Influence of external field on layer-thinning transitions in free-standing smectic-*A* films

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In the framework of a simple microscopic mean-field model for thin smectic-*A* liquid-crystal films with two boundary surfaces the effect of an external magnetic (or electric) field on the recently observed phenomenon of layer-thinning transitions in the free-standing smectic-*A* films upon heating is theoretically investigated. It is found that the external field increases the layer-thinning transition temperatures and decreases the first multilayer jump in the free-standing film thickness. The magnitudes of both magnetic and electric fields necessary for experimental verification of the results obtained are numerically estimated.
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Free-standing smectic films can be considered as a stack of smectic layers with two free boundary surfaces. One can produce smectic films consisting of 2–1000 layers, which make them a convenient object for the investigation of low-dimensional effects [1–3]. The combination of the surface-induced ordering and finite-size effects in these films gives rise to the appearance of phenomena that are not observed in bulk liquid-crystal (LC) samples. For example, Rosenblatt and Amer [4] reported an anomalously high temperature of existence of the smectic-*A* (Sm-*A*) phase in the free-standing film of octylcyanobiphenyl. Heinekamp *et al.* [5] observed the smectic-*C** (Sm-*C**) phase in the free-standing film of DOBAMBC at the temperature significantly higher than that of the Sm-*C**- Sm-*A* transition in the bulk. The observation of smectic-*I* (Sm-*I*) layers in the smectic-*C* (Sm-*C*) film has been reported in Ref. [6] and the Sm-*A*–smectic-*B* (Sm-*B*) phase transition in boundary layers of the Sm-*A* film has been found in high-precision calorimetry measurements [7].

A different remarkable phenomenon in the smectic-*A* free-standing films has been observed by Stoebe *et al.* [8,9]. It has been found that above the bulk Sm-*A*–isotropic (Sm-*A*–*I*) transition point the Sm-*A* free-standing films of members of the partially perfluorinated 5-*n*-alkyl-2-[4-*n*-(perfluoroalkyl-metheleneoxy)phenyl] pyrimidine homologous series undergo the 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 Sm-*A*–*I* transition. The temperatures of these layer transitions have been found to obey the simple power law

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

where L 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 Sm-*A* film exists, T_0 is the bulk Sm-*A*–*I* transition temperature, and $\beta \approx 0.74$.

A theoretical description of the layer-thinning transitions in the free-standing smectic-*A* films based on a simple microscopic mean-field model for thin LC film with two boundary surfaces has been offered in Ref. [10]. It has been shown that below a critical temperature $T_c(N)$ $[T_c(N)>T_0]$ the Sm-*A* phase occurs in the film. In this phase the distribution the free energy over the film layers 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 one. When the critical temperature $T_c(N)$ is reached, the N-layer Sm-*A* film becomes absolutely unstable to the occurrence of a ''quasismectic''-*A* film structure (QSm-*A*) in which the LC molecules in the interfacial film layers are orientationally and positionally ordered, but the order parameters 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 the interior ones into a surrounding isotropic reservoir 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, QSm-*A* structure in the N-layer film. Choosing a suitable value of the parameter determining the ''strength'' of the bulk Sm-*A*–*I* phase transition, the model allows one to obtain a sequence of the layer-thinning transitions ($25\rightarrow13\rightarrow11\rightarrow10\rightarrow9\rightarrow8\rightarrow\cdots$) very similar to the experimentally observed one. The small difference between theory and experiment is possibly due to the use of the mean-field approximation, which is the simplest approach to the phenomenon under consideration. In addition, for $N\leqslant13$ the relation between $t(N)$ and L [Eq. (1)], similar to experiment is found.

It is well known that external magnetic (or electric) fields have an effect on the orientational ordering and phase transitions in LCs [11–16]. Since, according to Ref. [10], the layer-thinning transitions in the free-standing smectic-*A* films are due to melting of the interior smectic layers, one can expect that these transitions and their characteristics (transition temperature and number of layers squeezed into the surrounding reservoir) are also sensitive to the external field. It should be also noted that the free-standing LC films under the external field are the systems in which a triple

combination of the field effect, the finite-size effect, and the surface effect occurs. Therefore, such systems are extremely interesting.

In this paper we present the results of a theoretical investigation of the influence of the external magnetic (or electric) field on the layer-thinning transitions in the free-standing smectic-*A* film performed in the framework of the model proposed in Ref. [10]. According to this model, the 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 $\vec{n}$ is aligned along the normal $\vec{\nu}$ to the boundary surfaces. The intermolecular interaction is simulated by the McMillan model pair potential [17]

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

where V_0 is the interaction constant, ϑ_{12} is the angle between long molecular axes, r_{12} is the distance between molecular centers, r_0 is the characteristic distance for the intermolecular interaction, and n_0 is the density of molecules. It should be noted that though this model pair potential is highly idealized and unrealistic, it allows us to obtain, in a mean-field approximation, a phase diagram qualitatively similar to the experimental ones [17]. Since in the framework of the 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 the two neighboring layers.

As for the interaction between the boundary free surfaces and the mesogenic molecules, the principle of independent surface action, proposed by Langmuir [18], states that each part of the molecule possesses a local free energy. Then, to minimize the free energy of the system, each molecule in the interfacial layers prefers to have the molecular groups with the lowest surface free energy exposed to the free surface. Hence the free surface should act on the LC molecules as an ''effective'' orienting field, which induces the homeotropic orientation in the free-standing smectic-*A* films. Further, the experiments on the surface tension of the free-standing LC films [19] show that the mechanism responsible for the surface tension is highly localized in the two outermost surface layers. Consequently, the above-mentioned effective orienting fields should be very short ranged, i.e., they act directly only on the molecules within the first and last film layers. Since we have no detailed information concerning the concrete coordinate dependence of the forces between the free surfaces and the LC molecules, we shall assume the external orienting fields to be spatially independent. Such short-range external orienting fields were used in previous papers on the interfacial smectic structures [20,21] and can be written as

$$W_1(\vartheta_1) = -W_0(3/2\cos^2\vartheta_1 - 1/2), \tag{3}$$

$$W_N(\vartheta_N) = -W_0(3/2\cos^2\vartheta_N - 1/2), \tag{4}$$

where ϑ_1 (ϑ_N) is the angle between long axes of the molecules within the first (last) layer and the normal $\vec{\nu}$ to the boundary surfaces of the film and W_0 is the interaction constant.

By analogy with the McMillan theory [17], we can expand the pair potential (2) in a Fourier series with a characteristic period l along the z axis parallel to $\vec{\nu}$ and keep the first two terms of this expansion. Then, in a mean-field approximation, one can obtain the single-particle pseudopotentials $V_i(z_i,\vartheta_i)$ ($i=1,N$) for the molecules within each film layer given by Eqs. (4)–(7) in Ref. [10]. These pseudopotentials are the functions of the ''local'' orientational q_i and smectic σ_i order parameters determined by self-consistent equations (8)–(10) in Ref. [10]. If the free-standing LC film is placed, for example, into an external, magnetic field $\vec{H}$ aligned parallel to the normal $\vec{\nu}$, then the energy of the interaction between the LC molecules and this field must be added to the single-particle pseudopotentials $V_i(z_i,\vartheta_i)$. This energy for molecules within the ith film layer is given by [11]

$$\Delta V_i(H,\vartheta_i) = -(1/3)\chi_a H^2(3/2\cos^2\vartheta_i - 1/2), \tag{5}$$

where χ_a is the LC diamagnetic susceptibility anisotropy per one molecule. If the free-standing film, formed of a LC with positive dielectric anisotropy, is placed into an external electric field $\vec{E}$ parallel to $\vec{\nu}$, then the product $\chi_a H^2$ in Eq. (13) must be replaced by $(\varepsilon_a/4\pi n_0)E^2$, where ε_a is the dielectric permittivity anisotropy of a LC with perfect orientational order [14–16]. The free energies F_i of the discrete film layers are determined by Eqs. (12)–(14) in Ref. [10] and the total free energy F of the N-layer film is equal to

$$F = \sum_{i=1}^{N} F_i. \tag{6}$$

We have performed a numerical investigation of self-consistent equations (8)–(10) in Ref. [10] for various values of the dimensionless parameter $h = \chi_a H^2/3V_0$ (in the case of the external electric field $h = \varepsilon_a E^2/12\pi n_0 V_0$) determining the effect of the external field on the phenomenon under consideration. The values of other parameters involved into our theoretical consideration, namely, the initial number N_0 of the film layers, the ratio of the interaction constants W_0/V_0, and the parameter α determining the strength of the bulk Sm-*A*–*I* transition in the McMillan theory [17], have been chosen to provide a reasonable agreement with experiment [8,9] performed in the absence of the external field. It has been found [10] that most appropriate values of the parameters N_0 and α are $N_0 = 25$ and $\alpha = 1.05$. As for the value of the ratio W_0/V_0, in choosing it we can be guided by the fact that the free-standing Sm-*A* films experimentally investigated were stable above the bulk Sm-*A*–*I* transition temperature. Consequently, it is reasonable to assume that the free surface enhances the liquid-crystalline ordering, i.e., the LC–free-surface interaction constant W_0 must be greater than the intermolecular interaction constant V_0 and we should set $W_0/V_0 > 1$. Therefore, as in Ref. [10], we will use $W_0/V_0 = 3$. Using these values, we have obtained, first of all, the dependence of the first layer-thinning transition temperature $T_c(N_0)$ on the external magnetic field. This multilayer jump in the free-standing film thickness is much stronger

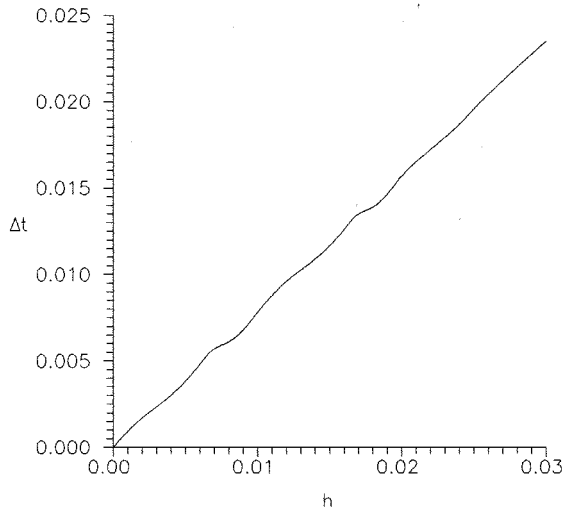

FIG. 1. Dependence of the relative shift of the first layer-thinning transition temperature on the dimensionless parameter h. $N_0=25$, $\alpha=1.05$, and $W_0/V_0=3$.

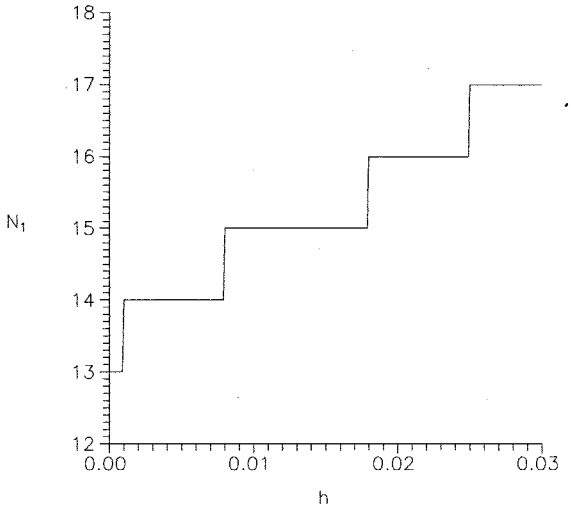

FIG. 2. Dependence of the number N_1 on the parameter h.

than all subsequent layer-thinning transitions and hence is of particular interest. As we have said before, at the critical temperature $T_c(N_0)$ the Sm-A phase becomes absolutely unstable in the N_0-layer film, i.e., $T_c(N_0)$ is a spinodal point for the free-standing smectic-A film of initial thickness. The dependence of the relative shift of the first layer-thinning transition temperature $\Delta t(N_0)=[T_c(N_0,h)-T_c(N_0)]/T_c(N_0)$, where $T_c(N_0,h)$ is the critical temperature for the free-standing film under the external field, on the parameter h is shown in Fig. 1. It is seen that $\Delta t(N_0)$ grows almost linearly with the parameter h, i.e., the shift of the first layer-thinning transition temperature is proportional to square of the external magnetic (or electric) field. It should be added that the relative shifts of the other layer-thinning transition temperatures $[\Delta t(N_1), \Delta t(N_2), \Delta t(N_3), \ldots]$ depend on the parameter h in an analogous manner.

We have also investigated the effect of the external field on the number N_1 of layers remaining in the film after the first layer-thinning transition. According to Ref. [10], in the absence of the external field the number N_1 must be such as to provide the existence of the stable Sm-A phase with the total free energy not exceeding that of the QSm-A phase in the N_0-layer film (the free energy of the isotropic phase in the surrounding reservoir was equal to zero). In the presence of the external field the situation changes, because the field induces a ''paranematic'' (PN) phase [12–16] in the reservoir. In this phase the orientational order parameter $q_{\mathrm{PN}}(h)$ is not equal to zero and hence the free energy $F_{\mathrm{PN}}(h)$ of the reservoir is also different from zero. Then the number N_1 must be such as to provide the sum of the free energy of the Sm-A phase in the N_1-layer film and the energy of the N_0-N_1 film layers, squeezed into the paranematic reservoir, not exceeding the total free energy of the QSm-A phase in the N_0-layer film. Consequently, we have to decrease the number of film layers [at the constant temperature $T_c(N_0,h)$] from the initial value N_0 to the final one N_1, for which one can obtain the solution of Eqs. (8)–(10) in Ref. [10] corresponding to the Sm-A phase with the total free energy (6) not exceeding that of the QSm-A phase in the N_0-layer film minus the free energy of N_0-N_1 film layers in the PN phase. The paranematic order parameter $q_{\mathrm{PN}}(h)$ induced by the external field in the isotropic phase at the temperature $T_c(N_0,h)$ and the free energy of a single film layer in the PN phase can also be determined by means of our model in the limit case of infinitely thick LC film ($N\to\infty$). Using the above-mentioned procedure, we have obtained the dependence of the number N_1 on the parameter h shown in Fig. 2. It is seen that this dependence is an increasing step-like function of h. Since the growth of N_1 is equivalent to the decrease of the first and very sharp jump in the free-standing film thickness, one can conclude that the external field ''moderates'' this multilayer-thinning transition in the free-standing smectic-A films.

Using the above-mentioned values of the parameters N_0, α, and W_0/V_0, we have plotted, as in Ref. [10], the dependence of $\log_{10}[T_c(N,h)-T_0]/T_0$ on $\log_{10}(N)$ for four different values of the dimensionless parameter h, namely, $h=0$, $h=0.01$, $h=0.02$, and $h=0.03$ (see Fig. 3, curves 1,2,3,4). It has been found that these values of h correspond to the following sequences of the layer-thinning transitions upon heating:

$25\to13\to11\to10\to9\to8\to\cdots$ for $h=0$,
$25\to15\to13\to12\to11\to10\to9\to\cdots$ for $h=0.01$,
$25\to16\to14\to13\to12\to11\to10\to\cdots$ for $h=0.02$,
$25\to17\to15\to14\to13\to12\to11\to\cdots$ for $h=0.03$.

One can see from Fig. 3 that all theoretical curves are similar to each other and for $N\leqslant10$ they are parallel to the analogous experimental dependence [8,9] (Fig. 3, curve 5), i.e., for $N\leqslant10$ the theoretical curves, independent of the magnitude of the external field, are well described by relationship (1) with the exponent β very similar to experimental one ($\beta\approx0.74$), i.e., this exponent is independent of the external field. However, for larger values of N ($N>10$) the theoretical dependences become sharper and do not obey this simple power law. Moreover, the stronger the external field, the larger the deviation of the theoretical curves from relationship (1). This result is qualitatively independent of the particular values of the parameters used in calculations and the discrepancy between theoretical curves and power law

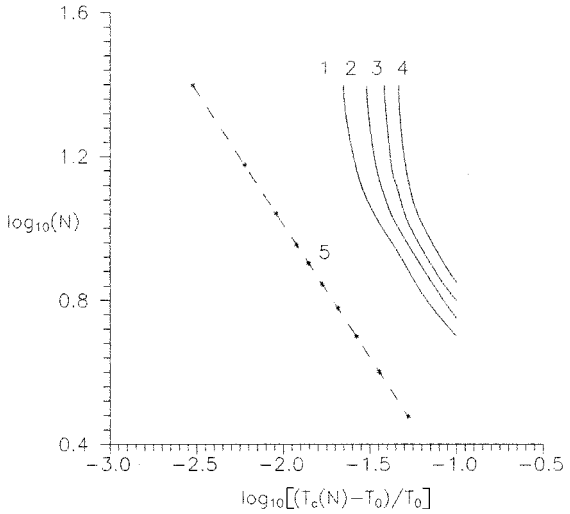

FIG. 3. Dependence of the layer-thinning transition temperature on the film thickness determined for different values of the parameter h. 1, $h=0$; 2, $h=0.01$; 3, $h=0.02$; 4, $h=0.03$; 5, experimental data [8,9].

(1) for thick films ($N>10$) is probably due to the use of the oversimplified mean-field approximation.

Finally, we can estimate numerically the magnitude of the magnetic (or electric) field necessary for the experimental observation of the effect of the external field on the layer-thinning transitions in the free-standing smectic-A films. Let us determine, for example, the magnitude H_1 of the magnetic field, which gives rise to an increase of the first layer-thinning transition temperature by ~ 1 K. According to experimental data [8,9], this increase corresponds to the relative shift Δt of the first layer-thinning transition temperature of the order of ~ 0.003. One can see from Fig. 1 that this shift corresponds to the magnitude of the parameter h of the order of ~ 0.005, which, in turn, leads us to

$$H_1 \sim (0.015 V_0/\chi_a)^{1/2}. \tag{7}$$

The magnitude of the constant V_0 can be estimated in the following way. According to the McMillan theory [17], for $\alpha=1.05$ the bulk Sm-A–I phase transition temperature is equal to $0.2249(V_0/K_B)$. The mesogenic compound studied in Refs. [8,9] exhibits the bulk Sm-A–I transition at the temperature $T_0 \approx 358$ K. Hence we obtain $V_0 \approx 2.2\times 10^{-13}$ erg. Substituting this value and a typical value of $\chi_a \approx 3\times 10^{-28}$ [11] into Eq. (7), we obtain $H_1 \sim 3.3\times 10^6$ G. Evidently such magnetic fields are not available now. As for the value of the electric field E_1 necessary to increase the first layer-thinning transition temperature by ~ 1 K, it can be obtained from Eq. (7) by replacing χ_a by $(\varepsilon_a/4\pi n_0)$. Using the value $\varepsilon_a \approx 20$ typical for a strongly polar [14], and the value $n_0 \approx 1.4\times 10^{21}\ \mathrm{cm}^{-3}$ typical for a LC [22], one can obtain $E_1 \approx 5\times 10^5$ V/cm, which is, according to recent experimental papers on the electric-field-induced transitions in LCs [14–16], a quite achievable value.

In conclusion, in the framework of a simple microscopic mean-field model for thin LC layer with two boundary surfaces [10] we have investigated theoretically the influence of the external magnetic (or electric) field on the recently observed [8,9] phenomenon of layer-thinning transitions in free-standing smectic-A films upon heating. It has been found that the external field increases the layer-thinning transition temperatures and decreases the first multilayer jump in the free-standing film thickness. The values of the magnetic and electric fields, necessary for the experimental observation of the effect of the external field on the phenomenon under consideration, are numerically estimated. The necessary value of the external electric field E_1 is found to be quite achievable.

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