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MODEL OF LAYER-BY-LAYER THINNING TRANSITION IN THIN FILMS

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Abstract Free-standing smectic liquid-crystal films exhibit an interesting phenomenon of layer-by-layer thinning transition where, instead of abrupt rupture of the film at or below Sm-A–isotropic transition temperature T_c, discrete jumps in film thickness are observed when temperature is increased, and the film eventually breaks at a temperature above the bulk value T_c [4]. Starting with a molecular pair interaction potential of the McMillan form and deriving therefrom a single effective potential, the behavior of thin films with changing temperature is studied. The film thickness experimentally found [4] to exhibit a clear functional relationship to temperatures of layer transitions, $h(t) = l_0 t^{-\nu}$, can be explained qualitatively, its exact form depending strongly on the parameters of the potential. Fluctuation profile of the order parameters within smectic layers is considered showing a critical behavior in the vicinity of the transition.

INTRODUCTION

One of the interesting aspects of interfacial phenomena [1] and surface ordering at interfaces in liquid crystals [2,3] is the formation, by many smectic liquid crystals, of free-standing films. As in the case of free surfaces of bulk liquid-crystal samples, the surface tension seems to induce order also at the film-vapor interfaces. T. Stoebe *et al.*

[4], studying free-standing films consisting of members of the partially perfluorinated 5-*n*-*alkyl*-2-[4-*n*-(*perfluoroalkyl*-metheleneoxy) phenyl] pyrimidine homologous series, discovered a *layer-by-layer thinning* transition taking place as the temperature was gradually increased. The film thickness h, in units of layers, exhibited a clear functional relationship to temperatures of the layer transitions,

$$h(t) = l_0 t^{-\nu} \tag{1}$$

with $t = [T_c(N) - T_0]/T_0$, $T_c(N)$ being the maximum temperature at which the N-layer film exists, l_0 is a constant, $T_c(N)$ the highest temperature at which the N-layer film exists, and T_0 some temperature very close to the bulk Sm-A–isotropic transition temperature T_c. Experimentally, the exponent ν was found to be 0.74.

SINGLE MOLECULE POTENTIAL

In treating the behavior of the smectic film, we proceed in much the same way as Mirantsev [5], generalizing his approach and including the study of fluctuations. In an N-layer film, let the i-th layer extend on the interval $z_i \in [(i-\frac{1}{2})d, (i+\frac{1}{2})d]$, i running from 0 to $N-1$, d being the layer-thickness. We start with a pair potential of the McMillan form, $V(r_{ij}) = -(V_0 c^3/n_0\pi^{3/2})\exp(-c^2 r_{ij}^2)$, V_0 being the interaction strength, $n_0 = N_{layer}/V_{layer}$ the density of molecules (the same in all layers), and $r_0 = 1/c$ the characteristic distance of the intermolecular interaction. By expanding $V(r_{ij})$ in Fourier series and performing the appropriate averaging procedure, we arrive at the expression

$$V_i(\mu_i, z_i) = -(V_0/3)[\textstyle\sum_j \beta_{ij}\eta_j + \alpha\cos(2\pi z_i/d)\sum_j \gamma_{ij}\sigma_j]P_2(\mu_i) \tag{2}$$

for the single molecule potential within the i-th layer, for $0 \le i \le N-1$. In (2), $\alpha = 2\exp[-(\pi/cd)^2]$, $\eta_j = \langle P_i(\mu_j)\rangle_j$ and $\sigma_j = \langle P_i(\mu_j)\cos(2\pi z_j/d)\rangle_j$ are local nematic and mixed nematic-smectic order parameters, respectively, and higher-order terms including $\sigma_j^{(n)} = \langle P_i(\mu_j)\cos(2\pi n z_j/d)\rangle_j$ have been neglected. Parameters $\beta_{ii} = \gamma_{ii} = 1$, the others β_{ij} and γ_{ij} are estimated to be $\beta_{i,i\pm1} \equiv \beta_1 = \exp[-(cd/2)^2]/(cd\sqrt{\pi})$ and $\gamma_{i,i\pm1} \equiv \gamma_1 =$

$-(2/\alpha)\exp[-(\pi/cd2\sqrt{2})]\beta_{i,i\pm1}$. The others β_{ij} and γ_{ij} vanish due to negligible coupling between molecules not in the same and the two neighboring layers, so the sums run over $j = i-1, i, i+1$. We note that $\beta_{i,i\pm1}$ and $\gamma_{i,i\pm1}$ are much smaller from $\beta_{ii} = 1$ and $\gamma_{ii} = 1$, respectively: the coupling between neighboring layers is the weaker the larger is d/r_0. This seems reasonable since, for a fixed r_0, the interaction between "centers of mass" of the molecules is weaker for longer molecules (large d). However, β_{ij} and γ_{ij} must be sufficiently large in order to obtain smectic ordering. Here, we take them intentionally as fitting parameters.

The surface effects are described by a two-parameter form

$$V_S(\mu_0, z_0; \mu_{N-1}, z_{N-1}) = -[W_0 + W_1 \cos(2\pi z_0/d) - (V_0/3)\,(\beta_{0,-1}\,\eta_{-1} + \alpha\,\gamma_{0,-1}\,\sigma_{-1})]P_2(\mu_0)$$

$$-[W_0 + W_1 \cos(2\pi z_{N-1}/d) - (V_0/3)\,(\beta_{N-1,N}\,\eta_N + \alpha\,\gamma_{N-1,N}\,\sigma_N)]P_2(\mu_{N-1}) \qquad (2')$$

where W_0 and W_1 are the nematic and smectic surface coupling strength constants, respectively. The former is related to reinforcing the homeotropic anchoring, the latter is stimulating the appearance of the surface-induced smectic layering. The terms in (2') including V_0 describe the coupling between layers in the bulk part of the film.

The free energy of the N-layer film is the $F = \sum_i F_i$, the sum running over all layers and F_i referring to individual layers. Using standard methods of statistical mechanics, $f_i = F_i/N_{layer}/(V_0/6)$ are found to be

$$f_i = [\eta_i(\eta_i + \beta_1(\eta_{i-1} + \eta_{i+1})) + \alpha\,\sigma_i\,(\sigma_i + \gamma_1(\sigma_{i-1} + \sigma_{i+1}))] - (6\,k_BT/V_0)\ln(Z_i/2d), \quad (3)$$

$$Z_i/2d = (1/2d)\int_{-1}^{1} d\mu_i \int_{(i-\frac{1}{2})d}^{(i+\frac{1}{2})d} dz_i \exp[-V_i(\mu_i, z_i)/k_BT] =$$

$$= \int_0^1 d\mu_i \exp[(V_0/3k_BT)P_2(\mu_i)\textstyle\sum_j \beta_{ij}\,\eta_j]\; I_0[(V_0/3k_BT)\alpha P_2(\mu_i)\textstyle\sum_j \gamma_{ij}\,\sigma_j],$$

where $I_0(z)$ is the modified Bessel function of the first kind. Analogous expression is found for the surface term.

The thinning process of the film is a non-equilibrium irreversible process. However, between jumps in film-thickness, the film has a fixed number of layers, and the process of heating takes place at constant pressure and volume until a subsequent

jump in layer-number occurs. The minimization condition for the Helmholtz free energy is justified for the process of heating between jumps in layer-number. The order parameter profiles as functions of temperature are therefore obtained by solving equations (3) for η's and σ's self-consistently and taking solutions with the lowest total free energy.

In order to investigate fluctuations, we expand the free energy up to quadratic terms. We can write $f = \sum_j f_j = f_0 + \sum_{ij} [\eta_i M_{n,ij} \eta_j + \sigma_i M_{s,ij} \sigma_j] \equiv f_0 + \sum_{ij} x_i M_{ij} x_j$ with $x = \eta \oplus \sigma$ and $\mathbf{M} = \mathbf{M}_n \oplus \mathbf{M}_s$ being direct sums. $\mathbf{M}$ is a symmetric matrix with non-zero elements on the diagonal and the first two off-diagonal positions. Because of the equipartition of energy among independent modes, the order parameter fluctuations within individual layers can be obtained from the diagonal elements of the inverse matrix $\mathbf{M}^{-1}$,

$$\langle x_j^2 \rangle = (6 k_B T/V_0) (\mathbf{M}^{-1})_{jj}. \tag{4}$$

RESULTS

The results obtained so far are preliminary and their complete explanation is yet to be done. They are in qualitative agreement with the results obtained previously by Mirantsev [5], and by Kranjc and Zumer [6] where use has been made of the Landau–de Gennes free energy density formalism. The parameters used in our calculation are α, β_1, γ_1, W_0 and W_1. In accordance with [5], we have taken $W_0/V_0 = 3$, $\alpha = 1.05$, and put $W_1 = W_0$, together with $\beta_1 = 0.9$, $\gamma_1 = 1$. Equations (3) and (4) yield a correct qualitative picture of the thinning process, consisting of consecutive Sm-A–*nematic*–*isotropic* phase transitions in core layers together with the appearance of accompanying increase in fluctuations.

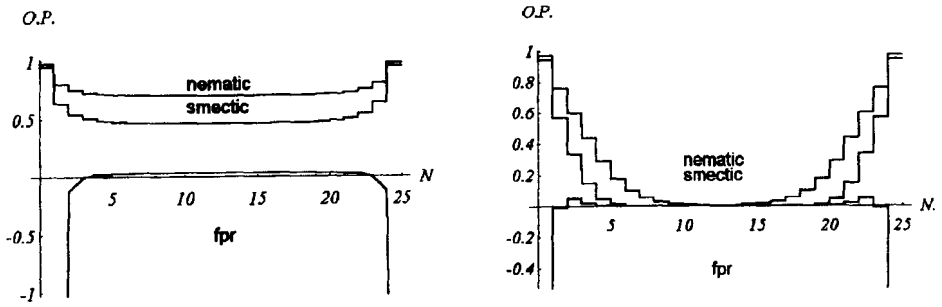

Figure 1

In Figure 1 the layer profiles of the order parameters η and σ (O.P.) together with the free energy (fpr) profiles (relevant to the distribution of forces within layers [5]) are shown at a particular phase transition (under and above $T_c(N)$) for a 25-layer film.

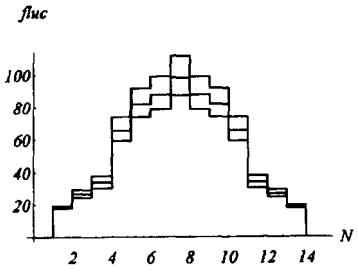

Figure 2

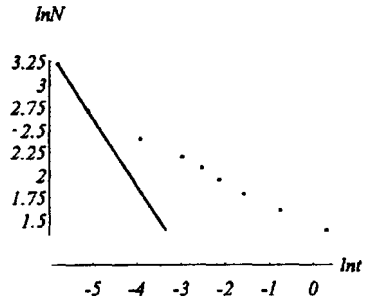

Figure 3

Figure 2 shows the corresponding fluctuation profiles (fluc) of the nematic order parameters as given by (4) for a 15-layer film for different temperatures in the vicinity of the transition. In Figure 3, the film thickness $h(t)$ as obtained from the above calculation (dots) is shown together with the experimental plot (solid line).

We note that the calculation yields essentially a power-law dependence of h on t of the form (1) with exponent 0.5 instead of experimentally found 0.74. This relationship, however, depends sensitively on the choice of the fitting parameters. Therefore, further study will be needed to clear up to what extent the mean field theory is capable to quantitatively explain the layer-by-layer thinning transition. In particular, one should find out whether it is possible to fit the experimental results with independent values of the parameters β_1, γ_1, W_0 and W_1, i.e. not using them as sheer fitting parameters, and whether it is sufficient to retain only the lowest terms in the Fourier expansion of the pair molecular potential.

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