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Squeezing-out dynamics in free-standing smectic films

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ABSTRACT

We have carried out a theoretical study of the dynamics of the squeezing-out of one layer from the *N*-layer free-standing smectic film (FSSF) coupled with a meniscus, during the layer-thinning process. Squeezing-out is initiated by a thermally activated nucleation process in which a density fluctuation forms a small void in the center of the circular FSSF. The pressure gradient develops between the squeezed-out and nonsqueezed-out areas and is responsible for the driving out of one or several layer(s) from the *N*-layer smectic film. The dynamics of the boundary between these areas in the FSSF is studied by the use of the conservation laws for mass and linear momentum with accounting for the coupling between the meniscus and the smectic film. This coupling has a strong effect on the dynamics of the squeezing-out process and may significantly change the time which is needed to completely squeezed-out one or several layer(s) from the *N*-layer smectic film.

1. Introduction

A unique property of smectic liquid crystals (LCs) is an ability to form free-standing smectic films (FSSFs) which can be spread across large openings and considered as a stack of smectic layers confined by a surrounding air [1,2] or water [3]. Surface ordering in FSSFs has generated considerable experimental [1,3–5] and theoretical [6–12] interest, because the competition between surface and finite-sized effects leads to unusual physical properties of FSSFs. 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 temperature than that in the interior [1,3–10]. The presence of the surface tension is responsible for intriguing surface ordering phenomena exhibited by these films, such as the layer-thinning transitions in such quasi-two-dimensional systems where the melting originates in the interior of the film and penetrates toward the surface.

In this work we have carried out a theoretical study of the dynamics of the squeezing-out of one layer from the *N*-layer FSSF having a layered smectic-A (SmA) structure, in which the long axes of molecules are normal to the planes containing the layers and the intermolecular spacing is roughly of the length of the molecule. The combination of surface and finite-size effects in FSSFs gives rise to existence of smectic films at temperatures above the bulk smectic-A-isotropic (AI) transition temperature T_{AI}(bulk), surface-enhanced ordering, and layer-thinning transitions [1,4,6–9]. 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 the temperature T is increased above T_{AI}(bulk) [1,4,6–9].

Different mean-field theories have been used to obtain a qualitative description of the layer-thinning transitions [6–12]. According to the set of mean-field approaches [6–12], thinning takes place when the smectic layer structure throughout the middle of the film vanishes. In an alternative theory [4], supported by experimental and theoretical studies [13–15], layer-thinning occurs in compounds which undergo first-order SmA-I transitions by spontaneous nucleation of dislocation loops, the growth of which causes a film to thin.

It has been shown that the layer-thinning transition can be modeled as the successive melting (transitions to the isotropic phase) and subsequent removal of interior layers of the film as the film temperature is increased in the range $T > T_{AI}$(bulk) [9–12]. That transition has been attributed to the high surface tension at the film-air interface which acts to promote smectic order at the surface resulting in the surface layers ordering at a higher temperature than in the interior [1,6,8,9]. As a result, the interior layer(s) is(are) squeezed-out by the bounding ones. It has been assumed that the dynamics of the squeezing-out process is initiated by a thermally activated nucleation process in which a density fluctuation forms a small hole (a cavity with melted phase) of critical radius in the center of the circular smectic film [16]. The hole inside the film is taken to be of circular shape with radius

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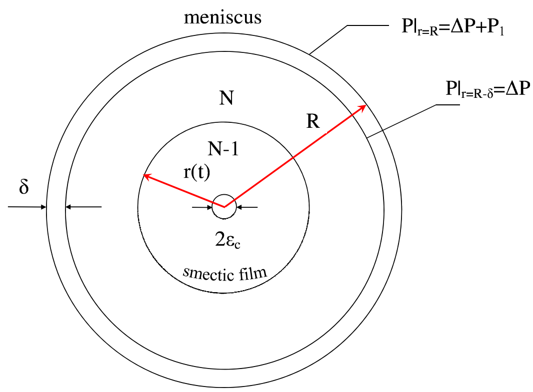

Fig. 1. Top view of the circular shape of the bounding line (or dislocation) between squeezed-out and nonsqueezed-out areas in the free-standing smectic film.

ϵ and with a thickness of the order of the molecular length d. The pressure gradient ∇P develops between the squeezed-out and nonsqueezed-out areas and is responsible for the driving out of one or several smectic layer(s) from the N-layer smectic film. The origin of ∇P is a disjoining pressure (DP) dropping [16] across the front of the moving boundary area during the layer-thinning transition $N \to N-1$.

In this work, the previously developed dynamical model [16], which describes the removal of one smectic layer from the N-layer smectic film during the layer-thinning process, will be supplemented by accounting for the effect of the meniscus. The dynamics of the bounding area during the layer-thinning transition $N \to N-1$ is studied by the use of the conservation laws for mass and linear momentum [17,18], with accounting for the boundary and initial conditions. The disjoining pressure (DP) is the main factor that is responsible for the driving out of one smectic layer from the N-layer smectic film. In turn, the DP is calculated in the framework of the extended McMillan's mean-field approach with anisotropic forces [19], where at the final stage of the removal of one smectic layer from the N-layer smectic film the effect of the meniscus is accounted for as an external field.

2. Model and calculations

In this work we investigate the dynamics of the bounding area of the circular shape, which is separated by the layer-thinning transition front, from the N-layer to $(N-1)$-layer smectic film in contact with a reservoir of the similar LC. This reservoir is necessary to provide a stable state of the smectic film. With that in mind, a free-standing Sm-A film composed of N discrete smectic layers with a thickness of the order of the molecular length d will be considered [9–12,16]. The geometry of the system is shown in Fig. 1. So, we are focused on the problem of evolution of the bounding area between the squeezed-out and nonsqueezed-out areas in the free-standing smectic film of the circular shape with the total area $A_0 = \pi R^2$, where R is the radius of the smectic film. We assume that squeezing-out starts from a thermally activated nucleation process in which a density fluctuation forms a small hole in the center of the circular smectic film [16]. The nucleus grows only when its size $\omega = \pi\epsilon^2 d$ exceeds a critical value ω_c, which is set by the competition between the bulk and surface thermodynamic forces. Let us investigate the dynamics of the bounding area during the layer-thinning transition $N \to (N-1)$, when the nucleation occurs in the center of the smectic film and the bounding line (which can be treated as dislocation) between the squeezed-out and nonsqueezed-out areas has the circular shape of radius $r(t)$, and the squeezed-out area $A(t) = \pi r^2(t)$ increases up to A_0.

Recently, it has been shown that during the thinning process all smectic layers are subjected to the compressive force acting across the free-standing smectic film upon heating to the isotropic temperature [6,9]. It has been shown that the pressure gradient ∇P, which develops between the squeezed-out and nonsqueezed-out areas, drives out the liquid crystal expulsion. The origin of ∇P is the disjoining pressure [11] P acting across the N-layer and $(N-1)$-layer smectic film, respectively. Taking into account that the disjoining pressure $P(N-1)$ acting across the $(N-1)$-layer film is greater then $P(N)$ acting across the N-layer smectic film [11,16], one can assume that the DP is responsible for the pressure gradient ∇P which drives the squeezed-out smectic layer in the zone far from the meniscus. In the bounding area close to the meniscus $(R-\delta \le r \le R)$ one should account for the effect of an additional pressure P_1 caused by coupling of the smectic film with the meniscus. Here P_1 is the pressure that the meniscus affects the smectic film and δ is the distance, counted from the smectic film/meniscus edge, where that effect occurs.

In these circumstances conservation laws for mass, linear momentum and torques must be hold. It should be pointed out that the layer-thinning process in free-standing smectic film is characterized by removal of interior isotropic layer(s) from the overheated film [9], so, we will account for only the continuity equation and the Navier–Stokes equation for the velocity field $\mathbf{v}(r,t)$.

It should be pointed out that the temperature T's effect both on the orientational $q_i(T)$ $(i=1,\ldots,N)$ and translational $\sigma_i(T)$ $(i=1,\ldots,N)$ order parameters (OPs) in thin $(N \le 25)$ FSSF has been investigated numerically [6,8–10]. According to these calculations, the distributions of the OPs across the smectic film, in the high-temperature region, are characterized by a sharp drop of both $q_i(T)$ and $\sigma_i(T)$ to zero with increasing distance (or number of layers) from the bounding surface toward the interior of the smectic film. Basing both on the behavior of the free energy and the OPs one can conclude that the interior layer(s) are melted and one deals with the isotropic layer(s).

Taking into account the thickness of one or several isotropic layer(s) one can assume that the mass density ρ is constant, and one deals with an incompressible isotropic layer(s). Incompressibility condition assumes that [16–18]

$$\nabla \cdot \mathbf{v} = 0, \tag{1}$$

whereas the Navier–Stokes equation takes the form [16]

$$\rho\frac{d\mathbf{v}(r,t)}{dt} = \rho\left[\frac{\partial \mathbf{v}(r,t)}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v}\right] = -\nabla_r P(r) + \nabla_r \sigma_{rz}(r,t), \tag{2}$$

where σ_{rz} is the stress tensor component corresponding to the viscous force. In our case, we choose the usual cylindrical coordinates with

$$\mathbf{v} = v(r,t)\hat{\mathbf{e}}_r, \tag{3}$$

and the gradient of the scalar field $P(r)$ is defined as

$$\nabla_r P(r) = \frac{\partial P(r)}{\partial r}\hat{\mathbf{e}}_r. \tag{4}$$

Here $\hat{\mathbf{e}}_r$ is the unit radial vector, and $v(r,t)$ is the radial component of the velocity vector $\mathbf{v}$. So, the coordinate system defined by our task assumes that the velocity $\mathbf{v}$ is directed parallel to the horizontal smectic layers. Substituting these expressions to Eqs. (1) and (2) gives

$$\frac{\partial v(r,t)}{\partial r} + \frac{1}{r}v(r,t) = 0, \tag{5}$$

$$\rho\left[\frac{\partial v(r,t)}{\partial t} + v(r,t)\frac{\partial v(r,t)}{\partial r}\right] = -\frac{\partial P(r)}{\partial r} + \frac{\partial \sigma_{rz}(r,t)}{\partial r} + \frac{\sigma_{rz}(r,t)}{r}, \tag{6}$$