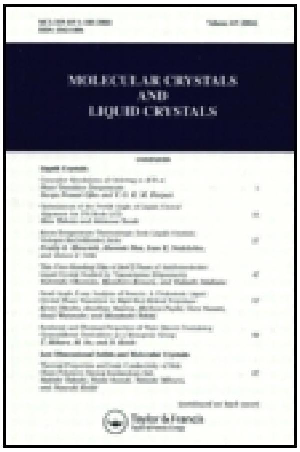

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Theory of Layer-Thinning Transitions in Free-Standing Smectic-a Films. Effect of External Fields

L. V. Mirantsev [a]

[a] Institute of the Problems of Mechanical Engineering, Academy of Sciences of Russia, St. Petersburg, 199178, Russia

Version of record first published: 04 Oct 2006

Mol. Cryst. Liq. Cryst., 1997, Vol. 304, pp. 265-273
Reprints available directly from the publisher
Photocopying permitted by license only

THEORY OF LAYER-THINNING TRANSITIONS IN FREE-STANDING SMECTIC-A FILMS. EFFECT OF EXTERNAL FIELDS

L.V. MIRANTSEV
Institute of the Problems of Mechanical Engineering, Academy of Sciences of Russia, St. Petersburg, 199178, Russia

Abstract In 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 (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.

1. INTRODUCTION

Free-standing smectic films can be considered as the stack of smectic layers with two free boundary surfaces. One can produce the smectic films consisted of 2-1000 layers, which make them a convenient object for investigation of low dimension effects [1-3]. The combination of the surface-induced ordering and finite-size effects in these films gives rise to appearance of phenomena which 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 8 OCB. 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 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].

New 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 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 25K higher than that of the bulk Sm A-I transition. The temperatures of these layer transitions have been found to obey the following 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 N layer Sm A film exists, T_0 is the bulk Sm A-I transition temperature and $\beta \approx 0.74$.

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, 11]. 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 another 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 "quasi-smectic"-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 opposite direction. One can imagine that the interfacial layers seek to squeeze the interior ones into surrounding isotropic reservoir thinning the film to a stable $N'(N' < N)$ layer smectic-A film. The free energy of 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 a parameter determining the "strength" of the bulk Sm A-I phase transition, the model allows to obtain the sequence of the layer-thinning transitions ($25 \rightarrow 13 \rightarrow 11 \rightarrow 10 \rightarrow 9 \rightarrow 8 \rightarrow \ldots$) very similar to the experimentally observed one. In addition, for $N \leq 13$ the relation between $t(N)$ and L similar to experimental Eq. (1) is found.

It is well known that external magnetic (electric) fields have an effect on the orientational ordering and phase transitions in LCs [12-17]. Since, according to ref. [10, 11], 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 noticed 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 theoretical investigation of an effect of the external magnetic (electric) field on the layer-thinning transitions in the free-standing smectic-A film performed in framework of the model proposed in ref. [10, 11]. 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 experimental observation of the effect of the external field on the phenomenon under consideration, are numerically estimated.

2. MODEL

According to the model offered in ref. [10, 11] the LC film with two boundary surfaces is assumed to consist of N discrete layers with thickness of order of the molecular length l. The film is also assumed to be homeotropically oriented, i.e. 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 [18]

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

where V_0 is the interaction constant, ϑ_{12} is the angle between long molecular axes, r_{12} is the distance between molecular centres, r_0 is the characteristic distance for the intermolecular interaction and n_0 is the density of molecules. Since in 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 the distance of 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. Further, since 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 two outermost surface layers, the interaction between the boundary free surfaces and the mesogenic molecules can be simulated by certain short-range 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 [20, 21]

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

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

where $\vartheta_1(\vartheta_N)$ 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 McMillan theory [18] one can expand the pair potential (2) in a Fourier series with characteristic period l along z-axis parallel to $\vec{\nu}$, and keeping the first two terms of this expansion, obtain the single-particle pseudopotential $V_i(z_i, \vartheta_i)$ for the molecules within the i-th film layer given by Eqs. (4)-(6) in ref. [10, 11]. The pseudopotentials $V_{2\leq i\leq N-1}$ are expressed in terms of "local"orientational q_j and smectic σ_j order parameters ($j=i$-1, i, $i+1$) for i-th film layer and its two neighbouring ones. These parameters are determined by the following equations:

$$q_i = < 3/2\cos^2\vartheta_i - 1/2 >_i, \tag{5}$$

$$\sigma_i = < (3/2\cos^2\vartheta_i - 1/2)\cos(2\pi z_i/l) >_i, \tag{6}$$

$$< G(z_i, \vartheta_i) >_i = \int_{(i-1)l}^{il} dz_i \int_{-1}^{+1} G(z_i,\vartheta_i) f_i(z_i,\vartheta_i) d\cos\vartheta_i / \int_{(i-1)l}^{il} dz_i \int_{-1}^{+1} f_i(z_i,\vartheta_i) d\cos\vartheta_i, \tag{7}$$

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

$$f_i(z_i,\vartheta_i) = A_i^{-1}\exp[-V_i(z_i,\vartheta_i)/K_BT], \tag{8}$$

where A_i is the normalization constant for i-th layer, T is the absolute temperature of the system and K_B is the Boltzmann constant. The pseudopotentials $V_1(V_N)$ for the first (last) film layer is expressed in terms of the order parameters $q_{1,2}(q_{N-1,N})$, $\sigma_{1,2}(\sigma_{N-1,N})$, and the energy $W_1(\vartheta_1)$ $(W_N(\vartheta_N))$ of interaction between the LC molecules and the boundary surfaces. If the free-standing LC film is placed into external, for example, magnetic field $\vec{H}$ aligned parallel to the normal $\vec{\nu}$, then the energy of 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 i-th film layer is given by [12]:

$$\Delta V_i(H,\vartheta_i) = -(1/3)\chi_a H^2(3/2\cos^2\vartheta_i - 1/2), \tag{9}$$

where χ_a is the LC diamagnetic susceptibility anisotropy per one molecule. If the free-standing film, formed of LC with positive dielectric anisotropy, is placed into external electric field $\vec{E}$ parallel to $\vec{\nu}$, then the product $\chi_a H^2$ in Eq. (9) must be replaced by $(\epsilon_a/4\pi n_0)E^2$, where ϵ_a is the dielectric permitivity anisotropy of LC with perfect orientational order [15-17]. The free energies F_i of the discrete film layers are determined by Eqs. (12)-(14) in ref. [10, 11] and the total free energy F of the N-layer film is equal to

$$F = \sum^N F_i, \tag{10}$$

3. THE RESULTS OF NUMERICAL CALCULATION AND DISCUSSION

We have performed numerical investigation of self-consistent Eqs. (5), (6) for various values of the dimensionless parameter $h=\chi_a H^2/(3V_0)$ (in case of the external electric field $h=\epsilon_a E^2/(12\pi n_0 V_0)$) 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 "strength" of the bulk Sm A-I transition in McMillan theory [18], have been chosen to provide a reasonable agreement with experiment [8, 9] performed in absence of the external field. It has been found [10, 11] that most appropriate values of the parameters N_0 and α are: $N_0=25$, $\alpha=1.05$. 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, 11] 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 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 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 of 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 (electric) field. It should be added, that the relative shifts of the other layer-thinning transition temperatures ($\Delta t(N_1)$, $\Delta t(N_2)$, $\Delta t(N_3)$...) depend on the parameter h in analogous manner.

We have also investigated the effect of the external field on number N_1 of the layers remaining in the film after the first layer-thinning transition. According to ref. [10, 11], in 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 isotropic phase in the surrounding reservoir we set to be equal to zero). In presence of the external field the situation is changed, because the field induces a "paranematic" (PN) phase [13-17] in the reservoir. In this phase the orientational order parameter $q_{PN}(h)$ is not equal to zero and, hence, the free energy $F_{PN}(h)$ 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 the film layers (at the constant

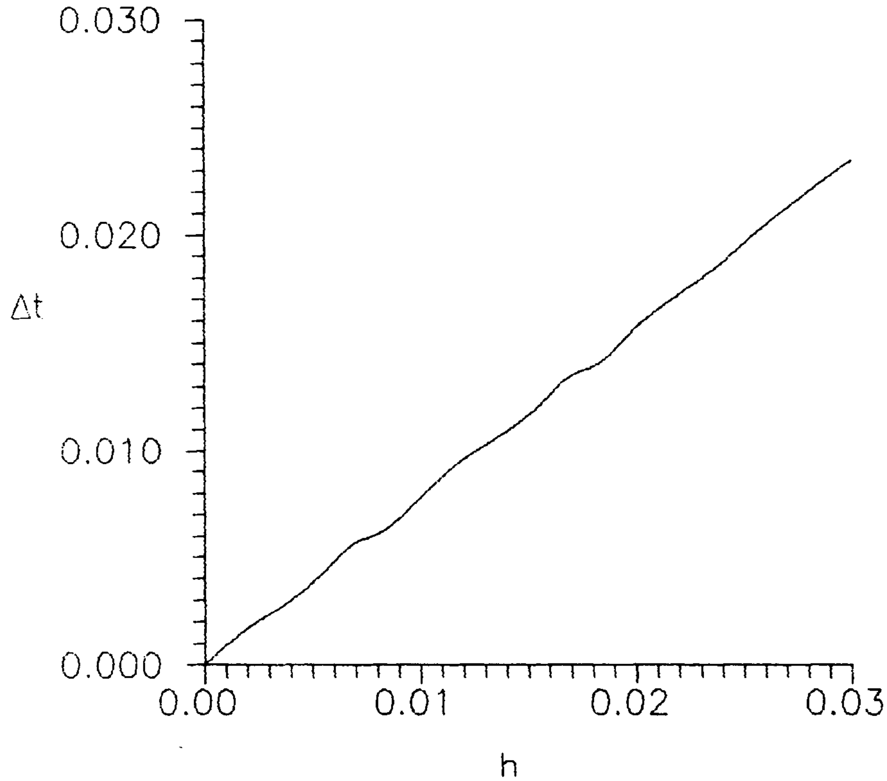

Figure 1. The dependence of the relative shift of the first layer-thinning transition temperature on the dimensionless parameter h. $N_0=25$, $\alpha=1.05$, $W_0/V_0=3$.

temperature $T_c(N_0, h)$) from initial value N_0 to final one N_1 for which one can obtain the solution of Eqs. (5), (6) corresponding to the Sm A phase with total free energy (10) 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 $q_{PN}(h)$ 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 be also 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 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.

Finally, we can estimate numerically the magnitude of the magnetic (electric) field necessary for 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 increasing of the

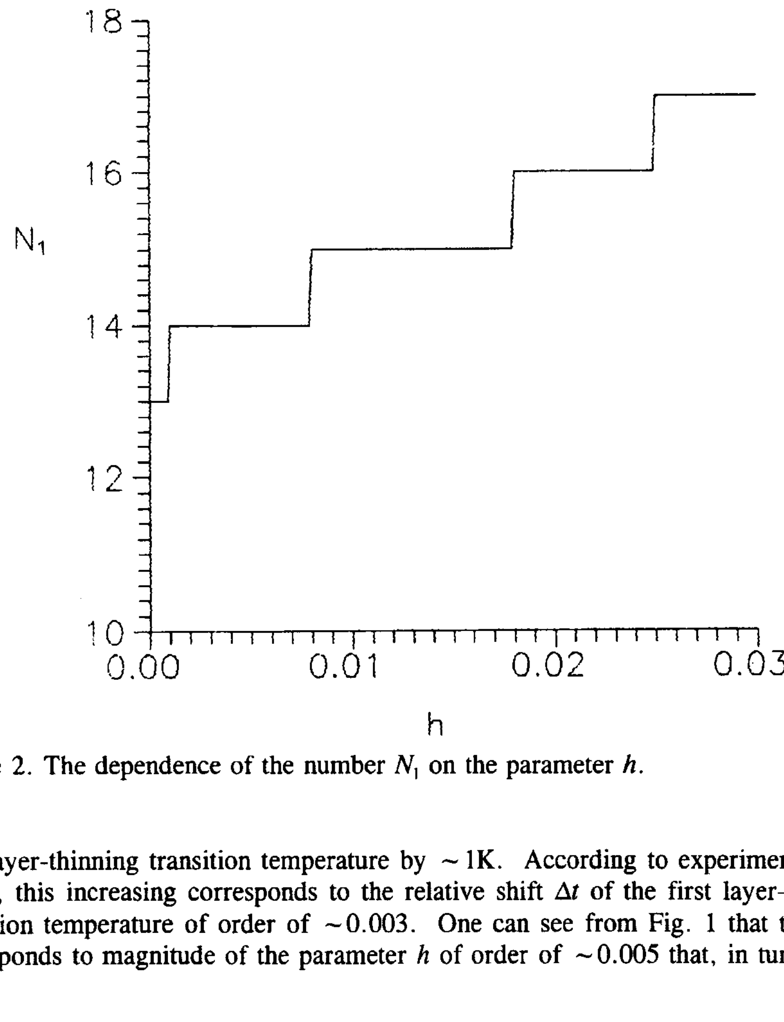

Figure 2. The dependence of the number N_1 on the parameter h.

first layer-thinning transition temperature by ~ 1K. According to experimental data [8, 9], this increasing corresponds to the relative shift Δt of the first layer-thinning transition temperature of order of ~ 0.003. One can see from Fig. 1 that this shift corresponds to magnitude of the parameter h of order of ~ 0.005 that, in turn, leads us to

$$H_1 \sim (0.015\, V_0/\chi_a)^{1/2}. \tag{11}$$

The magnitude of the constant V_0 can be estimated in the following way. According to McMillan theory [18], for $\alpha = 1.05$ the bulk Sm A-I phase transition temperature is equal to $0.2249 \times (V_0/K_B)$. The mesogenic compound studied in ref. [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 $\chi_a \approx 3 \times 10^{-28}$ [12] into Eq. (11), 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. (11) by replacing χ_a by $(\epsilon_a/4\pi n_0)$. Using the typical for strongly polar LC value $\epsilon_a \approx 20$ [15], and typical for LC value $n_0 \approx 1.4 \times 10^{21} cm^{-3}$ [22], one can obtain $E_1 \approx 5 \times 10^5$ V/cm, that is, according to recent experimental papers on the electric field-induced transitions in LCs [15-17], a quite achievable value.

4. CONCLUSION

In framework of a simple microscopic mean-field model for thin LC layer with two boundary surfaces [10, 11] we have theoretically investigated the influence of the external magnetic (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 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.

This work was supported by Russian Fund of Fundamental Investigations (Grant N 96-03-32417a).

REFERENCES

1. P. Pieranski, L. Beliard, J.P. Tournellec, X. Leoncini, C. Furtlehner, H. Dumoulin, E. Riou, B. Jouvin, J.P. Fenerol, Ph. Palaric, J. Heuving, B. Cartier and I. Kraus, *Physica A* **194**, 364 (1993).
2. C.C. Huang and T. Stoebe, *Adv. Physics* **42**, 343 (1993).
3. R. Geer, T. Stoebe and C.C. Huang, *Phys.Rev.E* **48**, 408 (1993).
4. C. Rosenblatt and N.M. Amer, *Appl.Phys.Lett.* **36**, 432 (1980).
5. S. Heinekamp, R.A. Pelcovits, E. Fontes, E.Y. Chen, R. Pindak and R.B. Meyer, *Phys.Rev.Lett.* **52**, 1017 (1984).
6. E.B. Sirota, P.S. Pershan, S. Amador and L.B. Sorensen, *Phys.Rev.A* **35**, 2283 (1987).
7. T. Stoebe, R. Geer, C.C. Huang and J.W. Goodby, *Phys.Rev.Lett.* **69**, 2090 (1992).
8. T. Stoebe, P. Mach and C.C. Huang, *Phys.Rev.Lett.* **73**, 1384 (1994).
9. T. Stoebe, A.J. Jin, P. Mach and C.C. Huang, *Mol.Cryst.Liq.Cryst.* **26**, 511 (1995).
10. L.V. Mirantsev, *Phys.Lett.A* **205**, 412 (1995).
11. L.V. Mirantsev, *Liq.Cryst.* **20**, 417 (1996).
12. H. Hama, *J.Phys.Soc.Jpn.* **54**, 2204 (1985).
13. C. Rosenblatt, *J.Phys.(Paris)Lett.* **42**, L9 (1981).
14. C. Rosenblatt, *Phys.Lett.A* **83**, 221 (1981).
15. I. Lelidis, M. Nobili and G. Durand, *Phys.Rev.E* **48**, 3818 (1993).
16. I. Lelidis and G. Durand, *Phys.Rev.E* **48**, 3822 (1993).
17. I. Lelidis and G. Durand, *Phys.Rev.Lett.* **73**, 672 (1994).

18. W.L. McMillan, *Phys.Rev.A* **4**, 1238 (1971).
19. P. Mach, S. Grantz, D.A. Debe, T. Stoebe and C.C. Huang, *J.Phys.II(Fr.)* **5**, 217 (1995).
20. Z. Pawlowska, G.F. Kventsel and T.J. Sluckin, *Phys.Rev.A* **36**, 992 (1987).
21. Z. Pawlowska, G.F. Kventsel and T.J. Sluckin, *Phys.Rev.A* **38**, 5342 (1988).
22. W.H. de Jeu, *Physical Properties of Liquid Crystalline Materials* (Gordon and Breach, 1980).