

## Effects of surface enhancement on fluctuation-induced interactions

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We examine the fluctuation-induced interaction energy  $\Delta f$  between the surfaces of a layered hexatic film within a quadratic-functional-integral approach. Both discrete and continuum formulations are studied. We find large corrections to the asymptotic behavior  $\Delta f(l) \propto l^{-2}$  for finite  $l$ , where  $l$  is the film thickness. A small field becomes relevant beyond a length scale  $\xi(h)$ , while an enhanced surface Frank constant is irrelevant above a length  $\xi(K)$ . Possible relevance of these results to recent experiments on layer-by-layer surface ordering in liquid-crystal films is discussed.

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It is well known that boundaries produce measurable effects on the global properties of physical systems [1]. In particular, they cause long-range interactions in systems whose fluctuations are correlated over long distances. For example, at a critical point, Fisher and de Gennes discovered corrections to the free energy of a system of size  $l$  that scale as  $1/l^2$  [2]. Since a spontaneously broken continuous symmetry also leads to long-range correlations, similar forces are present in superfluids or liquid crystals. The correlated fluctuations in a *smectic* liquid crystal lead to a long-range force between the surfaces of the film that decays asymptotically as  $\Delta W \propto l^{-p}$ , with  $p=2$ , where  $l$  is the film thickness [3–5]. On the other hand, the forces induced by orientational fluctuations are of shorter range, with  $p=3$  [4–6]. The magnitude of these interactions is proportional to  $k_B T$ , while their amplitudes are *universal*. There has been recent attention on fluctuation-induced long-range forces in critical systems and their connection to such phenomena as wetting [7] and layer-by-layer surface ordering in free-standing liquid-crystal films [8,9].

Liquid-crystal films provide an additional interesting feature in that their surfaces are typically more ordered than the bulk. This is because of the surface tension between the film and the surrounding gas which inhibits fluctuations of the molecules close to the surface [10]. Recent heat-capacity experiments on free-standing liquid-crystal films near smectic-*A* to surface-stabilized smectic-*I*, and smectic-*A* to surface stabilized smectic-*B* transitions reveal a layer-by-layer ordering that starts at the surface and proceeds into the bulk [9]. On approaching the bulk transition, the number of (bond orientationally) ordered layers close to the surface diverges as  $l(t) \propto t^{-\nu}$ , where  $t$  is the reduced temperature. At the Sm-*A*–Sm-*I* transition [8],  $\nu \approx 0.373 \pm 0.015$ , while  $\nu \approx 0.32 \pm 0.01$  for the Sm-*A*–Sm-*B* transition [9].

The continuous growth of the ordered hexatic region from the surface is reminiscent of *complete wetting* [11]. If the net force between the boundaries of the ordered region decays as  $1/l^p$ , the exponent  $\nu$  takes the value of  $1/p$ . This is obtained by equating the repulsive interaction, which favors thick layers, with the force due to the additional chemical-potential cost of creating the metastable ordered phase. The latter force is attractive (prefers  $l=0$ ), and the chemical-potential difference is assumed to be proportional to  $t$ . For example, van der Waals forces lead to  $\nu = \frac{1}{3}$ , which is close to the value observed for the Sm-*A*–Sm-*B* transition, but somewhat less than that seen at the Sm-*A*–Sm-*I* transition.

A possible explanation of the continuous layering transitions is that the molecular fluctuations gradually increase from the surface into the bulk. This in turn sets up a profile of coupling constants for the hexatic-order parameter that increases on approaching the surface. Each layer orders at the transition temperature corresponding to that layer. However, the similarity to complete wetting suggests that we may try to identify repulsive interactions that favor the thickening of the ordered layer, even if homogeneous. A difference between the dielectric constants of two phases will indeed lead to a van der Waals interaction that could account for the observations. However, we shall show that the forces induced by the additional bond-orientational fluctuations in smectics *B* and *I*, also falling off as  $1/l^3$ , are at least as strong as the van der Waals forces. If these forces are indeed responsible for the observations, they may also account for the different exponents observed for Sm-*I* and Sm-*B* ordering: As these forces originate in the modification of fluctuations by boundaries, the molecular tilt of the Sm-*I* phase could result in changes not present in the Sm-*B* phase. In this paper, we focus on the fluctuation-induced interaction  $\Delta f(l)$ , and investigate its

dependence on different surface-enhancement operators. We find that any surface enhancement introduces a characteristic length scale  $\xi$  [12]. For films much thicker or much thinner than  $\xi$ , the well-known asymptotic behaviors  $\Delta f \propto l^{-2}$  are obtained [4,5,6,13]. However, we show that large corrections to these asymptotic regimes appear for finite  $l/\xi$ , and relate our results to the heat-capacity findings cited above.

After the hexatic order is established, the fluctuations of the bond angles,  $\theta_i(r)$ , in a *homogeneous* film are governed by the quadratic Hamiltonian [14]

$$\beta\mathcal{H}_0 = \int_a^L d^2r \left[ \frac{a^2 K_A}{2} \sum_{i=0}^n (\nabla\theta_i(r))^2 + \frac{J}{2} \sum_{i=0}^{n-1} [\theta_{i+1}(r) - \theta_i(r)]^2 \right]. \quad (1)$$

The index  $0 \leq i \leq n$  labels the layer number, and  $r$  is the location within the two-dimensional layer. The short-distance cutoff  $a$  is approximately the size of a molecule, while  $L$  is the size of the film.  $K_A$  is the effective Frank constant of each layer, and  $J$  measures the interplane coupling, both measured in units of  $a^{-2}$ . [Equation (1) disregards amplitude fluctuations and topological defects.] The surface tension between the film and the surrounding gas reduces fluctuations in the neighborhood of the surface [10], and makes the Hamiltonian inhomogeneous. We shall model these effects by adding appropriate enhancement operators to Eq. (1) that act only on the boundary layers, such as

$$\beta\mathcal{H}_S = \int_a^L d^2r \left[ \frac{a^2}{2} [K_{A,0}^S (\nabla\theta_0)^2 + K_{A,n}^S (\nabla\theta_n)^2] + \frac{1}{2} (h_0\theta_0^2 + h_n\theta_n^2) \right]. \quad (2)$$

For liquid-crystal compounds of the *n*-alkyl-4'-(*n*-alkoxy)biphenyl-4-carboxylate (*nmOBC*) homologous series which develop a Sm-*A*–Sm-*B* transition, the evolution of the heat-capacity peaks with film thickness is well reproduced by a model with enhanced surface Frank constant  $K_A^S$  [15–17]. On the other hand, for the compound 4-(*n*-nonyloxy)benzylidene-4(*n*-butyl)aniline (9O.4) which undergoes a Sm-*A*–Sm-*I* transition, the tilting of molecules on the surface Sm-*I* phase generates an ordering field on the hexatic-order parameter [18]. As the tilt of the molecules on the surface is much more pronounced than in subsequent layers, and reinforced by the fact that the Sm-*I* phase does not exist in bulk, we consider an ordering field that acts only on the surface layer. Such a field adds a term  $h\theta^2/2$  to the Hamiltonian density. The geometry appropriate to the layer-by-layer ordering transitions is indicated in Fig. 1. It is clear that the environments of the top and bottom hexatic layers are in fact very different and the enhancement operator will mostly act at the hexatic-gas boundary. This is the origin of the difference between the two boundaries in the above equation.

We shall initially derive the results appropriate to an enhanced field, and subsequently discuss the generaliza-

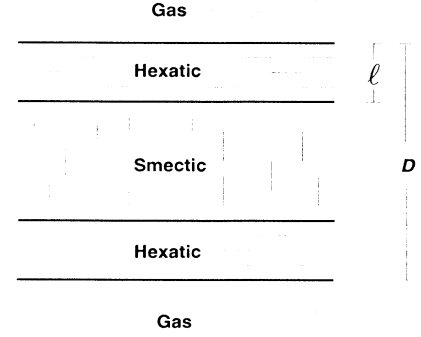


FIG. 1. Geometry of a liquid-crystal film that develops a surface-hexatic-ordered phase. Surface tension inhibits fluctuations in the gas-film interface and its vicinity. The hexatic phase can be tilted, as in the Sm-*I* phase, or untilted, as in the Sm-*B* phase. We assume that the thickness of the smectic bulk phase is large enough so that the effective interaction between the surface phases can be disregarded.

tion to enhanced surface Frank constants. The quadratic Hamiltonian (including the surface-ordering term) is partially diagonalized by Fourier transforming with respect to  $r$ ,

$$\beta\mathcal{H} = \frac{1}{2} \int_{2\pi/L}^{2\pi/a} d^2q \left[ \sum_{i,j=0}^n \theta_i(q) \mathbf{M}_{ij}(q) \theta_j(-q) \right], \quad (3)$$

where the only nonzero elements of  $\mathbf{M}$  are

$$\begin{aligned} M_{0,0} &= a^2 K_A q^2 + h_0 + J \equiv a_0, \\ M_{n,n} &= a^2 K_A q^2 + h_n + J \equiv a_n, \\ M_{i,i} &= a^2 K_A q^2 + 2J \equiv b \quad (\text{for } i \neq 0 \text{ or } n), \\ M_{i+1,i} &= M_{i,i+1} = -J. \end{aligned}$$

The total free energy is obtained from

$$\frac{f}{k_B T} = \frac{1}{2} \int d^2q \sum_m \ln \lambda_m = \frac{1}{2} \int d^2q \ln \det \mathbf{M}, \quad (4)$$

where  $\lambda_m$  are the eigenvalues of  $\mathbf{M}$ . Following standard matrix algebra [19],

$$\det \mathbf{M} = a_0 a_n T_{n-1} - (a_0 + a_n) J^2 T_{n-2} + J^4 T_{n-3} \quad (n > 1), \quad (5)$$

where

$$T_j = b^j \frac{\eta_+^{j+1} - \eta_-^{j+1}}{\eta_+ - \eta_-} \quad (6)$$

and

$$\eta_{\pm} = \frac{1 \pm [1 - 4(J/b)^2]^{1/2}}{2}. \quad (7)$$

Through numerical integration we confirm that the total free energy has, as expected, the following functional dependence on  $n$  [20]:

$$f = n f_B + f_S + \Delta f(n). \quad (8)$$

Here  $f_B$  is the extensive part of the free energy, and, in the limit of  $n \rightarrow \infty$ , gives the bulk free-energy density. The surface contributions appear in  $f_S$ , and  $\Delta f(n)$  is the fluctuation-induced interaction energy that vanishes as  $n \rightarrow \infty$ . We start by analyzing the behavior of the interaction energy as a function of  $n$ , for the three possible limiting cases of (I)  $h_0 = h_n = 0$  (free-surfaces), (II)  $h_0, h_n \rightarrow \infty$  (Dirichlet boundary conditions), and (III)  $h_0 = 0, h_n \rightarrow \infty$  (mixed boundary conditions). Note that in a renormalization-group treatment (see below), these conditions appear as the only possible fixed points [2,21]. Figure 2 depicts the  $n$  dependence of  $\Delta(n) = (a^2 K_A / J) [\Delta f(n) / k_B T] n^2$  for these cases. In the limit of  $n \gg 1$ , we recover the asymptotic values of  $\Delta(n) = \Delta_i$ , with  $\Delta_I = \Delta_{II} = \zeta(3) / 16\pi$  (attractive), and  $\Delta_{III} = -\frac{3}{4} \Delta_i$  (repulsive), as previously obtained within continuum approaches [4–6,13]. [Here  $\zeta(x)$  is the Riemann's  $\zeta$  function.] For finite  $n$ , there are corrections to the asymptotic limits, which, in all cases, initially scales as  $1/n$ .

We first concentrate on the symmetric case of equal finite surface fields ( $h_0 = h_n$ ). The evolution of the interaction energy with  $n$  is *nonmonotonic*. For small  $h/J$ , we can obtain a universal form for the interaction energy by using the scaling variable  $x = n / \xi(h)$  to collapse the data as shown in Fig. 3, where  $\xi(h) = J/h$  is the length scale characterizing a surface field. Note that the limits of  $x \rightarrow 0$  and  $x \rightarrow \infty$  recover, respectively, the asymptotic values of cases I and II. However, large deviations are observed for finite  $x$ . There is excellent data collapse for large  $x$ , but only a slow convergence to  $\Delta(x \rightarrow \infty) = \Delta_{II}$ . The fixed-point behavior obtained by renormalization-group techniques is only reached for  $n \gg \xi(h)$ , and this must be regarded as quite a general condition for the applicability of the renormalization-group arguments to layered systems. For small  $x$ , there are nonuniversal con-

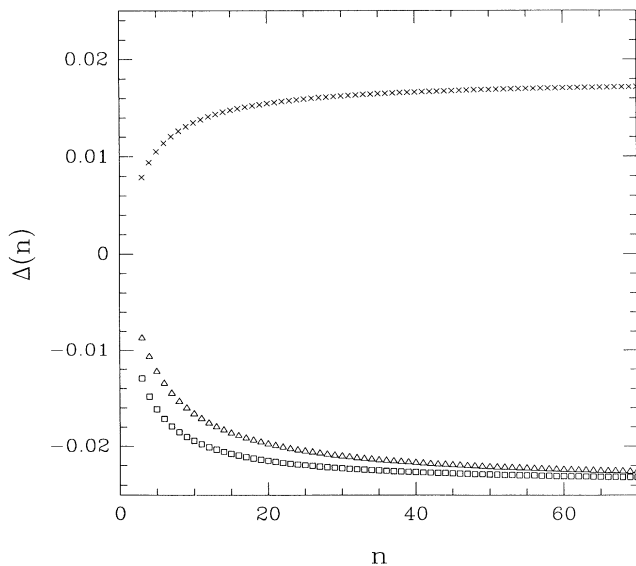


FIG. 2.  $\Delta(n) = (a^2 K_A / J) [\Delta f(n) / k_B T] n^2$  vs  $n$  for free surfaces (triangles), Dirichlet-Dirichlet boundary conditions (squares), and mixed boundary conditions (crosses).

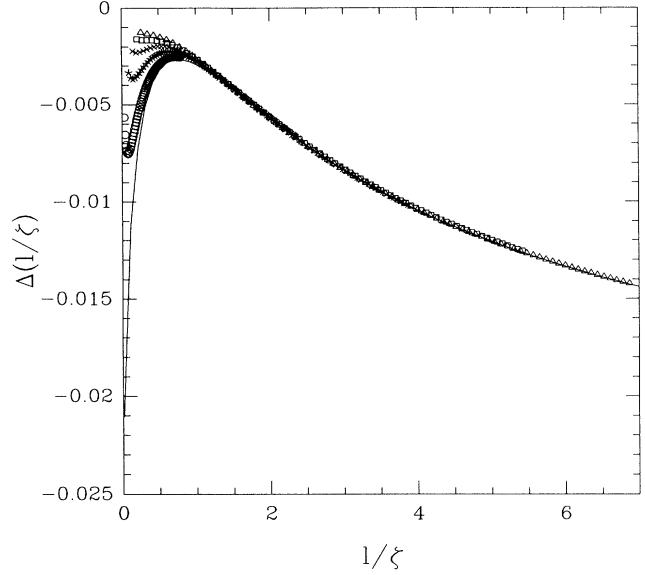


FIG. 3.  $\Delta(l/\xi(h)) = (a^2 K_A / J) [\Delta f(l/\xi(h)) / k_B T] l^2$  vs  $l/\xi(h)$  for discrete layered hexatic films.  $h/J = 1$  (triangles), 0.7 (squares), 0.5 (crosses), 0.3 (stars), and 0.1 (open circles). Here  $\xi(h) = (J/h)d$ , with  $d$  the interlayer spacing,  $l = nd$ , and  $h_0 = h_n = h$ . The data collapse for large  $l/\xi(h)$ , but nonuniversal behavior is observed for small  $l/\xi(h)$ . The solid line is obtained from Eq. (16) after disregarding all nonuniversal contributions.

tributions, and the data collapse does not work well. The minimum value of  $\Delta$  at  $x = 0$  is achieved only in the joint limit of  $n \gg 1$  and  $nh/J \rightarrow 0$ . Note that even for fields as small as  $h/J = 10^{-1}$ , large deviations are observed and the interaction amplitude reaches only to about  $\Delta_I/3$ .

Similar patterns are also obtained in the other two cases. A film adsorbed on a substrate that inhibits fluctuations is modeled by  $h_0 = 0$  on the free surface, and a finite  $h_n$  at the substrate. This is also the case for the surface-stabilized Sm-*I* phase in Fig. 1, where  $h_0 = 0$  at the interface between the Sm-*A* and Sm-*I* phases and  $h_n$  is finite at the Sm-*I*-gas boundary. Figure 4 shows the corresponding data collapse for the interaction energy. Note that the  $x \rightarrow 0$  and  $x \rightarrow \infty$  limits recover, in this case, type-I and type-III values, respectively, and in between there is a film thickness of order  $n^* \simeq \xi(h)$ , where the sign of the interaction energy changes. There are again large corrections to the asymptotic values, and a breakdown of data collapse for small  $x$ . The other situation of interest corresponds to a film deposited over a substrate, but with tilted surface phases. Both surfaces are subjected to hexatic ordering fields, but with  $h_n \gg h_0$ . We can model this situation by choosing a finite  $h_0$ , and infinite  $h_n$ . As indicated in Fig. 5, the  $x \rightarrow 0$  and  $x \rightarrow \infty$  limits reproduce type-III and type-II cases, and there is a similar crossover in between.

Most of the above features can be understood by studying the continuum version of the model. It is straightforward to show that the eigenmodes are obtained from the differential equation

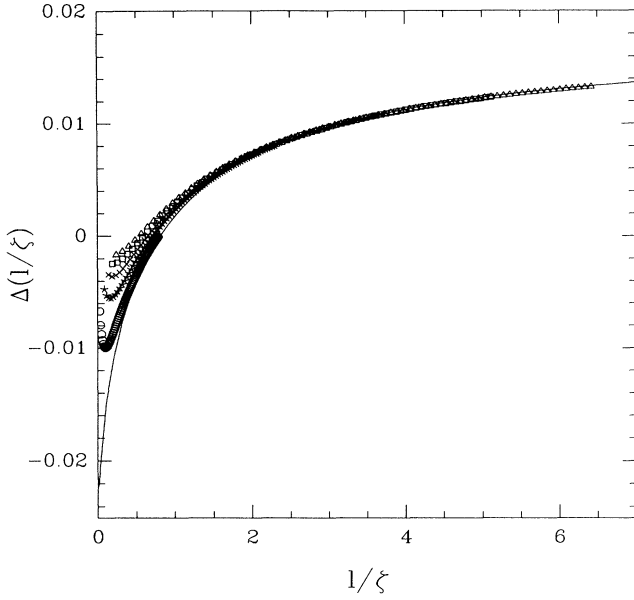


FIG. 4. Same as Fig. 3, with  $h_0=0$ , and  $h=h_n$ .

$$a^2 K_A q^2 \theta(z) - d^2 J \frac{\partial^2 \theta(z)}{\partial z^2} = \lambda \theta(z), \quad (9)$$

where  $d$  is the interlayer distance on the original discrete model, and  $z$  runs from 0 to  $l=nd$ . The surface operators appear in the boundary conditions

$$(a^2 K_A q^2 + h_0) \theta(0) - dJ \frac{\partial \theta(0)}{\partial z} = \lambda \theta(0) \quad (10)$$

and

$$(a^2 K_A q^2 + h_n) \theta(l) + dJ \frac{\partial \theta(l)}{\partial z} = \lambda \theta(l). \quad (11)$$

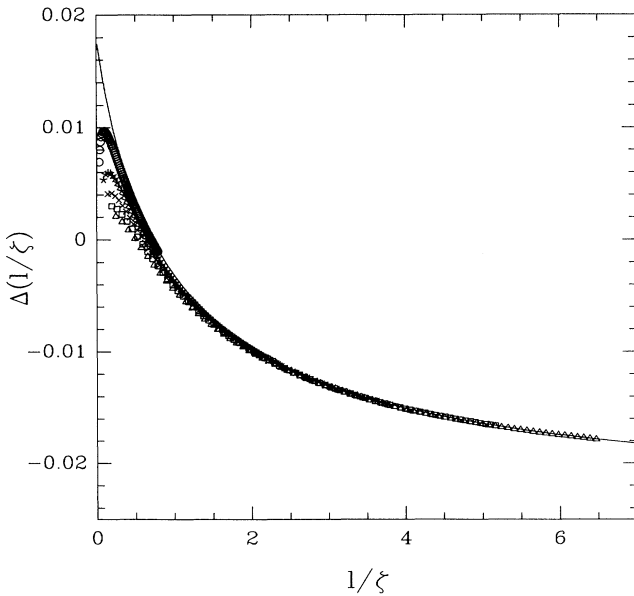


FIG. 5. Same as Fig. 3, with  $h_0=h$ , and  $h_n \rightarrow \infty$ . Note that the universal line has a large but finite derivative as  $1/\xi(h) \rightarrow 0$ .

Equation (10) and (11) continuously interpolate between boundary conditions  $h_i \rightarrow 0$  and  $h_i \rightarrow \infty$ , but with an eigenvalue-dependent mixing parameter. The eigenvalues of Eq. (9) subject to these boundary conditions are

$$\lambda_m = a^2 K_A q^2 + J \omega(m)^2, \quad (12)$$

where  $\omega(m)$  are the solutions of

$$\omega(m) l/d + \arctan(\Phi_0) + \arctan(\Phi_n) = m\pi \quad (m=0, 1, \dots), \quad (13)$$

with

$$\Phi_i = \frac{J \omega(m)^2 - h_i}{J \omega(m)}. \quad (14)$$

The free energy in Eq. (4) is formally divergent in the continuum limit. The divergences are determined by the asymptotic distribution of the eigenvalues  $\lambda_m$  [22], and appear in the volume and surface contributions. They can be removed by the introduction of a suitable cutoff in the integration over  $q$ . The interaction energy can be obtained by standard regularization techniques, such as by the cutoff [1,23], Green's function [24],  $\zeta$  function [25], or the dimensional-regularization [26] methods. Although there is no analytical proof, all these methods are expected to be equivalent [27]. We computed the interaction energy by applying the Poisson summation formula [28], which naturally removes the surface and volume terms [3,6], and replaces the discrete summation over  $m$  by an integral over  $\omega$ . After transforming the integral by parts, the interaction energy is found to be

$$\begin{aligned} \Delta f(l) &= -\frac{k_B T}{2} \int_{2\pi/L}^{2\pi/a} \frac{d^2 q}{(2\pi)^2} \int_{-\infty}^{\infty} d\omega \sum_{n=1}^{\infty} \frac{e^{2\pi i n m(\omega)}}{2\pi i n} \frac{\partial \ln \lambda}{\partial \omega}. \end{aligned} \quad (15)$$

The integration over  $\omega$  can be performed by noting that the integrand has a single pole at  $\omega = i a q \sqrt{K_A/J}$ . After evaluating the pole and some algebra, we finally obtain

$$\begin{aligned} \Delta(x_0, x_n) &\equiv l^2 \left[ \frac{a}{d} \right]^2 \left[ \frac{K_A}{J} \right] \frac{\Delta f(l; x_0, x_n)}{k_B T} \\ &= \frac{1}{4\pi} \int y dy \ln [1 - e^{-2y} G(y, x_0) G(y, x_n)], \end{aligned} \quad (16)$$

where  $x_i = l/\xi(h_i)$ , with  $\xi(h_i) = Jd/h_i$ , and

$$G(y, x_i) = \frac{y - l/\xi(h_i) - y^2 d/l}{y + l/\xi(h_i) + y^2 d/l}. \quad (17)$$

The limits of integration in Eq. (16) are

$$2\pi \frac{l}{d} \frac{a}{L} \sqrt{K_A/J} < y < 2\pi \frac{l}{d} \sqrt{K_A/J}.$$

The main contribution to the integral in Eq. (16) comes from the region of small  $y$ , and hence the upper limit can

be put to infinity for  $2\pi l\sqrt{K_A/J}/d \gg 1$ . As the integrand vanishes at  $y=0$ , we can put the lower limit at zero. The resulting expression has a universal dependence on  $h_0$  and  $h_n$  in the limit of  $x_i \gg d/l$ . This implies the existence of another characteristic thickness,  $\xi' \approx d\sqrt{J}/h$ , below which nonuniversal corrections appear. (Parenthetically, we point out that these two characteristic length scales  $\xi'$  and  $\xi(h) = dJ/h$  are smaller than the thickness  $\xi_h$  that governs the universal nonmonotonic behavior of the mean angle fluctuations [29]). In Fig. 6, we illustrate the full behavior of Eq. (16) as a function of  $l/\xi(h)$  for several values of  $h_0 = h_n = h$ . The agreement with the results obtained in Fig. 3, even in the *nonuniversal* regime, is quite impressive. Disregarding all nonuniversal contributions (terms of order  $y^2$ ), Eq. (16) is an excellent fit to the universal line of the data collapse (the solid lines in Figs. 3–6). The preasymptotic regimes of the universal line have the following analytical forms:

(a) When  $x_0 = x_n = x$ ,

$$\Delta(x) = \begin{cases} -\frac{1}{4\pi} \left[ \frac{\xi(3)}{4} + x \ln x \right] & \text{for } x \ll 1 \\ -\frac{\xi(3)}{16\pi} \left[ 1 - \frac{4}{x} \right] & \text{for } x \gg 1. \end{cases} \quad (18)$$

(b) When  $x_0 = 0, x_n = x$ ,

$$\Delta(x) = \begin{cases} -\frac{1}{4\pi} \left[ \frac{\xi(3)}{4} + \frac{x}{2} \ln x \right] & \text{for } x \ll 1 \\ \frac{3\xi(3)}{64\pi} \left[ 1 - \frac{2}{x} \right] & \text{for } x \gg 1. \end{cases} \quad (19)$$

(c) When  $x_0 \rightarrow \infty, x_n = x$ ,

$$\Delta(x) = \begin{cases} \frac{1}{4\pi} \left[ \frac{3\xi(3)}{16} - x \ln 2 \right] & \text{for } x \ll 1 \\ -\frac{\xi(3)}{16\pi} \left[ 1 - \frac{2}{x} \right] & \text{for } x \gg 1. \end{cases} \quad (20)$$

Note that there are divergent derivatives at  $x=0$  in the cases where a uniform fluctuation mode is present (free surfaces). If one takes into account the finite size of the layers, the derivative at  $x=0$  becomes proportional to  $\ln(L/a)$ , and diverges only in the thermodynamic limit,  $L/a \rightarrow \infty$ . Logarithmic divergences are characteristic of systems with quasi-long-range order [30]. For  $x > 1$ , the corrections to the asymptotic behavior are quite large for the symmetric case, and can be disregarded only for  $x \gg 4$  [ $l \gg 4\xi(h)$ ]. The asymptotic decay,  $f(l) \propto l^{-2}$ , is similar to that of the van der Waals interaction [11]. The fluctuation-induced force between the surfaces of the film is obtained from  $\Delta F = -\partial\Delta f(l)/\partial l$ , which asymptotically has the form  $\Delta F = B_{FIF}/l^3$ . For typical liquid crystals, parameters  $d = 30 \text{ \AA}$ ,  $a = 4 \text{ \AA}$ ,  $K_A/J \approx \frac{1}{2}$ , and  $k_B T = 4 \times 10^{-21} \text{ J}$ , the coefficient  $B_{FIF}$  is approximately  $0.5 \times 10^{-20} \text{ J}$ . This estimate indicates that these forces are comparable to the van der Waals interactions be-

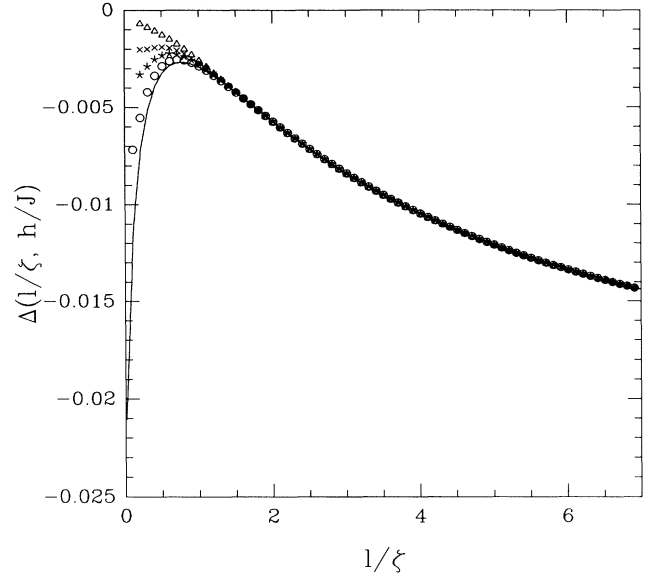


FIG. 6. The amplitude  $\Delta$  as obtained in the continuum limit from Eq. (16). Both universal and nonuniversal behaviors of the original data of the discrete layered model are reproduced. The definitions are the same as in Fig. 3.

tween the surface layers of free-standing liquid crystals, where  $B_{vdW} \approx 10^{-20} \text{ J}$  [31].

The above analysis can be extended to enhanced surface Frank constants, a more appropriate description of the 3(10)OBC compound which undergoes a Sm-*A*–Sm-*B* transition. The interaction energy has the same form as in Eq. (16), except for the absence of nonuniversal corrections. The scaling variable in this case is  $x = l/\xi(K)$ , with  $\xi(K) = dK_A^S/K_A$ ,  $K_A^S$  being the surface Frank constant. (Note that this length is again different from length scales identified in earlier works governing the universal nonmonotonic behavior of the mean angle fluctuations [29], or the bulk transition temperature [17]. Actually it is the same as the distance from the surface for which the angle fluctuation profile has a maximum [29]). The general expression for the interaction energy in the presence of both enhanced surface Frank constants and surface-ordering fields is obtained from Eq. (16) after replacing  $G(y, x_i)$  by

$$G'(y, \xi(h_i), \xi(K_i)) = \frac{y - l/\xi(h_i) - y^2 \xi(K_i)/l}{y + l/\xi(h_i) + y^2 \xi(K_i)/l}. \quad (21)$$

The above equation indicates that in the presence of both types of surface enhancement, it is the surface field that controls the true asymptotic behavior, no matter how weak. The effects of an enhanced Frank constant are felt only for films with a thickness smaller than  $\xi' = d\sqrt{(J/h)(K_A^S/K_A)} = \sqrt{\xi(h)\xi(K)}$ . This observation is easily explained by carrying out a scaling analysis of Eqs. (1) and (2). The homogeneous Hamiltonian is invariant under a rescaling of distances by a factor of  $b$ , and the field  $\theta$  by  $b^{-1/2}$ . Under such rescaling, the surface operators transform as  $K_A^S = b^{-1}K_A^S$  and  $h' = bh$ . The surface field is a *relevant* operator that grows under rescaling and

asymptotically leads to Dirichlet boundary conditions. By contrast, the enhanced Frank constant is an *irrelevant* operator, and only an infinite enhancement can cause such a boundary condition. The two operators have comparable effects at scales of the order of  $\xi'$ .

We now reexamine the experimental findings on layer-by-layer ordering in the light of the above results. As in the case of wetting a repulsive potential,  $U(l)$  is necessary to overcome the chemical potential cost of creating the ordered layer. First note that the interaction induced by the smectic fluctuations (suggested in Ref. [9]) is not appropriate to the experimental geometry of Fig. 1, as smectic fluctuations are present in both phases. (Such an interaction should be quite important for fluid to smectic transitions as it is longer ranged than the van der Waals interaction.) The van der Waals interaction has the right sign, but is proportional to the difference between the polarizabilities of the phases. Since this difference is probably much smaller between two smectic phases than between a smectic phase and the surrounding gas, the magnitude of this interaction should be less than the estimate of  $B_{\text{vdW}} \approx 10^{-20}$  J presented earlier. Thus if the inhomogeneities in the coupling constants can be ignored, the fluctuation-induced forces due to the additional hexatic ordering will be quite important. Such interactions are only repulsive for mixed boundary conditions. As the fluctuations at the hexatic-smectic boundary are free, the surface-enhancement operators must be sufficiently strong to suppress the fluctuations at the hexatic-gas interface. We shall examine the cases of Sm-B and Sm-I ordering separately.

The appropriate surface operator for the Sm-B phase has  $h=0$  and  $K_A^S/K_A > 1$ . (The Sm-A–Sm-B interface will be treated as a free surface.) Heat-capacity measurements show that the peak bulk-transition temperature turns around at thickness of about 20 layers [16]. Although not quite the same, we shall use this length scale as an estimate of  $\xi(K) = dK_A^S/K_A$ . The experimental measurements of Ref. [8] correspond only to the ordering of the first four layers. This is clearly not a sufficient range for the identification of a power-law behavior. Nevertheless, the results are likely to correspond to the regime of  $x = l/\xi(K) \ll 1$ . The ordered region experiences mixed boundary conditions leading to a repulsive interaction favoring further growth of the hexatic phase. However, at longer length scales [of the order of  $\xi(K)$ ], the surface enhancement becomes irrelevant, and the interaction changes sign as in Fig. 5. If correct, this scenario predicts that the Sm-B film may grow continu-

ously only up to a finite thickness as in incomplete wetting phenomena [11]. The fact that only the ordering of the first four layers is experimentally observed may be related to this picture. Further experiments may thus shed light on this point.

Reference [9] identifies the successive appearance of Sm-I order in up to ten layers. The effect of the Sm-I–gas boundary is described by Eq. (2), with both operators present. We have no *a priori* estimate of the magnitude of these enhancement operators, and hence of  $\xi(h)$  and  $\xi(K)$ . Due to the relevance of  $h$ , the interaction is indeed repulsive for thick films, and continuous growth of the film is possible. For films of thickness  $l < \xi(K)$ , the enhanced Frank constant takes over, again leading to a repulsive interaction. The two regimes overlap for  $\xi(h) < \xi(K)$ , and the interaction should be well described by a power law. On the other hand, if  $\xi(K) \ll \xi(h)$ , there is an intermediate regime where the potential is attractive, with a minimum around  $\xi' = \sqrt{\xi(h)\xi(K)}$ . The continuous growth of the Sm-I phase up to ten layers seems to rule out the latter possibility, and suggest  $\xi(h) \lesssim \xi(K)$ . The deviations observed from the  $\frac{1}{3}$  power law could be due to preasymptotic corrections. Better estimates of the ratios  $J/h$ ,  $K_A^S/K_A$ , and  $K_A/J$  are necessary to settle the behavior of the interaction.

In conclusion, we studied the interactions induced by fluctuations of orientational order in layered liquid-crystal films. Finite-surface enhancement operators lead to large corrections in the asymptotic power-law behavior and cause nonmonotonic forces. The results can be summarized in terms of universal functions of the scaled thickness  $l/\xi$ , where  $\xi$  is due to the appropriate surface-enhancement operator. We obtained analytical expressions for the interaction energy in the continuum limit, in excellent agreement with the data obtained by direct numerical integration. The results were further discussed in the context of layer-by-layer surface ordering in the Sm-A–Sm-I transition of 9O.4, and the Sm-A–Sm-B transition of 3(10)OBC compounds.

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