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Behaviour of free-standing smectic A films upon heating

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In the framework of a previously proposed microscopic mean-field model for thin smectic A liquid crystal films with two boundary surfaces, the behaviour of free-standing smectic A films upon heating is investigated theoretically. It is shown that the model accounts for both the film rupture and layer-thinning transitions with increasing temperature. A close correlation between the behaviour of the film upon heating and the surface tension is found. The model accounts also for essential features of the layer-thinning transitions for thick and thin free-standing smectic A films of various liquid crystal compounds.

1. Introduction

A unique property of smectic liquid crystals is the ability to form free-standing films (FSFs), which can be considered as stacks of several smectic layers with two free boundary surfaces. Their surface area can be as large as several cm^2, and the film thickness can be varied from thousands of molecular layers down to two, and even one smectic layer [1, 2]. This makes the FSF a convenient system for investigation of the crossover from 3D to 2D behaviour [3, 4]. The combination of the surface-induced ordering and finite-size effects in these films gives rise to the appearance of phenomena which are not observed in bulk liquid crystal (LC) samples [5–8].

One of the most remarkable of these phenomena is the layer-thinning transition. For most LC compounds, FSFs prepared in the smectic A (SmA) temperature range rupture upon heating above the bulk SmA–isotropic (SmA–I) or SmA–nematic (SmA–N) transition temperatures. In 1994, however, Stoebe *et al.* [9] found that above the bulk SmA–I transition point the SmA FSF (FSAF) of one member of the partially perfluorinated 5-*n*-alkyl-2-(4-*n*-perfluoroalkylmetheleneoxyphenyl)-pyrimidine homologous series, namely H10F5MOPP, exhibits a series of thinning transitions with increasing temperature. For example, the initially 25 layer film 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 SmA–I transition. Later, Demikhov *et al.* [10] observed similar thinning behaviour above the bulk SmA–N transition point of LC 50.6 (4-*n*-pentyloxybenzylidene-4-*n*-hexylaniline). To date, such phenomena have been found by different research groups in several LC compounds [11–14], and one can summarize their essential features.

It is convenient to divide all LCs exhibiting layer-thinning transitions into two groups, namely LCs undergoing the bulk SmA–I phase transition, and those having the SmA–N–I phase sequence. As a rule, compounds from the first group are perfluorinated, i.e. they have one hydrogeneous alkyl and one fluorinated alkyl tail, for example, H8F(2,1)MOPP [13], or two fluorinated alkyl tails, for example, F3MOCPH11OB [14]. Conventional LCs with two hydrogeneous alkyl tails do not exhibit layer-thinning transitions and rupture above the bulk SmA–I transition temperature [13]. There is a close correlation between the behaviour of a FSAF upon heating above the bulk SmA–I transition point and the measured values of the surface tension. The perfluorinated compounds, exhibiting layer-thinning transitions, show a significantly lower surface tension ($\sim 13\,\mathrm{dyn\,cm^{-1}}$ [15]) than the conventional LCs (~ 20–$25\,\mathrm{dyn\,cm^{-1}}$ [16]) that rupture upon heating. Further, the thinning transitions in 'thick' FSAFs (number of the film layers $N > 10$) of compounds from the first group may occur in multilayer steps of variable size, and thus can be termed 'irregular' [14]. For film thicknesses less than 10 layers, the film loses a single layer per transition, and each transition occurs at a reproducible temperature. Therefore such thinning transitions can be termed 'regular', or layer-by-layer transitions [14]. Finally, the series of regular thinning transitions can be characterized by the simple power law expression

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

where h is the film thickness (in units of layers), t is the reduced temperature $t = [T_c(N) - T_0]/T_0$, $T_c(N)$ is the maximum temperature at which the N-layer film can exist, and T_0 is very close to the bulk SmA–I transition

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temperature. The exponent β ranges from ~ 0.6 to ~ 0.7 [9, 13, 14].

Now, let us turn to the second group of compounds exhibiting layer-thinning transitions. For such compounds the existence of these phenomena is not related to perfluorination, and the layer-thinning transitions can occur in conventional LC materials with two hydrogeneous alkyl tails [10–12]. The surface tension of these LCs is equal to about 20–25 dyn cm^{-1} [12], much higher than that of perfluorinated compounds from the first group. Further, the thinning transitions in LCs having the bulk nematic phase are more regular than those in mesogens exhibiting the bulk SmA–I phase transition. For example, 16-, 17-, 24-, and even 48-layer FSAFs demonstrate layer-by-layer transitions [10, 12], whereas for LC materials from the first group such regular transitions can occur only in FSAFs with thicknesses less than 10 layers. The temperatures of these transitions have also been found to obey the power law (1) with exponent β similar to that for perfluorinated compounds from the first group.

A theoretical description of layer-thinning transitions in free-standing smectic A films based on a simple microscopic mean-field model for thin LC films with two boundary surfaces was proposed for the first time in [17, 18]. Later, other models for thinning transitions were offered in [19, 20]. Up to now, however, a complete understanding of these phenomena is absent. In particular, it is not clear why FSAFs of some LCs undergo layer-thinning transitions, whereas FSAFs of most liquid crystalline compounds rupture with increasing temperature. It is obvious, that a successful theoretical model of layer-thinning transitions should account for this fact and answer the following questions:

(i) Why do LC compounds without the bulk nematic phase exhibit layer-thinning transitions only after perfluorination, whereas for LC materials having the bulk SmA–N–I phase sequence perfluorination is not necessary, and the layer-thinning transitions can occur in conventional LC compounds with two flexible hydrogeneous alkyl tails?

(ii) Why for sufficiently thick ($N > 10$) films of LCs without the bulk nematic phase are the thinning transitions 'irregular', i.e. show irreproducible behaviour, and may occur in multilayer steps of variable size, whereas for film thicknesses less than 10 layers these transitions are 'regular', occurring layer-by-layer at reproducible temperatures?

(iii) Why for LC materials having the bulk nematic phase are the layer-thinning transitions more regular then those for LC compounds without the nematic phase, and even sufficiently thick ($N > 20$) FSAFs exhibit layer-by-layer transitions?

In this paper we present the results of a recent numerical investigation of the model proposed in [17, 18], and show that this model accounts for all the above-mentioned features of behaviour of FSAFs upon heating above the bulk SmA–I or SmA–N transition temperature. It has been found that this behaviour depends crucially on the strength W_0 of the effective short range external field, which simulates the orienting action of the boundary free surfaces on the LC molecules within the first and last film layers. If this field is not sufficiently 'strong' ($W_0 <$ a certain critical value W_0^c), then heating the film above some critical temperature $T_c(N)$ gives rise to melting of the smectic layers in the whole film volume, resulting in turn in film rupture. On the contrary, when the anisotropic interaction between the LC molecules and the boundary free surfaces is 'strong' enough ($W_0 \geqslant W_0^c$), heating the film above $T_c(N)$ gives rise to the appearance of a 'quasi-smectic' (QSmA) film structure composed of the melted interior film layers and the interfacial layers maintaining the orientational and positional order. In this case the ordered interfacial film layers seek to squeeze out the melted interior layers, giving rise to the thinning transition. Since the above-mentioned external orienting field gives a negative contribution to the total interfacial free energy of FSAFs, then the surface tension of films exhibiting layer-thinning transitions should be lower than that of FSAFs rupturing upon heating. Moreover, the model predicts that for LC materials having the bulk nematic phase, the ratio W_0^c/V_0, where V_0 is the intermolecular interaction constant, could be significantly smaller than that for compounds undergoing the bulk SmA–I phase transition. Hence, the surface tension of LC compounds from the first group should be significantly lower than that of those from the second group. This result allows us to reveal a rôle of perfluorination in the layer-thinning transitions. Perfluorination significantly lowers the LC surface tension and this provides a possibility of thinning transitions in LC compounds without the bulk nematic phase. As for LC materials having the bulk nematic phase, they can exhibit thinning transitions at values of the surface tension higher than that for compounds from the first group and do not need perfluorination.

The model accounts also for the 'irregularity' of the layer-thinning transitions in 'thick' ($N > 10$) FSAFs of compounds from the first group, and the 'regularity' of these transitions in the 'thin' ($N \leqslant 10$) films. It has been found that for sufficiently thick films there are two temperatures characterizing the stability of the SmA film structure and the occurrence of the QSmA structure. At the first temperature $T_c^b(N)$ ('binodal' point) the QSmA structure becomes energetically more favourable than the SmA structure, and when the second temperature $T_c^s(N)$ ('spinodal' point) is reached, the N-layer FSAF becomes absolutely unstable to the occurrence of the QSmA structure. The SmA to QSmA transition and, hence, the thinning transition, should occur at the temperature $T_c(N)$ which can range from $T_c^b(N)$ to $T_c^s(N)$, and the model predicts that the number of film layers squeezed into the surrounding reservoir depends on the value of $T_c(N)$. If $T_c(N)$ is close to the binodal point $T_c^b(N)$, then the film should lose one smectic layer per transition, whereas near the spinodal point $T_c^s(N)$, the thinning transition occurs in a multilayer step. Near the binodal point $T_c^b(N)$ the difference ΔF between the free energies of the SmA and QSmA film structures is small, and because of a sufficiently high smectic–isotropic interfacial excess free energy, the probability of QSmA structure nucleation in thick FSAFs is negligibly low. This probability grows with increasing temperature and becomes sufficiently high near the spinodal point $T_c^s(N)$. Therefore, in thick FSAFs the QSmA structure could appear only in a 'highly superheated' metastable SmA phase. Then 'non-thermodynamics factors' such as impurities, ions, etc., become very important to this process, giving rise to high irregularity of the thinning transition in thick FSAFs (the transition temperature and discontinuity in the film thickness are variable and can change from run to run). The model predicts also that the width of the SmA metastability interval, $T_c^s(N) - T_c^b(N)$, decreases with decreasing film thickness N; beginning from a certain thickness N' ($N' \leqslant 10$), this interval degenerates to a point. Then for sufficiently thin films ($N \leqslant 10$) the QSmA structure should appear at the binodal point $T_c^b(N)$, and hence the thinning transition occurs in a regular layer-by-layer manner. Moreover, numerical calculations show that the binodal points are well described by the power law (1) with an exponent β similar to experimental value.

Further, the model predicts that for thick FSAFs of LC compounds having the bulk nematic phase, the width of the SmA metastability interval, $T_c^s(N) - T_c^b(N)$, is much smaller than that for FSAFs of the same thickness but consisting of LC materials without the bulk nematic phase. Moreover, when the bulk SmA–N first order phase transition is sufficiently weak, this width can be equal to zero even for a film thickness > 20 layers. Thus, the model also accounts for the occurrence of regular layer-by-layer thinning transitions for sufficiently thick FSAFs of LCs having the bulk nematic phase.

2. Rupture and thinning transitions as two possible scenarios of behaviour of FSAFs above the bulk SmA–I or SmA–N transition temperature

According to the FSAF model proposed in [17, 18], an LC film with two boundary surfaces 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 $\mathbf{n}$ is aligned along the normal $\boldsymbol{\nu}$ to the boundary surfaces. The intermolecular interaction is simulated by the McMillan model short range pair potential [21], and the molecules within each layer are assumed to interact only with the molecules of the same layer and those of the two neighbouring layers. The action of the boundary free surfaces on the LC molecules is simulated by an 'effective' orienting field (see equation (3) in [17, 18]) which induces a homeotropic orientation in the FSAF. These fields are assumed to be very short range, and they act directly only on the molecules within the first and last film layers. By analogy with McMillan theory, in a mean-field approximation, the single particle pseudopotentials $V_i(z_i, \vartheta_i)$, and, hence the distribution functions $f_i(z_i, \vartheta_i)$ ($i = 1, N$) for the molecules within each film layer are obtained (see equations (4–7), and (11) in [17, 18]). These pseudopotentials are the functions of the 'local' orientational q_i and smectic σ_i order parameters determined by self-consistent equations (8, 9) in [17, 18]. The free energies F_i of the discrete film layers and the total free energy F of the N-layer film are determined by equations (12–14) and (15), respectively, in [17, 18].

The numerical solution of the self-consistent equations (8, 9) allows us to determine the local order parameters q_i and σ_i at a given number N of film layers, the temperature T, the model parameter α, which in the framework of McMillan theory, determines the type and 'strength' of the phase transition for the bulk LC sample, and the ratio W_0/V_0. Then, using equations (12–15), one can determine the free energy profile and the total free energy F of the film, respectively. Thus, we can obtain all the information about the thermodynamic properties of a FSAF and investigate its behaviour upon heating.

First, let us investigate the dependence of such a behaviour on 'strength' of an orienting action of the boundary free surfaces on the LC molecules within the outermost film layers. Since in the framework of the model this orienting action is simulated by the external fields given by equation (3) in [17, 18], we should investigate the behaviour of the FSAF upon heating for various magnitudes of the ratio W_0/V_0 at fixed values of both the number N of film layers and the model parameter α. As in [17, 18], we set the initial number of film layers at $N_0 = 25$ and the parameter α equal, at first, to 1.05 (the bulk SmA–I phase transition occurs).

The numerical solution of the self-consistent equations (8, 9) in [17, 18] shows that, independent of the value of W_0/V_0, for a temperature $T < T_c^b(N_0)$ with $T_c^b(N_0) > T_0$, the stable SmA phase occurs in the film under consideration, see figure 1 in [17, 18]. Both the orientational and smectic order parameters are different from zero in each film layer. The free energy profile in the SmA phase is

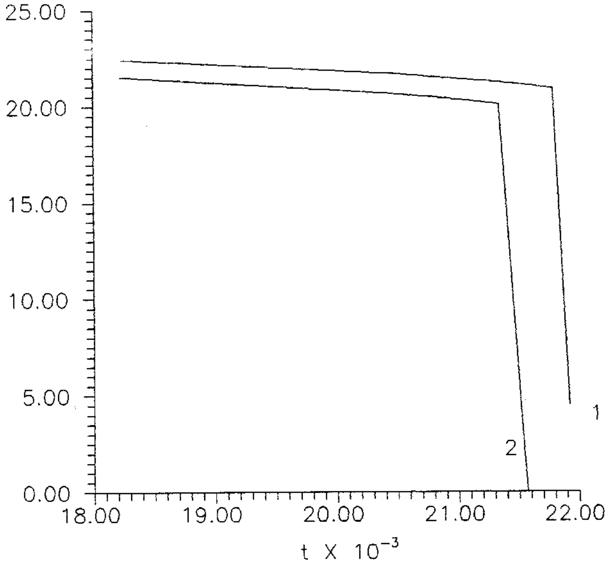

Figure 1. Typical behaviour of the effective thickness L^* of a well smectic ordered region in a 25-layer FSAF upon heating above $T_c^b(N_0)$. It is shown that a sharp decay of L^* occurs near the spinodal point $T_c^s(N_0)$: $\alpha = 1.05$. Curve 1, $W_0/V_0 = 1.8$; curve 2, $W_0/V_0 = 1$.

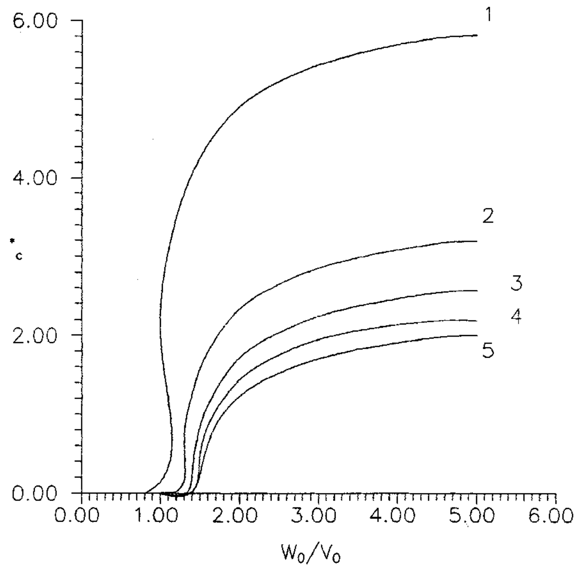

Figure 2. Dependence of L_c^* on the ratio W_0/V_0 for different values of the parameter α: $N_0 = 25$. Curve 1, $\alpha = 0.9$; curve 2, $\alpha = 1$; curve 3, $\alpha = 1.05$; curve 4, $\alpha = 1.1$; curve 5, $\alpha = 1.2$.

a monotonic function of the distance from the boundary free surface, see figure 3 (curve 1) in [17, 18]. As for the effective force acting on the film layers, this force for each layer of one half of the film is directed towards the first boundary surface and the forces acting on all layers of the other half of the film are directed towards the second surface. In other words, in the SmA phase all film layers are subjected to attractive forces from the boundary surfaces.

When the critical temperature (binodal point) $T_c^b(N_0)$ is reached and the SmA phase becomes unstable (the order parameter profiles shown in figure 1 in [17, 18] do not provide an absolute minimum of the total free energy F), the behaviour of the N_0 layer of the FSAF depends crucially on the value of the ratio W_0/V_0. When this value is sufficiently large, the system under consideration should undergo a discontinuous transition to a 'quasi-smectic' A phase (QSmA). The orientational and smectic order parameter profiles in the QSmA phase, which for $T > T_c^b(N_0)$ provide a minimum value of F, are shown in figure 2 in [17, 18]. Though 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 part of the film, whereas the interfacial film layers hold the smectic order. Therefore, one can consider the 'quasi-smectic' state of the film as a composite structure with a melted interior part and a 'hard' smectic membrane, which preserves the film from rupture. In the QSmA phase, however, the monotonic character of the free energy profile 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, see figure 3 (curve 2) in [17, 18]. The presence of these maxima results from the first 2–3 interfacial film layers being subjected to attractive forces from the boundary surfaces, whereas the interior layers are subjected to forces acting in the opposite direction. As a

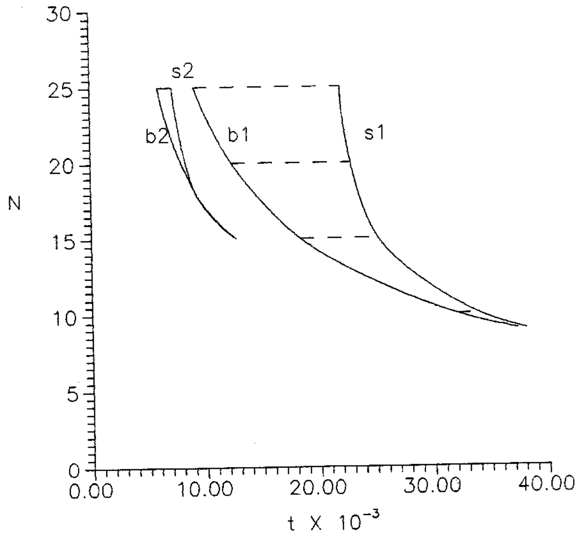

Figure 3. Dependences of the reduced binodal t^b and the reduced spinodal t^s temperatures on the number N of film layers: $W_0/V_0 = 1.8$. b1 and s1 are the binodal and spinodal temperatures, respectively, for $\alpha = 1.05$; b2 and s2 are the analogous temperatures for $\alpha = 0.9$.

result, the melted interior film layers are squeezed by the hard smectic membrane. According to the estimation made in [17, 18], the average pressure acting on the interior film layers can be comparable with atmospheric pressure. Consequently, some of the melted interior layers can be squeezed into the surrounding reservoir producing a stable smectic A film with a fewer number of layers. In other words, the SmA–QSmA transition in the free-standing film could be accompanied by the thinning transition.

For smaller values of the ratio W_0/V_0, the model predicts another scenario of behaviour of a FSAF upon heating. In this case, when the critical temperature $T_c^b(N_0)$ is reached, the absolute minimum of the total free energy F of the film is provided by a solution of the self-consistent equations (8, 9) in [17, 18] corresponding to almost complete disappearance of the smectic order in the whole volume of the film. Now the hard membrane, which in the QSmA phase preserves the film from rupture, is absent, and film rupture is inevitable.

Two possible scenarios of behaviour of the film upon heating can be illustrated by figure 1, in which an effective thickness L^* (in terms of the molecular length l) of a 'well smectic ordered' region in the 25-layer free-standing film vs. the reduced temperature t is shown for sufficiently 'strong' ($W_0/V_0 = 1.8$) and 'moderate' ($W_0/V_0 = 1.0$) orienting actions of the boundary free surface on the LC molecules. Here L^* is defined as

$$L^* = \left(\sum_{i=1}^{N0} \sigma_i\right) \Big/ \sigma_{AI} \qquad (2)$$

where σ_{AI} is the value of the bulk smectic order parameter at the SmA–I transition temperature T_0, given by McMillan's theory [21] for $\alpha = 1.05$. The effective thickness L^* can be considered as the number of 'full-bodied' smectic layers in the film. It is seen that for both 'strong' and 'moderate' interactions between the LC molecules and the boundary surface, heating of the FSAF above the critical temperature $T_c^b(N_0)$ should give rise to a sharp decrease of the effective thickness L^*. For the 'strong' interaction, however, L^* decays to a finite value different from zero (the SmA–QSmA transition), whereas for the 'moderate' interaction, L^* decreases to nearly zero (film rupture).

One can expect that there is a certain critical value of the LC molecule-boundary surface interaction constant W_0^c which separates two possible scenarios of behaviour of the FSAF upon heating above $T_c^b(N_0)$. For $W_0 > W_0^c$, the thinning transition should occur, whereas for $W_0 < W_0^c$, film rupture should be observed. To find this critical value, we have determined, for different values of the interaction constant W_0 and the model parameter α, an effective thickness L_c^* of the hard smectic membrane which remains in the free-standing film after melting of the smectic order in its interior. For symmetric reasons, this thickness can be defined as $L_c^* = L^*/2$. The dependence of L_c^* on the ratio W_0/V_0 for different values of the parameter α is shown in figure 2 (for $\alpha \leqslant 0.98$, according to the McMillan theory, the bulk SmA–N transition occurs, and the parameter σ_{AI} in equation (2) must be replaced by the bulk smectic order parameter σ_{AN} at the SmA–N transition temperature). It is seen that in the case of 'strong' interaction between the LC molecules and the boundary surfaces ($W_0 > 2V_0$) the magnitude of L_c^* depends weakly on W_0 for all values of the parameter α under consideration ($0.9 \leqslant \alpha \leqslant 1.2$), and it saturates at $W_0 \sim 5V_0$. The maximum value of the 'hard' smectic membrane thickness L_c^* ranges from ~ 2 smectic layers, for $\alpha = 1.2$ up to ~ 6 smectic layers for $\alpha = 0.9$. When $W_0 < 2V_0$, a decrease of W_0 gives rise to a sharp decrease in the thickness L_c^* to nearly zero at values of W_0 ranging from $\sim 0.8V_0$, for $\alpha = 0.9$, up to $\sim 1.5V_0$ for $\alpha = 1.2$. If a minimum effective thickness of the 'hard' smectic membrane (which is capable of preserving the film with a melted interior from rupture) is assumed to be equal to the thickness l of a single smectic layer, then one can find from figure 2 that the critical value W_0^c for the LC molecule-boundary surface interaction constant should range from $\sim 1.2V_0$, for $\alpha = 0.9$, up to $\sim 1.8V_0$ for $\alpha = 1.2$.

The above theoretical results suggest to us that behaviour of a FSAF upon heating above the bulk SmA–I or SmA–N transition point depends crucially on the strength of the orienting action of the boundary free surfaces on the LC molecules. When this orienting action is sufficiently strong ($W_0 > W_0^c$), the thinning transition should occur. In the opposite case ($W_0 < W_0^c$), the heating

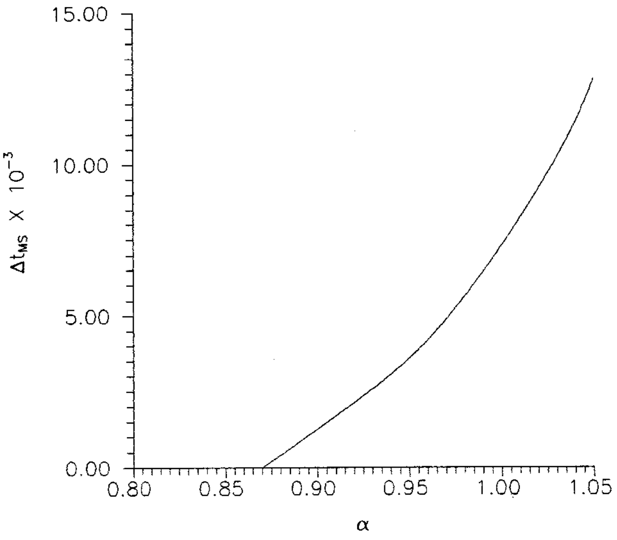

Figure 4. Dependences of the reduced width Δt_{MS} of the metastability region on the parameter α for a 25-layer FSAF: $W_0/V_0 = 1.8$.

of the FSAF above a certain critical temperature gives rise to the melting of the smectic order in the whole film volume, and film rupture is observed. Moreover, from results shown in figure 2, one can conclude that for LC compounds having a bulk nematic phase ($\alpha < 0.98$), the critical value W_0^c should be significantly lower than for LCs exhibiting the bulk SmA–I transition. Since, according to the model, the orienting interaction between LC molecules and the boundary free surface gives a negative contribution to the total film-vapour interfacial free energy (see equation (3) in [17, 18]), the surface tension for a FSAF exhibiting the thinning transitions should be lower than that for a FSAF that ruptures upon heating. Furthermore, FSAFs of LC compounds having a bulk nematic phase could give thinning transitions for values of the surface tension higher than those necessary to observe these transitions in films of LC materials without a bulk nematic phase.

These predictions of the model are in good qualitative agreement with results from experiments on the behaviour of FSAFs upon heating. As said in the Introduction, among numerous LC compounds exhibiting the bulk SmA–I transition, only several perfluorinated materials give thinning transitions. These perfluorinated LCs are significantly lower surface tensions (~ 13 dyn cm^{-1} [15]) than conventional non-perfluorinated compounds (~ 20–25 dyn cm^{-1} [16]) that rupture upon heating. A comparison of these experimental results with the above model predictions not only allows us to quote the qualitative agreement between them, but also enables us to explain the importance of fluorination in the thinning transitions. Apparently, fluorination of the end groups of the flexible molecular tails provides the strength of orienting action of the boundary free surface on the LC molecules necessary for the occurrence of thinning transitions in LC compounds without a bulk nematic phase.

On the other hand, for LC materials having a bulk nematic phase, the existence of thinning transitions is not related to fluorination, and these phenomena can be observed for conventional LCs with two hydrogeneous alkyl tails [10–12]. The surface tension of such compounds is equal to about 20–25 dyn cm^{-1}, much higher than that of perfluorinated LCs exhibiting thinning transitions. These experimental results are also in qualitative agreement with the model predictions because, as said above, in LC materials with a bulk nematic phase, thinning transitions can be observed at a strength of orienting action of the boundary free surface on the LC molecules lower than that necessary for compounds without a bulk nematic phase. Consequently, the surface tension of FSAFs of the former materials can be higher than that of FSAFs of the latter materials.

3. Regular and irregular thinning transitions

Now let us turn to the problem of regularity of the thinning transitions. As said in the previous section, when the effective orienting action of the boundary free surfaces on the LC molecules is sufficiently strong, the model predicts the occurrence of the critical temperature $T_c^b(N)$ (the binodal point), above which the N-layer FSAF becomes unstable to the appearance of the QSmA structure and the subsequent thinning transition. In addition, the model predicts the occurrence of the second critical temperature (the spinodal point) $T_c^s(N)$ $[T_c^s(N) \geqslant T_c^b(N)]$, above which the N-layer FSAF is absolutely unstable (there is no solution which gives the local smectic order parameters different from zero in each film layer), and the transition to the QSmA structure and, as a consequence, the thinning transition become inevitable. Therefore, within a temperature range $T_c^b(N) \leqslant T \leqslant T_c^s(N)$, the N-layer FSAF can be considered as a metastable state, and the thinning transitions can be, in principle, observed at any temperature $T_c(N)$ from this metastability region. The dependences of the reduced binodal ($t^b = [T_c^b(N) - T_0]/T_0$) and reduced spinodal ($t^s = [T_c^s(N) - T_0]/T_0$) temperatures on the number N of film layers are shown for $\alpha = 1.05$ (curves b1 and s1) and for $\alpha = 0.9$ (curves b2 and s2), respectively, in figure 3. It is seen that for both LCs, the first of which exhibits the bulk SmA–I phase transition ($\alpha = 1.05$) and the second has the bulk nematic phase ($\alpha = 0.9$), the reduced width of the metastability region $\Delta t_{MS} = t_c^s(N) - t_c^b(N)$ decreases with decreasing film thickness, and beginning from a certain critical number N' of film layers, this region degenerates to a point. For thick FSAFs of the first LC, however, the metastability region is much wider than for similar FSAFs of the second material. Moreover, for LCs exhibiting the bulk SmA–I transition, the critical number ($N' \sim 10$) of film layers is significantly smaller than that ($N' \sim 18$) for materials having the bulk nematic phase. Numerical investigation of the model shows also that for LCs undergoing a 'weak' enough bulk SmA–N first order phase transition, the metastability region can degenerate to a point even for sufficiently thick FSAFs, such as the 25-layer film. This fact can be illustrated by figure 4, in which the reduced width of the metastability region Δt_{MS} is plotted vs. the model parameter α for the 25-layer FSAF. It is seen that Δt_{MS} decreases with decreasing α and reaches zero at $\alpha \approx 0.87$. Since in the framework of the McMillan theory [21] the 'strength' (the transition enthalpy) of the bulk SmA–I or SmA–N first order phase transition is proportional to the parameter α, one can conclude that the width of the metastability region decreases, and the critical number N' of film layers increases with weakening of the bulk phase transition.

As said above, the thinning transition can occur, in principle, at any temperature $T_c(N)$ within the metastability region. However, both the probability of the transition and the number of film layers squeezed into the surrounding reservoir depend strongly on $T_c(N)$. The number N_1 of layers remaining in the film after thinning must be such as to provide the existence of the stable SmA phase with total free energy not exceeding that of the QSmA phase in the free-standing film of initial thickness [17, 18]. In the opposite case the film should obtain some energy from outside. The numerical investigation of the model shows that near the binodal point $T_c^b(N)$, this condition can be satisfied by squeezing a single film layer into the surrounding reservoir, whereas sufficiently above this temperature, the film should lose several layers. For example, for $\alpha = 1.05$, near the spinodal point the initially 25-layer FSAF should thin down to 13 layers. As for the probability of the thinning transition, according to the model, this transition is caused by the appearance of the QSmA structure in the film, and, hence, the probability under consideration should be directly proportional to that of nucleation of the QSmA phase in the FSAF. This probability can be, in turn, estimated in a manner similar to that proposed in [2, 22].

Let us consider the FSAF of a LC without the bulk nematic phase ($\alpha \geqslant 0.98$) at the temperature T within the metastability region $T_c^b(N) \leqslant T \leqslant T_c^s(N)$, i.e. when the SmA–QSmA transition can, in principle, occur. For simplicity, a nucleus of the QSmA phase in the N-layer FSAF can be assumed to have a cylindrical form. Then the energy required to create such a nucleus of radius R can be approximately written as

$$E_R \approx 2\pi R N_I l \gamma_{AI} - \pi \Delta F R^2, \tag{3}$$

where N_I is the number of 'isotropic' layers in the composite QSmA structure, γ_{AI} is the isotropic–smectic A interfacial tension, and ΔF is the difference between the free energies of the SmA and QSmA film structures per unit area. Using equation (3), one can find an energy barrier

$$E_c \approx \pi (N_I l \gamma_{AI})^2 / \Delta F \tag{4}$$

and, hence, the frequency of thermally creating nuclei of the QSmA phase of critical radius $R_c \approx (N_I l \gamma_{AI})/\Delta F$ per unit area of the film. This frequency will be

$$f = f_0 \exp(-E_c / K_B T) \tag{5}$$

where K_B is the Boltzmann constant, and f_0 is assumed, according to [2, 22], to be $f_0 \sim$ (speed of sound)/ [(molecular diameter) × (molecular cross section)] $\sim 2 \times 10^{27}\,\mathrm{s}^{-1}\,\mathrm{cm}^{-2}$.

Though for the present there are no well established data on the isotropic–smectic A interfacial tension γ_{AI}, one can estimate this value in the following way. There are a number of experimental data on the isotropic–nematic interfacial tension γ_{NI} for various LCs [23–26], and typically $\gamma_{NI} \sim 10^{-1}\,\mathrm{dyn\,cm}^{-1}$. On the other hand, theoretical investigation [27] of interfacial SmA structures shows that the magnitude of γ_{AI} should be an order higher than that of γ_{NI}. Then we can set $\gamma_{AI} \sim 1\,\mathrm{dyn\,cm}^{-1}$. Inserting this value and $l \approx 30\,\mathrm{\AA}$ into equation (5), one obtains

$$f \approx 2 \times 10^{27} \exp\left(-\frac{2048 N_I^2}{\Delta F T}\right) \mathrm{s}^{-1}\,\mathrm{cm}^{-2}. \tag{6}$$

Now, using equation (6), let us calculate the frequency f as a function of temperature within the metastability region for sufficiently thick (25-layer) FSAFs at $\alpha = 1.05$. The number N_I of isotropic layers in the QSmA phase may be determined from figure 2 in [17, 18] and, as easily seen, one can set $N_I \approx 10$. The typical value of the temperature T is, according to [9, 13, 14], about 350–360 K. The difference ΔF between the free energies of the SmA and QSmA states of the film within the metastability region (which, according to figure 3, ranges from $t \approx 10^{-2}$ to $t \approx 2.2 \times 10^{-2}$ can be directly obtained from the model. The resulting frequency f, as a function of the reduced temperature within the metastability region of the 25-layer FSAF is shown in figure 5. It is seen that not far from the binodal point, this frequency is negligibly small, and reaches a value comparable with unity at $t \sim 1.9 \times 10^{-2}$, i.e. not far from the spinodal point. Consequently, in sufficiently thick FSAFs of LC materials exhibiting the bulk SmA–I phase transition, the

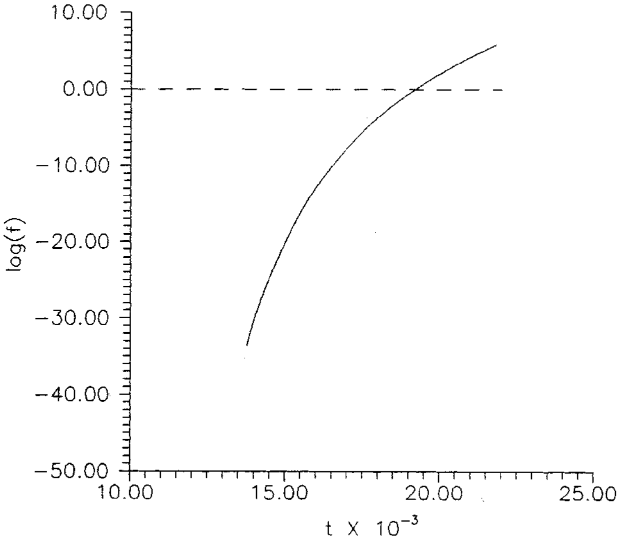

Figure 5. Temperature dependence of the frequency f of thermally creating nuclei of the QSmA phase of critical radius R_c per unit area for a 25-layer FSAF. $\alpha = 1.05$; $W_0/V_0 = 1.8$; $N_I = 10$; $\gamma_{AI} = 1\,\mathrm{dyn\,cm}^{-1}$.

QSmA structure should appear only in a 'highly superheated' metastable SmA phase. Then 'non-thermodynamic factors', such as, impurities, ions, etc., can play a very important role for the SmA–QSmA transition. As a result, the transition temperature and, hence, the discontinuity in the film thickness are variable and an change from run to run. Thus, the model accounts for the experimentally observed high irregularity of thinning transitions in thick FSAFs [9, 13, 14].

Further, the model accounts for the observable regular character of the thinning transitions in sufficiently thin FSAFs [9, 13, 14]. As said above, the width of the metastability region decreases with decreasing film thickness (see figure 3) and, beginning from the critical number N' (for $\alpha = 1.05$, $N' \sim 10$) of film layers, this region degenerates to a point. Therefore, for $N \leqslant 10$, the SmA–QSmA transition temperature should be a reproducible value coinciding with the binodal point $T_c^b(N)$. Hence, the film should lose a single layer per transition. Thus, the thinning transitions in a FSAF with $N \leqslant 10$ should be 'regular' layer-by-layer in type. One can also see that the numerically calculated dependence of a reduced binodal temperature t^b on the number N of film layers (see figure 6, curve 1) is well described by the power law (1), which characterizes the experimentally observed regular thinning transitions. Moreover, the corresponding exponent $\beta \approx 0.7$ is found to be very similar to the experimental value [9, 13, 14].

Let us turn to FSAFs of LC compounds having the bulk nematic phase ($\alpha \leqslant 0.98$). As easily seen from figure 3, the metastability regions of the SmA phase for such films are much narrower than those for FSAFs of LCs exhibiting the bulk SmA–I phase transition. Further, beginning from a certain sufficiently large number N' of film layers (for $\alpha = 0.9$, $N' \sim 18$), the metastability region for these films should degenerate to a point. Since, as has been shown above, irregularity of the thinning transitions in thick FSAFs is due to the existence of 'wide' metastability regions of the SmA phase, one can conclude that the thinning transitions in thick FSAFs of LCs having the bulk nematic phase should be more 'regular' than those in FSAFs of the same thickness, but formed from LC compounds without a bulk nematic phase. Moreover, if the bulk SmA–N phase transition is sufficiently 'weak', then the metastability region of the SmA phase degenerates to zero even for thick enough ($N > 20$) films (see figure 4). Consequently, for LCs exhibiting 'weak' bulk SmA–N phase transitions, a sufficiently thick FSAF can demonstrate regular layer-by-layer thinning transitions. Thus, the model accounts for the experimentally observed regular layer-by-layer thinning transitions in 16-, 17- [10], 24-, and even 48-layer [12] FSAFs of LCs having a bulk nematic phase. In addition, the model predicts that the temperatures of the thinning transitions in these FSAFs should obey the power law (1) (see curve 2 in figure 6) with exponent β similar to that for FSAFs of LC without the bulk nematic phase. This theoretical result is also in agreement with experimental observations [10–12].

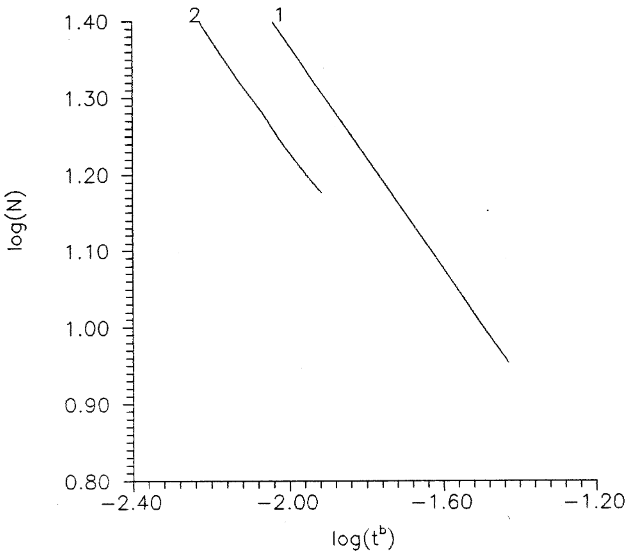

Figure 6. Log–log plot of the dependence of the reduced binodal temperature t^b on the number N of film layers: $W_0/V_0 = 1.8$. Curve 1, $\alpha = 1.05$; curve 2, $\alpha = 0.9$.

4. Conclusion

We present the results of recent theoretical investigations of the behaviour of FSAFs upon heating; these have been performed in the framework of the previously proposed microscopic mean-field model for thin LC films with two boundary surfaces [17, 18]. It has been shown that the model allows us to account for the essential features of this behaviour, which depends crucially on the strength of the orienting action of the boundary free surfaces on the LC molecules within the outermost film layers. If the effective short range external field simulating this action is not sufficiently 'strong', then film heating above some critical temperature $T_c(N)$ gives rise to melting of the smectic layers in the whole film volume, resulting, in turn, in film rupture. On the contrary, when the orienting action of the boundary free surfaces on the LC molecules is 'strong' enough, film heating above $T_c(N)$ gives rise to the appearance of the 'quasi-smectic' film structure composed of melted interior film layers and interfacial layers maintaining the smectic order. The interfacial film layers squeeze out a few melted interior layers into the surrounding reservoir, giving rise to the thinning transition. It has been shown that the surface tension of films exhibiting thinning transitions should be lower than that of FSAFs rupturing upon heating. This prediction of the model is in qualitative agreement with experiment [15]. The model accounts for the experimentally observed [13, 14] 'irregularity' of the thinning transitions in the 'thick' ($N > 10$) films of LC materials exhibiting the bulk SmA–I phase transition. It predicts also that the thinning transitions in a 'thin' ($N \leqslant 10$) FSAF should be regular layer-by-layer in type. In addition, the model predicts that for LC compounds having a bulk nematic phase, regular layer-by-layer thinning transitions can occur even in sufficiently thick ($N > 10$) films. These theoretical results are also in a qualitative agreement with experimental observations [9–14].

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