than the intermolecular interaction constant V_0 and we should set $W_0/V_0 > 1$. Henceforth, we will use $W_0/V_0 = 3$. It should be noted that numerical calculations show a very weak dependence of the results obtained on the concrete value of the ratio W_0/V_0.

The numerical solution of equations (8, 9) shows that for $T < T_c(N_0)$ $(T_c(N_0) > T_0)$, where $T_c(N_0)$ is a critical temperature for the N_0 layer film, the S_A phase occurs in the film under consideration. Typical orientational and smectic order parameter profiles for $T < T_c(N_0)$ are shown in figure 1. It is seen that both orientational and smectic order parameters are different from zero in each film layer and their magnitudes in the first interfacial layers exceed those in the interior layers. As for the free energy profile in the N_0 layer S_A film, it is a monotonic function of distance from the boundary surface (figure 3, curve 1). If an effective force $P = -\partial F(z)/\partial z$ is defined (in the case of discrete layers the effective force P_i acting on the ith layer can be defined as $-(F_{i+1} - F_i)/((i+1-i)l) = (F_i - F_{i+1})/l$), then, as follows from figure 3 (curve 1), this force for each layer of one half of the film is directed towards the nearest boundary surface and the forces acting on all layers of the other half of the film are directed towards the second boundary surface. In other words, in the N_0 layer S_A film, for $T < T_c(N_0)$, all film layers are subjected to attractive forces from the boundary surfaces.

When the critical temperature $T_c(N_0)$ is reached, the N_0 layer S_A film becomes absolutely unstable and the system under consideration undergoes a discontinuous transition to a composite structure with melted interior layers. The orientational and smectic order parameter profiles in the composite structure are shown in figure 2.

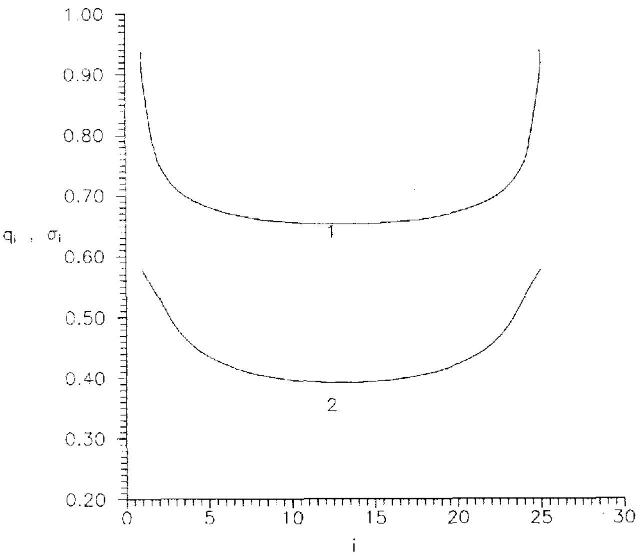

Figure 1. The orientational and smectic order parameter profiles in the S_A phase in a free-standing LC film at $T = 0{\cdot}2298\,(V_0/K_B)\,(T < T_c(N_0)) = 25$, $\alpha = 1{\cdot}05$. (1): the orientational order parameter; (2): the smectic order parameter.

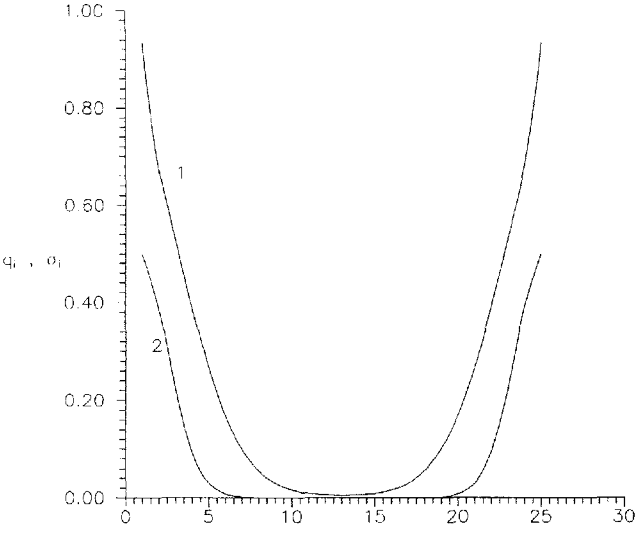

Figure 2. The orientational and smectic order parameter profiles in the QS_A phase at $T_c(N_0) = 0{\cdot}2299\,(V_0/K_B)$. $N_0 = 25$, $\alpha = 1{\cdot}05$. (1): the orientational order parameter; (2): the smectic order parameter.

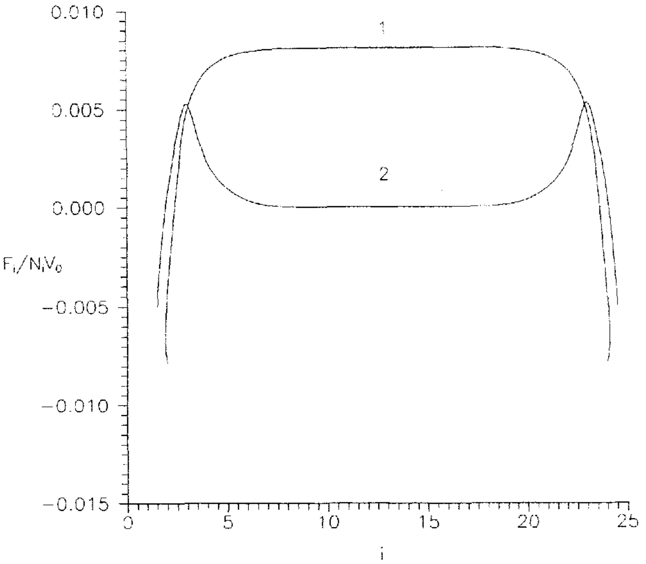

Figure 3. The free energy profiles in the free-standing LC film in the S_A phase and QS_A phase. $N_0 = 25$, $\alpha = 1{\cdot}05$. (1): the S_A phase at $T = 0{\cdot}2298\,(V_0/K_B)$; (2): the QS_A phase at $T_c(N_0) = 0{\cdot}2299\,(V_0/K_B)$.

It is seen that although both the orientational and smectic order parameters in the first interfacial layers are different from zero, they decay rapidly to nearly zero with distance from the boundary surface. In fact, the isotropic phase occurs in the interior film layers. In the composite structure, the monotonic character of the free energy profile (figure 3, curve 2) is drastically distorted. Now the distribution of the free energy over the film layers has two maxima which are symmetric with respect to the centre of the film. The presence of these maxima results in the first 2–3 interfacial film layers being subjected to attractive forces from the boundary surface, whereas the interior layers are subjected to forces acting in the opposite direction. As a result, the interior film layers are squeezed by the interfacial layers.

Let us estimate the pressure acting on the interior layers. In order to do this we can use curve 2 in figure 3. According to this curve, the free energy per single layer achieves its maximum value $\sim 5 \times 10^{-3} N_i V_0$ in the third layer ($i = 3$) and then decays to nearly zero for $i = 5$. Hence, the free energy per single film layer decreases from $\sim 5 \times 10^{-3} N_i V_0$ at a distance of two molecular lengths, i.e. $\sim 5 \times 10^{-7}$ cm. The number of molecules N_i within a single layer with unit surface (1 cm^2) can be estimated as $n_0 l$, where $n_0 \approx 1{\cdot}5 \times 10^{21}\,\mathrm{cm}^{-3}$. Taking $l \approx 2{\cdot}5 \times 10^{-3}$ cm, we obtain $N_i \approx 3{\cdot}75 \times 10^{14}\,\mathrm{cm}^{-2}$. The magnitude of the constant V_0 can be estimated in the following way. According to McMillan theory [17], for $\alpha = 1$–$1{\cdot}2$, the bulk S_A–I phase transition temperature ranges from $0{\cdot}2213 \times (V_0/K_B)$ to $0{\cdot}2368 \times (V_0/K_B)$. The mesomorphic compound studied in [16] exhibits the bulk S_A–I transition at the temperature $T_0 \approx 358$ K. Hence we obtain $V_0 \approx (2{\cdot}1 - 2{\cdot}2) \times 10^{-13}$ erg and $N_i V_0 \approx 80\,\mathrm{erg\,cm}^{-2}$. Then the average pressure acting on the interior film layers can be roughly estimated as $\sim 5 \times 10^{-3} N_i V_0 / 5 \times 10^{-7}$ cm, $\sim 8 \times 10^5\,\mathrm{dyn\,cm}^{-2}$ or $8 \times 10^4\,\mathrm{N\,m}^{-2}$ that is comparable with atmospheric pressure. Consequently, the interfacial smectic layers can squeeze interior isotropic layers into the surrounding reservoir producing a stable smectic A film with a fewer number of layers.

One can then ask: what is the number, N_1, of layers in the free-standing smectic A film after the thinning transition? The answer to this question is the following: the number of layers remaining in the film after thinning must be the number that produces a stable S_A film with total free energy not exceeding that of the composite N_0 layer film with melted interior layers. Consequently, we have to decrease the number of film layers (at the constant temperature $T_c(N_0)$) from the initial value N_0 to a final value N_1 for which one can obtain the solution of equations (8, 9) corresponding to the S_A phase with total free energy (15) not exceeding that of the QS_A phase in the N_0 layer film. This number, depending on the value of the parameter α, is: $N_1 = 15$ for $\alpha = 1$; $N_1 = 13$ for $\alpha = 1{\cdot}05$; $N_1 = 12$ for $\alpha = 1{\cdot}1$; $N_1 = 10$ for $\alpha = 1{\cdot}2$.

After this first thinning transition, the S_A phase with the order parameter profiles similar to those shown in figure 1 occurs in the film until the second critical temperature $T_c(N_1)$ ($T_c(N_1) > T_c(N_0)$) is reached. At this temperature, the interior layers of the film undergo a melting transition which, in turn, gives rise to one more squeezing of the melted interior layers into the surrounding reservoir. Using the above mentioned procedure, we can again obtain the number N_2 of layers remaining in the film after the second thinning transition. Reiterating this procedure for subsequent values of the film thickness, we have obtained the following sequences of layer-thinning transitions upon heating:

$$25 \to 15 \to 13 \to 12 \to 11 \to 10 \to 9 \to \ldots \text{ for } \alpha = 1;$$

$$25 \to 13 \to 11 \to 10 \to 9 \to 8 \to \ldots \text{ for } \alpha = 1{\cdot}05;$$

$$25 \to 12 \to 11 \to 10 \to 9 \to 8 \to \ldots \text{ for } \alpha = 1{\cdot}1;$$

$$25 \to 10 \to 9 \to 8 \to \ldots \text{ for } \alpha = 1{\cdot}2.$$

It is easily seen that the layer-thinning transitions obtained for $\alpha = 1{\cdot}05$ are almost similar to the experimental ones [16]. Using this value of the parameter α, we have plotted the dependence of $\log[(T_c(N) - T_0)/T_0]$ on $\log(N)$ (figure 4, curve 1) and compared it with the analogous experimental dependence [16] (figure 4, curve 2). It is found that for $N \leqslant 13$, the theoretical curve is well described by relationship (1), with an exponent $\beta \approx 0{\cdot}7$ very similar to the experimental value ($\beta \approx 0{\cdot}74$). One can see from figure 4 that for $N \leqslant 13$, both theoretical and experimental curves are parallel to each other. However, the absolute values of the parameter $t(N)$ given by theory are about 3–4 times larger than the experimental values, and for $N > 13$, the theoretical dependence becomes sharper and approaches the well known Kelvin law, namely, $t(N) \sim N^{-1}$. Possibly this discrepancy is due to utilization of the mean-field approximation which is the simplest approach to the phenomenon under consideration.

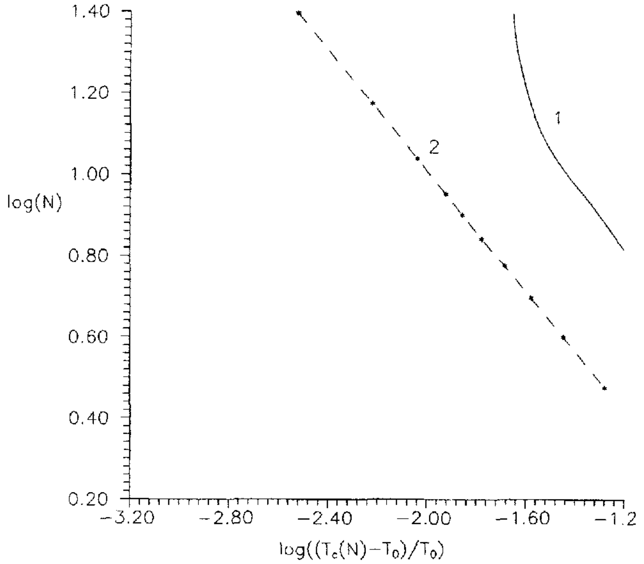

Figure 4. The dependence of the layer-thinning transition temperature on the film thickness. (1): theoretical curve ($\alpha = 1{\cdot}05$, $T_0 = 0{\cdot}2249$ (V_0/K_B)); (2): experimental data [16].

4. Conclusion

We offer a simple macroscopic mean-field model for a thin LC film with two boundary surfaces. This model accounts for the recently observed phenomenon of layer-thinning transitions in free-standing smectic A films upon heating [16]. It is shown that this phenomenon is due to the melting of interior layers in the film above the bulk S_A–I transition temperature. In the composite S_A film with melted interior layers, the orientationally and positionally ordered interfacial layers squeeze several isotropic interior layers into the surrounding reservoir. The number of layers remaining in the film after squeezing must be that needed to provide the existence of a stable S_A phase with free energy not exceeding that of the composite structure in the film of initial thickness. The theory predicts the sequence of layer-thinning transitions in free-standing S_A films very similar to that observed experimentally.

References

[1] Horn, R. G., Israelachvili, J. N., and Perez, E., 1981, *J. Phys. (Paris)*, **42**, 39.
[2] Miyano, K., 1979, *Phys. Rev. Lett.*, **43**, 51.
[3] Miyano, K., 1979, *J. chem. Phys.*, **71**, 4108.
[4] Mada, H., and Kobayashi, S., 1979, *Appl. Phys. Lett.*, **35**, 4.
[5] Mada, H., and Kobayashi, S., 1981, *Mol. Cryst. liq. Cryst.*, **66**, 57.
[6] Van Sprang, H. A., 1983, *J. Phys. (Paris)*, **44**, 421.

[7] Deriagin, B. V., Popovski, Iu. M., and Altoiz, B. A., 1982, *Dokl. Akad. Nauk SSSR*, **262**, 853.

[8] Als-Nielsen, J., Christensen, J., and Pershan, P. S., 1982, *Phys. Rev. Lett.*, **48,** 1107.

[9] Pershan, P. S., and Als-Nielsen, J., 1984, *Phys. Rev. Lett.*, **52,** 759.

[10] Pershan, P. S., Braslau, A., and Weiss, A., 1987, *Phys. Rev. A*, **35,** 4800.

[11] Ocko, B. M., Braslau, A., Pershan, P. S., Als-Nielsen, J., and Deutsch, M., 1986, *Phys. Rev. Lett.*, **57,** 94.

[12] Rosenblatt, C., 1984, *Phys. Rev. Lett.*, **53,** 791.

[13] Ocko, B. M., 1990, *Phys. Rev. Lett.*, **64,** 2160.

[14] Rosenblatt, C., and Amer, N. M., 1980, *Appl. Phys. Lett.*, **36,** 432.

[15] Heinekamp, S., Pelcovits, R. A., Fontes, E., Chen, E. Y., Pindak, R., and Meyer, R. B., 1984, *Phys. Rev. Lett.*, **52,** 1017.

[16] Stoebe, T., Mach, P., and Huang, C. C., 1994, *Phys. Rev. Lett.*, **73**, 1384.

[17] McMillan, W. L., 1971, *Phys. Rev. A*, **4,** 1238.

[18] Pawlowska, Z., Kventsel, G. F., and Sluckin, T. J., 1987, *Phys. Rev. A*, **36,** 992.

[19] Pawlowska, Z., Kventsel, G. F., and Sluckin, T. J., 1988, *Phys. Rev. A*, **38,** 5342.