Possibility of a roughening transition at the boundary of a smectic and wetting of the free liquid surface by the smectic

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It is shown that smooth and rough phases are defined at the boundary of a smectic liquid crystal, despite the fact that the absolute position of the boundary fluctuates without bound in each phase. A phase transition between the two falls in the usual Kosterlitz-Thouless class. Long-range elastic correlations in a smectic film of thickness h cause an attraction of the film boundaries which falls off as h^{-1}. It is because of this attraction that the wetting of the free surface of the isotropic phase by the smectic is observed to be incomplete. Layer-by-layer growth of such a film may persist at temperatures well above the temperature of the roughening transition of an isolated boundary between a smectic and an isotropic phase.

1. INTRODUCTION

There is a fairly well-developed theory for the roughening transition at the surface of an ordinary crystal[1,2] and for wetting transitions and layered growth of crystalline[3,4] and liquid[3,5,6] wetting films. On the other hand, the extent to which these effects are specific to boundaries and films of smectic liquid crystals[7] has not been studied, to the best of my knowledge. This is a timely problem, particularly in connection with the development of the method of grazing-angle x-ray reflection, which has made it possible for Als-Nielsen, Pershan, *et al.*[8,9] to study the wetting of the free surface of a liquid in the *nCB* (cyanobiphenyl) homologous series. Near the line of the bulk first-order *I–A* transition (Fig. 1), a wetting *A*-phase film forms at the free surface of the *I* phase. The *A*-phase film undergoes a layered growth as the transition line is approached. The wetting is incomplete; the maximum thickness is five layers.[8] As the triple point is approached (Fig. 1), the layering transitions weaken. Near the second-order transition (Fig. 1), one observes a critical wetting[3] of the free surface: The film thickness h is proportional to the correlation length of the interior, ξ_b, and increases without bound[9] ($h \propto \xi_b \to \infty$).

In this paper I examine certain aspects of roughening and wetting effects in smectic liquid crystals which are associated with the particular nature of their long-wavelength Hamiltonian (elastic theory)[7]:

$$H_{el}(\{u\}) = {}^1/_2 \int d^3r[\bar{B}(\partial u/\partial z)^2 + K_1(\Delta_\| u)^2]. \tag{1}$$

Here $u = u(r)$ is the local displacement of the layers of the smectic, which are oriented parallel to the x,y plane on the average; $\Delta_\| \equiv (\partial/\partial x)^2 + (\partial/\partial y)^2$; and $\bar{B}$ is the elastic modulus of the smectic, which vanishes in the nematic phase, in contrast with the first Frank constant K_1, which is a measure of the stiffness corresponding to distortions of the nematic order.

The absence of terms $\sim (\nabla_\| u)^2$ from the Hamiltonian H_{el} leads to strong fluctuations of the field $\{u\}$: In the long-wavelength limit, the integral

$$\langle u^2 \rangle \propto \int dk_z\, d^2k_\| (k_z^2 + \lambda^2 k_\|^4)^{-1}, \qquad \lambda = (K_1/\bar{B})^{1/2},$$

diverges, and there is no translational order. Nevertheless, a long-range topological order does exist in the smectic. The ideal layered structure is restored by the smooth mapping $\mathbf{r} \to \mathbf{r}' = (x, y, z, -u(\mathbf{r}))$. For this reason, a dislocation in a smectic is defined as a topological structural defect.[7] A surface topological defect, an elementary step,[1] is defined in a corresponding way: As a state of a semi-infinite smectic which corresponds to a minimum of the free energy under the condition that in the limit $x \to -\infty$ its boundary is localized near smectic layer j, while in the limit $x \to +\infty$ it is localized near layer $j \pm 1$. A step defined in this manner is stable if the number of particles in the smectic is fixed. In the low-temperature phase, in which the boundary is smooth, the free energy per unit length of the step, γ, is positive, so loops of steps of only finite size arise. The boundary is accordingly characterized by a long-range topological order: Being localized at some point $\mathbf{x}_\| = (x,y)$ near layer j, the boundary will follow this layer even off to an infinite distance from $\mathbf{x}_\|$. The surface fluctuates along with the layer. As the temperature rises, γ may vanish at the point of the Kosterlitz-Thouless transition.[1,2] The steps which are created spontaneously in the high-temperature rough phase destroy the long-range topological order. Evidence for the existence of a smooth phase of the surface of the smectic in this sense comes from observations of macroscopic steps on the surface of a drop of smectic spreading out on a solid substrate.[1]

In Sec. 2, which follows, this physical picture is realized on the basis of a sine-Gordon model, which has been used successfully to describe roughening transitions in ordinary crystals[2] and which is also exceedingly convenient for incorporating size effects in studies of layering transitions in thin films.[4,6] We know[2] that this model is valid on sufficiently large longitudinal length scales for $T \gtrsim T_c$, where the right side is the temperature of the roughening transition, while for a diffuse boundary, for which the width of the transition layer satisfies $\xi_b \gg d$, it is valid on all length scales $\geqslant \xi_b$. We will show that both below and above the temperature of the roughening transition the boundary of the smectic undergoes unbounded logarithmic fluctuations, which are characteristic of the rough phase of the boundary of an ordinary crystal,[1,2] but the macroscopic stiffness of the boundary, which determines the amplitude of these fluctuations, is discontinuous at the point of the transition.

In Sec. 3 we then examine the size correction to the free energy of phonon fluctuations in a thin smectic film bounded by homeotropic surfaces, i.e., by surfaces which are parallel

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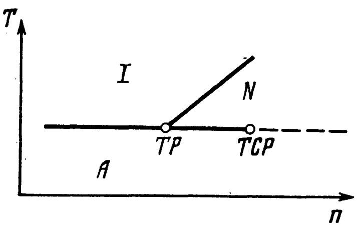

FIG. 1. Topology of the phase diagram of the nCB (cyanobiphenyl) homologous system. Solid lines—First-order transitions; dashed line—second-order transition; TP, TCP—triple and tricritical points, respectively.

to the smectic layers. We have shown previously that the corresponding correction $V_{\text{hyd}}(h)$ for a liquid film[5] and an ordinary crystal[10] falls off as the reciprocal square of the thickness: $V_{\text{hyd}}(h)\propto h^{-2}$, i.e., in the manner of a Van der Waals (photon) correction. In a smectic, however, according to (1), the dispersion relation for long-wave phonons, $\omega^2\propto(k_z^2+\lambda^2k_\parallel^4)$ differs qualitatively from that for phonons in ordinary crystals in liquids, $\omega^2\propto(k_z^2+k_\parallel^2)$. We will show that the corresponding size correction satisfies $V_{\text{hyd}}\propto h^{-1}$ and it is therefore the longest-range correction in systems without free charges (cf. Ref. 3).

In the final section of this paper (Sec. 4), we take a qualitative look at the relationship between the layered growth of a thin smectic film and the smoothness of the surfaces bounding it. We will show that a smectic film, in contrast with a film of an ordinary crystal,[4] can undergo a layered growth above the roughening temperature of one of its boundaries.

2. ROUGHENING TRANSITION

The assertion above that there are no qualitative differences between the fluctuations in the smooth and rough phases at the boundary of a smectic is actually contained in the book by de Gennes.[7] It was pointed out there that in the limit of an infinitely strong coupling of the surface with the smectic layers, i.e., under the assumption that the displacements of the surface layer, $u_0(\mathbf{x})$ [$\mathbf{x}=(x,y)$ is a vector in the plane of the boundary], are equal to the boundary displacements $z_0(\mathbf{x})$ and that a capillary wave $\delta z_0\exp(ikx)$ causes elastic distortions which decay slowly into the interior,

$$u(r)=\delta z_0\exp(ikx)\exp(-\lambda k^2 z)$$

with an energy $\varepsilon_b=(\bar{B}K_1)^{1/2}k^2|\delta z_0|^2$. The strong coupling of the boundary with the bulk structure (which is equivalent to the assumption $\gamma=\infty$ implying that steps are impossible) leads simply to a finite renormalization of the surface stiffness,

$$\sigma=\sigma_t\equiv\alpha_0+(\bar{B}K_1)^{1/2}\equiv\alpha_0+\sigma_b, \tag{2}$$

which appears in the Hamiltonian of the capillary fluctuations,

$$H_{\text{cap}}=\int d^2x\cdot{}^1/_2\sigma(\nabla z_0)^2, \tag{3}$$

and which does not alter the form of the logarithmic correlation function which follows from (3),

$$\langle[z_0(\mathbf{x}_2)-z_0(\mathbf{x}_1)]^2\rangle\propto\ln|\mathbf{x}_1-\mathbf{x}_2|.$$

In particular, the boundary remains delocalized: $\langle\delta z_0^2\rangle=\infty$. Here α_0 is the free surface energy of the boundary. Since it is assumed that the layers fluctuate along with the boundary, the anisotropy of the surface energy[11] does not contribute to the stiffness. In a crystal, the corresponding bulk elastic energy has the behavior $\varepsilon_b=\text{const}\cdot k\gg\sigma k^2$ in the limit of small k. Accordingly, in the theory of the roughening transition of ordinary crystals[1,2] the crystalline layers are assumed to be immobile, and $\langle\delta z_0^2\rangle$ turns out to be finite in the smooth phase.

In general we would have $u_0\neq z_0$ and the interaction of the boundary with the smectic structure would lead to a periodic variation of the free energy of the boundary in the direction of the relative coordinate $y=z_0-u_0$

$$\alpha=\alpha_0+\delta\alpha[(z_0-u_0)/d],$$

where $\delta\alpha(x+1)=\delta\alpha(x)$ and d is the period of the smectic structure. Since the modulation of the density of the smectic is described well by a single harmonic,[7] it is reasonable to set

$$\delta\alpha(x)=v(1-\cos(2\pi x)),$$

i.e., (cf. Ref. 2),

$$\alpha=\alpha_0+v\{1-\cos[2\pi(z_0-u_0)/d]\}. \tag{4}$$

Having assumed relative fluctuations z_0 and u_0, we must also take account of the sensitivity of α to the relative orientation of the boundary and the plane of the layers, expressed by the angle φ:

$$\alpha=\alpha_0+{}^1/_2W\varphi^2, \tag{5}$$

where W is the energy of the homeotropic orientation.[7] Using the expression $\sigma=\alpha+\partial^2\alpha/\partial\varphi^2$ to convert from the surface energy to the stiffness,[11] we find the following Hamiltonian for surface fluctuations:

$$H_{\text{cap}}=\int d^2x\left\{\frac{1}{2}\alpha_0(\nabla z_0)^2+\frac{1}{2}W[\nabla(z_0-u_0)]^2+\delta\alpha\left(\frac{z_0-u_0}{d}\right)\right\}. \tag{6}$$

Our analysis is meaningful only at length scales greater than the bulk correlation length ξ_b (i.e., the short-wave limit of the configuration integral $\Lambda\approx\xi_b^{-1}$). We will ignore the probability for the creation of dislocation loops with a length scale greater than ξ_b. Correspondingly, we will describe bulk effects by means of the elastic Hamiltonian H_{el} in (1). Since this Hamiltonian quadratic, the configurational integration over all u other than u_0 reduced to a minimization of H_{el} with respect to u under the condition $u_0=\text{const}$. In the leading order in ∇u_0 we find [cf. (2) and (3)]

$$H_b=\int{}^1/_2\sigma_b(\nabla u_0)^2d^2x; \tag{7}$$

incorporating the surface irregularity in the order parameter contributes only to the higher-order terms of the expansion.

The sum $\alpha_0(\nabla z_0)^2+\sigma_b(\nabla u_0)^2$ in $H_{\text{cap}}+H_b$ is conveniently transformed by analogy with the two-body problem of classical mechanics,[12] by going over to $y=z_0-u_0$ and $R=(\sigma_0z_0+\sigma_bu_0)/(\sigma_0+\sigma_b)$. Summing (4), (6), and (7), we find $H=H_0+H_i$, where H_0 is the Hamiltonian of the free field, (3), with the stiffness $\sigma=\sigma_t$ from (2), and

$$H_i = \int \{{}^1/_2\tilde{\sigma}(\nabla y)^2 + v[1-\cos(2\pi y/d)]\}d^2x \qquad (8)$$

is the Hamiltonian of the sine-Gordon model[2] with the stiffness

$$\tilde{\sigma} = W + \alpha_0\sigma_b/(\alpha_0+\sigma_b). \qquad (9)$$

The coordinate R is thus always characterized by logarithmic correlations,[2] causing a delocalization of the boundary as a whole (in general, this is a natural result, since we have $\langle u^2\rangle = \infty$ in the interior).

On the other hand, H_i describes an ordinary Kosterlitz-Thouless roughening transition in terms of the relative coordinate.[2] In the smooth phase we have $\langle y^2\rangle < \infty$. The step is defined as a topological defect; the macroscopic sample grows in a laminar fashion.[2,11] On macroscopic scales we have $y = 0$, $z_0 = u_0 = R$, and the observable stiffness if σ_t, given by (2). In the rough phase, the renormalization erases the periodic potential and maps H_i into H_R—the Hamiltonian (3) with $\sigma = \sigma_R > \tilde{\sigma}$. Correspondingly, we have $\langle y^2\rangle = \infty$, and there are no macroscopic steps or laminar growth. The stiffness of the boundary observable at macroscopic scales is determined by a minimization of $H_0 + H_i$ with respect to $u_0(x)$ at a given $z_0(x)$:

$$\sigma = \sigma_R\sigma_t^2/(\sigma_b^2+\sigma_t\sigma_R) < \sigma_t. \qquad (10)$$

The value of σ_R at the point of the transition on the side of the rough phase is related to the temperature T_c by the universal relation[1,2]

$$k_BT_c = 2\sigma_R d^2/\pi; \qquad (11)$$

in the smooth phase we have $\sigma_R = \infty$. The observable stiffness σ thus has a discontinuity $\Delta\sigma$ at T_c, given by

$$\frac{\Delta\sigma}{\sigma_t} = \left[1 + \frac{\pi T_c}{2}\,\frac{\alpha_0+\sigma_b}{\sigma_b^2 d^2}\right]^{-1}. \qquad (12)$$

This discontinuity becomes progressively more noticeable as σ_b/α_0, increases. The general expression for the temperature dependence $\sigma(T)$ with allowance for the square-root singularity[1,2]

$$\sigma_R(T_c) - \sigma_R(T) \propto (T-T_c)^{1/2},$$

is shown in Fig. 2.

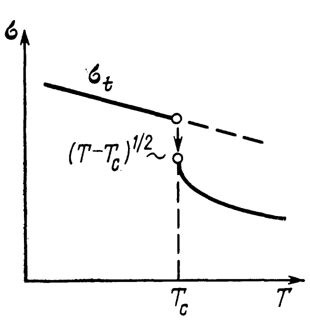

FIG. 2. Schematic temperature dependence of the macroscopic stiffness of the smectic boundary near a roughening transition.

3. HYDRODYNAMIC INTERACTION OF THE BOUNDARIES OF A SMECTIC FILM AND EQUILIBRIUM OF THIS FILM AT THE FREE SURFACE OF A LIQUID

The behavior $V_{\text{hyd}} \propto h^{-1}$ for the size component of the free energy of the phonon excitations in a smectic film oriented parallel to molecular layers can be found on the basis of some simple considerations. In a film of infinite thickness, both boundaries—which we assume for simplicity are smooth—fluctuate. They do so independently. They are characterized by stiffnesses $\sigma_j = \alpha_j + \sigma_b$ [see (2)], where α_j is the free energy of boundary j ($j = 1,2$). In a film of finite thickness h, in contrast, at wavelengths greater than the characteristic crossover scale $\xi_c \sim (\lambda h)^{1/2}$, the spectrum of capillary fluctuations is completely different. A symmetric capillary mode corresponds to bending of the film as a whole and is characterized by a stiffness $\sigma_s = \alpha_1 + \alpha^2$, while the elastic energy $\sim K_1hk^4 \ll \sigma_s k^2$ can be ignored in this limit. On the other hand, elastic effects generate a gap $\varepsilon_\alpha \sim \overline{B}/h$ in the spectrum of an antisymmetric mode. The contribution to the free energy which comes from these pronounced changes in the spectrum has the natural form

$$V_{hyd} \sim k_BT/\xi_c^2 \sim k_BT/\lambda h. \qquad (13)$$

In a quantitative calculation it is necessary to incorporate the size quantization of the bulk acoustic mode in the film. Such a calculation can be carried out by the method of Ref. 5, with allowance for the particular nature of the bulk dispersion relation

$$\omega^2 = (\overline{B}k_z^2 + K_1k_\parallel^4)/\rho,$$

which follows from (1). Matching the elastic wave in the smectic with a wave which is damped with distance into the interior of the bordering fluid at the boundary (on the basis of the equality of the pressures and the normal displacements; cf. §62 in Ref. 13), we find the conditions

$$u^{-1}\partial_{\mathbf{n}}u = (\rho_j\omega^2 - \alpha_jk_\parallel^3)/(\overline{B}k_\parallel) = \psi_j(k_\parallel, \omega) \qquad (14)$$

at the jth (smooth) boundary of the film. Here $\mathbf{n}$ is the inward normal to the boundary, and ρ_j is the density of the bordering fluid (a smooth boundary with a solid is modeled by the limit $\alpha_j \to \infty$, i.e., $u_j = 0$). Following Ref. 5, we find from (14) the dispersion relation

$$k_zh + \operatorname{arctg}[\psi_1(k_\parallel, \omega)/k_z] + \operatorname{arctg}[\psi_2(k_\parallel, \omega)/k_z] = \pi m.$$

The free energy of the phonon excitations is

$$k_BT\sum_{m,k_\parallel}\ln(\hbar\omega/k_BT).$$

The size correction to this free energy is the correction for the discrete nature in the sum over m. Applying the Poisson formula[14] and transforming the integrals over k_z by parts, we find

$$V_{hyd} = -k_BT\int\sum_{l=1}^{\infty}(2\pi il)^{-1}\int_{-\infty}^{\infty}\exp\left[2il\left(k_zh + \operatorname{arctg}\frac{\psi_1}{k_z} + \operatorname{arctg}\frac{\psi_2}{k_z}\right)\right]\frac{\partial\ln(\hbar\omega/k_BT)}{\partial k_z}dk_z\frac{d^2k_\parallel}{(2\pi)^2}.$$

Closing the contour of the integration over k_z in the upper half-plane, we find that the asymptotic expression for $V_{\text{hyd}}(h)$ is determined by the pole in the integrand at $k_z = i\lambda k_\parallel^2$. Hence

$$V_{hyd}=-k_BT\sum_{l=1}^{\infty}(2l)^{-1}\int\exp\left\{2l\left[-\lambda k_\parallel^2h+\operatorname{arcth}\frac{\psi_1(k_\parallel,\omega=0)}{\lambda k_\parallel^2}+\operatorname{arcth}\frac{\psi_2(k_\parallel,\omega=0)}{\lambda k_\parallel^2}\right]\right\}\frac{d^2k_\parallel}{(2\pi)^2}.$$

Substituting in

$$\psi_j(k_\parallel,\ \omega=0)/\lambda k_\parallel^2=-\alpha_j/\sigma_b$$

from (14), we finally find

$$V_{hyd}=-\frac{1}{16\pi}\operatorname{Li}_2\left(\frac{\alpha_1-\sigma_b}{\alpha_1+\sigma_b}\frac{\alpha_2-\sigma_b}{\alpha_2+\sigma_b}\right)\frac{k_BT}{\lambda h},\qquad(15)$$

where[15]

$$\operatorname{Li}_2(x)=\sum_{n=1}^{\infty}x^nn^{-2};\qquad \operatorname{Li}_2(1)=\pi^2/6.$$

Since the free energy α_1 of the A/I boundary (and, especially, the larger energy of the boundary with the gas, α_2) contains a contribution from nematic degrees of freedom, which is unrelated to the weak smectic order, and since we have $\sigma_b\propto\overline{B}^{1/2}$, it is reasonable to assume $\alpha^2\gg\alpha_1>\sigma_b$, so that we have $V_{\rm hyd}<0$.

In the limit $\alpha_1,\alpha_2\gg\sigma_b$ (near the tricritical point TCP in Fig. 1), the argument of Li_2 approaches 1, and we have

$$V_{hyd}=-\frac{\pi}{96}\frac{k_BT}{\lambda h}=-0{,}033\frac{k_BT}{\lambda h}.\qquad(16)$$

4. LAMINAR TRANSITIONS IN A THIN SMECTIC FILM

The laminar growth of a macroscopic smectic film is equivalent to the smoothness of both of its boundaries: The lines of first-order transitions which correspond to a thickening of the film by one layer terminate at the critical points at the temperature $T_{c,\infty}=T_c$. In a film of finite thickness, the temperatures $T_{c,j}$ experience a size shift for two reasons. 1. The surface energy $\alpha(h)$ given by (4) acquires a size component $V(h)$ with $d^2V/dh^2>0$ for thicknesses near equilibrium. Under the condition

$$d^2V/dh^2>\max|d^2\alpha/dh^2|$$

the barriers which separate the thicknesses $h_j=jd$ are suppressed, and the growth becomes continuous. This effect lowers the critical temperatures: $T_{c,j}<T_c$. It is apparently this situation which prevails in films of an ordinary crystal.[4] 2. A specific feature of a smectic liquid crystal is that (as is clear from Sec. 2) the driving force for the transition to the rough phase consists not only of capillary fluctuations but also of elastic fluctuations of surface layers. Under the conditions $\sigma_b\ll\alpha_0\sim W$, the presence of these fluctuations [i.e., the finite value of σ_b in (9)] reduces the effective stiffness $\tilde\sigma$ in (8) from $\tilde\sigma^0=W+\alpha_0$ to $\tilde\sigma^\infty=W+\sigma_b$, i.e., possibly by severalfold. On the other hand, elastic waves with wavelengths greater than the crossover length $\xi_c=(\lambda h)^{1/2}$ are suppressed in the film according to (13). More precisely, minimizing the functional (1) in the film leads to a size dependence of the constant σ_b in (7):

$$\sigma_b(h)=\sigma_b^\infty\frac{\alpha_2+\sigma_b^\infty\operatorname{sh}(k_\parallel^2\lambda h)}{\alpha_2\operatorname{sh}(k_\parallel^2\lambda h)+\sigma_b^\infty\operatorname{ch}(k_\parallel^2\lambda h)}.$$

It thus increases from $\sigma^b_\infty=(K_1\overline{B})^{1/2}$ at $k_\parallel\xi_c\gtrsim1$ to $\sigma_b^0=\alpha_2\gg\sigma_b^\infty$ at $k_\parallel\xi_c\ll1$. Here we are considering fluctuations of the weaker boundary of the film (A/I in Ref. 8), and α_2 is the energy of the opposite boundary, which is stronger (A with the gas in Ref. 8), so we have $\alpha_2>\alpha_1(\equiv\alpha_0)$. At $k_\parallel\sim\xi_c^{-1}$, the stiffness $\tilde\sigma$ of the effective Hamiltonian (8) thus undergoes a crossover from $\tilde\sigma^\infty$ at large $k_\parallel$ to $\tilde\sigma^0\gg\tilde\sigma^\infty$ at $k_\parallel$.

The critical point of the laminar transition is determined qualitatively (cf. Ref. 6) by the relations among four lengths: ξ_c, the capillary length

$$\xi_{cap}=[\alpha_1/(d^2V/dh^2)]^{1/2},$$

and the correlation lengths $\xi_\parallel^\infty$ and $\xi_\parallel^0$, which are determined by Hamiltonian (8) with $\sigma_b=(K_1\overline{B})^{1/2}$ (i.e., $h=\infty$) and $\sigma_b=\infty$ (i.e., $h=0$), respectively. The latter quantities increase near the corresponding critical points $T_c^\infty<T_c^0$ from their finite values in the smooth phase to infinite values in the rough phase. The laminar growth disappears when the length $\xi_\parallel$ becomes greater than $\xi_{\rm cap}$; as $\xi_\parallel$ we must choose $\xi_\parallel^\infty$ if $\xi_{\rm cap}<\xi_c$ or $\xi_\parallel^0$ if $\xi_{\rm cap}>\xi_c$.

Since we have $V(h)=O(h^{-1})$, the length $\xi_{\rm cap}=O(h^{3/2})$ increases with increasing thickness more rapidly than ξ_c does. Accordingly, if the thickness of the wetting film is quite large, despite the incompleteness of the wetting, the film will grow in a laminar fashion up to $T_c\approx T_c^0$, which may be considerably higher than T_c^∞, the temperature of the transition to the rough phase of an isolated boundary. The limit $h\to\infty$ is ambiguous. In the interval $T_c^\infty<T<T_c^0$, laminar transitions formally persist at any finite thickness, but they are exceedingly weak at large h.

5. DISCUSSION AND CONCLUSIONS

In summary, working in a model which incorporates the interaction of the boundary with a smectic structure through a periodic component of the surface energy, (4), and an orientation-dependent component, (5), we have demonstrated the existence and nature of the smooth and rough phases of the boundary of the smectic and the transition between these phases. Fluctuations in the absolute position of the boundary are not bounded in either phase, but in the smooth phase the boundary is localized with respect to the strongly fluctuating smectic layers. The roughening phase transition falls in the same universality class, the Kosterlitz-Thouless class, as that for ordinary crystals.[1,2] The correlation function for the displacements of the boundary,[1,2]

$$\langle[z_0(\mathbf{x}_1)-z_0(\mathbf{x}_2)]^2\rangle\propto T\sigma^{-1}\ln|\mathbf{x}_1-\mathbf{x}_2|,\qquad(17)$$

which is found experimentally from x-ray scattering by the boundary,[16] is of the same qualitative form in the two phases, but the macroscopic boundary stiffness σ, which determines the amplitude (17), is discontinuous at the point of the roughening transition (Fig. 2). This discontinuity can also be observed in measurements of the frequency of long capillary waves at the surface of a smectic in experiments on inelastic scattering of light. In contrast, the vanishing of the free energy of the step and the transition from the laminar growth of a macroscopic sample to continuous growth occur extremely gradually, as in the case of an ordinary crystal[1,2] (the linear energy of the step is

$$\gamma \propto \xi_{\parallel}^{-1} \propto \exp[-\mathrm{const}(T_c-T)^{-1/2}]),$$

so these characteristics are not convenient for detecting the transition.

The possibility of diagonalizing the Hamiltonian of the problem, $H=H_0+H_i$ [(3) + (8)], stems from the circumstance that the Hamiltonians (7) and (3) are identical in form, i.e., from the circumstance that fluctuations in the elastic degrees of freedom of the smectic are qualitatively similar to capillary fluctuations of a free boundary: the correlations are logarithmic in each case. It is the case of frozen *logarithmic* distortions of a crystal lattice which was studied in Ref. 17, where a Kosterlitz-Thouless roughening transition was also found. The question of whether a smooth phase of the boundary is possible and the question of the nature of the roughening transition in this case, in which there are fluctuations in the displacements of the bulk structure (thermal or frozen) which are stronger than logarithmic, remain open. Such fluctuations might be realized, for example, as frozen phasons in quasicrystals (cf. Ref. 18).

It was then shown that the circumstance that the phonon correlations in smectics are of longer range then in ordinary crystals and liquids leads to a size correction to the free energy of a thin smectic film, $V_{\mathrm{hyd}}(h) \propto h^{-1}$, given by (13). This correction is the one of longest range among all known corrections in three-dimensional systems without free charges or dipoles. The quantity $\sigma_b \propto \overline{B}^{1/2}$, i.e., a quantity determined by the weak smectic order, is apparently always smaller than the surface energies $\alpha_{1,2}$, which contain components from other (stronger) degrees of freedom. We thus have $V_{\mathrm{hyd}}<0$, and the wetting of the smectic is always incomplete (cf. Ref. 5). The long-range attraction of the boundaries limits the growth of the film toward the line of the first-order transition (Fig. 1), in agreement with experiments.[8] The only exceptional case might be a smectic film bordered on one side by a nematic liquid crystal (near line TP–TCP in Fig. 1); the free energy of the extremely weak N/A boundary may be smaller than σ_b. In such a case, V_{hyd} would be positive and would promote complete wetting.

In any case, as the tricritical point (TCP in Fig. 1) is approached we have $\lambda \propto \overline{B}^{-1/2} \to \infty$ and therefore $V_{\mathrm{hyd}} \to 0$, and the incomplete wetting gives way to a critical wetting.[9]

Finally, the interaction of elastic and capillary fluctuations in a smectic film may substantially raise the temperature of the critical points for laminar transitions in a film from that of an isolated weak boundary of a film. The situation here is opposite that in a crystalline film, in which laminar transitions disappear below the roughening temperature of the half-space.[4]

Accordingly, the laminar growth of a wetting smectic film at the surface of an I phase[8] is not equivalent to a smoothness of an isolated A/I boundary. The latter can be rough near the triple point TP (Fig. 1). On the other hand, the continuous growth of an A film at the boundary of an N half-space[8,9] is evidence that the A/N boundary is in a rough state. In this connection, the continuous weakening of laminar transitions as the point TP is approached from the side of the I phase may be evidence of complete wetting of the A/I boundary by the N-phase film, which thickens without bound as TP is approached (cf. the corresponding situation at the boundary of a crystal with a gas which is undergoing surface melting[6]).

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