



Surface tension, disjoining pressure and layer compression of free-standing smectic films in water



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ABSTRACT

Using the extended McMillan's mean field approach with anisotropic forces a numerical study of the surface tension, disjoining pressure and layer compression of free-standing smectic film composed of decylcyanobiphenyl (10CB) molecules immersed in water has been carried out. We obtained that the smectic-A-isotropic transition occurs through a series of layer-thinning transitions causing the films to thin one layer at time, as well as a stepwise reduction and increase of the values of the surface tension and disjoining pressure per 10CB molecule as the temperature is raised to the isotropic value. Reasonable agreement between the theoretically predicted and the experimentally obtained data has been obtained.

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1. Introduction

Competition between surface and finite-sized effects leads to unusual physical properties of free-standing smectic films (FSSFs), both in air and water environments [1–5]. In particular, it has been shown that the surface film tension acts to promote smectic order at the surface resulting in the surface layers ordering at a higher temperatures than that in the interior [3,6]. The surface tension is clearly of fundamental importance to the stability of these films. Moreover, the presence of the surface tension is believed to be responsible for intriguing surface ordering phenomena exhibited by these films. Unlike the preferential surface melting exhibited by conventional solids, FSSF/vapor interface appears to enhance the order of the surface layers so they become ordered at temperatures well above the bulk smectic-A (Sm-A)-isotropic (AI) transition temperature $T_{AI}(\text{bulk})$ [1]. In such quasi-two-dimensional systems the melting originates in the interior of the film and penetrates toward the surface.

A great variety of phenomena can be obtained in thin FSSFs: layer-thinning transitions [1], stepwise reduction of heat capacity [1,6], and sawtooth behavior of the surface tension upon heating the FSSFs above $T_{AI}(\text{bulk})$ [3,5]. In particular, it was shown that the

AI transition occurs through a series of layer-thinning transitions, causing the films to thin in a stepwise manner as a temperature T is increased above $T_{AI}(\text{bulk})$, and the film thickness reduction is suitably described by a power-law expression $N(t) \sim t^{-\nu}$, where N is the number of layers, $t = (T_{AI}(N) - T_{AI}(\text{bulk})) / T_{AI}(\text{bulk})$ is the reduced temperature, $T_{AI}(N)$ is the temperature corresponding to the layer-thinning transition in N -layer smectic film, and ν is the critical exponent value belonging to the interval [0.52, 0.82], for different liquid crystal (LC) compounds [2].

Different mean-field theories have been used to obtain a qualitative description of the layer-thinning transitions [5–11], but the theoretical thinning temperatures were much larger than the experimental values [2]. Common features of all these theories are the existence of enhanced smectic ordering at the free surfaces of the film and the fact that thinning occurs when the smectic ordering in the interior of the film becomes sufficiently weak. Apart from details of the models used, the main differences among the theories are in the description of the kinetic processes by which layer-thinning occurs: i.e., whether this is by uniform squeezing-out of the melted interior [5–8,10,11], or via spontaneous nucleation of dislocation loops between domains of differing thickness [9].

Recently, the thinning effect in thin smectic films, composed of decylcyanobiphenyls (10CB) and dodecylcyanobiphenyls (12CB) molecules in water on heating to the isotropic temperature has been observed [4]. It was shown that these stable smectic films can be prepared in water with the help of a surfactant that induces homeotropic anchoring of LC molecules at the film/water interfaces. These films undergo a one-step thinning transition in

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which the film thickness decreases in a stepwise fashion until the films rupture at ~ 2 K above $T_{AI}(\text{bulk})$ [4]. This behavior is different from the case of FSSFs in air: on heating to the isotropic phase, the FSSFs in air either just rupture, for the vast majority of LC compounds, or show a layer-by-layer thinning transition, for LC compounds possessing the partially fluorinated alkyl chains. So, it clear indicates that the film's environment plays a crucial role in formation of the thinning effect and FSSFs present unusual physical properties which are associated with the interplay of surface and finite-size effects.

The theoretical description of the layer-thinning transitions in thin smectic films composed of cyanobiphenyl molecules immersed in water as the temperature is raised above $T_{AI}(\text{bulk})$ has been done in the framework of the extended McMillan's mean-field approach [12] with anisotropic forces [13]. But at current moment there is no theoretical description of the surface tension (ST) and disjoining pressure (DP) in FSSFs immersed in water and heated above $T_{AI}(\text{bulk})$. The theoretical description of these phenomena in thin smectic films composed of cyanobiphenyl molecules immersed in water is the main objective of the present work.

2. Model and calculations

With that in mind, a free-standing smectic-A film composed of N discrete smectic layers with a thickness $L = Nd$, where d is the molecular length, and with the total number of particles $M = \sum_{i=1}^N N_i$ will be considered. Here the number of molecules per layer N_i is assumed to be the same for all layers. The molecules within each layer are assumed to interact only with molecules of the same layer and those of the two neighboring ones. In the framework of that approach, the effective anisotropic potentials Φ_i ($i = 1, \dots, N$) within the i th smectic-A layer can be introduced [5,6]

$$\begin{aligned}\Phi_1(z_1, \beta_1) &= -\frac{V_0}{3} \left[\frac{W_0}{V_0} q_1 + q_2 + \alpha \cos\left(\frac{2\pi z_1}{d}\right) \left(\frac{W_0}{V_0} \sigma_1 + \sigma_2 \right) \right] P_2(\cos \beta_1), \\ \Phi_{1 < i < N}(z_i, \beta_i) &= -\frac{V_0}{3} \left[\sum_{j=i-1}^{i+1} q_j + \alpha \cos\left(\frac{2\pi z_i}{d}\right) \sum_{j=i-1}^{i+1} \sigma_j \right] P_2(\cos \beta_i), \\ \Phi_N(z_N, \beta_N) &= -\frac{V_0}{3} \left[\frac{W_0}{V_0} q_N + q_{N-1} + \alpha \cos\left(\frac{2\pi z_N}{d}\right) \left(\frac{W_0}{V_0} \sigma_N + \sigma_{N-1} \right) \right] P_2(\cos \beta_N),\end{aligned}\quad (1)$$

where q_i and σ_i ($i = 1, \dots, N$) are the orientational and translational order parameters (OPs) corresponding to the i th layer, z_i denotes the distance along the z -axis normal to the i th smectic plane, β_i is the polar angle between the long axis of the molecule belonging to the i th layer and the z direction, $P_2(\cos \beta_i)$ is the second-order Legendre polynomial, V_0 is the parameter of the system which determines the scale of the nematic-isotropic transition temperature and fixes the temperature scale of the model, W_0 is the parameter corresponding to the pair interactions in the bounding LC/water layers, and $\alpha = 2 \exp[-(\pi r_0/d)^2]$ is the extra one parameter of the system which can be varied between 0 and 2, and reflects the length of the *alkyl* tails of calamatic molecules [14]. Here r_0 is a characteristic length associated with the rigid core of

the molecule. Physically, this model indicates that we replace V_0 by $W_0 > V_0$ within the first and last layers, whereas for all interior layers $1 < i < N$ the interaction coefficient V_0 has not changed.

It should be pointed out that most LC molecules tend to align planar at the interface to an immiscible liquid, such as water, thereby preventing the generation of freely suspended films in their usual configuration in which the smectic layers are parallel to the two film surfaces. However, a homeotropic anchoring at LC/water interfaces can be attained by the use of suitable surfactants [4]. Moreover, by controlling the amount of surfactant adsorbed at the interface, it is possible to tune the anchoring strength W_0 , i.e., the strength of the ordering surface field.

The set of OPs q_i and σ_i corresponding to the i th layer of the smectic-A film composed of a stack of N smectic layers is described in Ref. [6], and can be obtained by solving the system of $2N$ nonlinear self-consistent equations (2)–(4) (Ref. [6]), at a given number of film layers N , temperature T , and two parameters α and W_0/V_0 of the model. Having obtained the set of OPs q_i and σ_i ($i = 1, \dots, N$), one can calculate the full dimensionless Helmholtz free energy per unit particle as $f = (1/N) \sum_{i=1}^N f_i$, where $f_i = F_i/N_i V_0$ is the dimensionless Helmholtz free energy corresponding to the i th layer, and can be calculated by using relations [6]

$$\begin{aligned}f_1 &= \frac{1}{6} \left[\frac{W_0}{V_0} q_1 \left(\frac{W_0}{V_0} q_1 + q_2 \right) + \alpha \frac{W_0}{V_0} \sigma_1 \left(\frac{W_0}{V_0} \sigma_1 + \sigma_2 \right) - 2\theta \ln Q_1 \right], \\ f_{1 < i < N} &= \frac{1}{6} \left[q_i \sum_{j=i-1}^{i+1} q_j + \alpha \sigma_i \sum_{j=i-1}^{i+1} \sigma_j - 2\theta \ln Q_i \right], \\ f_N &= \frac{1}{6} \left[\frac{W_0}{V_0} q_N \left(\frac{W_0}{V_0} q_N + q_{N-1} \right) + \alpha \frac{W_0}{V_0} \sigma_N \left(\frac{W_0}{V_0} \sigma_N + \sigma_{N-1} \right) - 2\theta \ln Q_N \right],\end{aligned}\quad (2)$$

where $Q_i = \frac{1}{d} \int_{(i-1)d}^{id} dz \int_0^1 h_i(x, z) dx$ ($i = 1, \dots, N$) is the partition function of the i th layer, $h_i(z_i, \beta_i) = \mathcal{A}^{-1} \exp[-(\Phi_i/k_B T)]$ is the one-particle distribution function of the i th layer, \mathcal{A} is the normalization constant, $\theta = k_B T/V_0$ is the dimensionless temperature of the system, k_B is the Boltzmann constant, and T is the absolute temperature of the system.

The dimensionless surface tension γ of the smectic film per molecule at constant volume $v = V/M$ is given by [5,15]

$$\gamma = \left(\frac{\partial f}{\partial a} \right)_{p, v, \theta} = - \left(z \frac{\partial f}{\partial z} \right)_{p, v, \theta}, \quad (3)$$

where a is the dimensionless area per molecule at constant p, v , and θ . Here $p = -(\partial f/\partial v)$ is the dimensionless pressure per molecule. Notice that the surface tension $\Gamma = \left(\frac{\partial F}{\partial A} \right)_{p, V, T} = -\frac{1}{A} \left(z \frac{\partial F}{\partial z} \right)_{p, V, T}$ was calculated using the fact that $V = ANd = \text{const}$, and A is the LC/water interface area.

Having obtained the set of f_i ($i = 1, \dots, N$), one can also calculate the disjoining pressure [5]

$$P(N, T) = -\frac{\Delta F}{L} = -V_0 n_0 \frac{\Delta f}{N}, \quad (4)$$

acting on the film layers from the bounding surfaces. Here the value of $\Delta f = f(N-1) - f(N)$ can be obtained for any N -layer smectic film

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