Pseudo-Casimir Structural Force Drives Spinodal Dewetting in Nematic Liquid Crystals

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We analyze theoretically the fluctuation-induced force in thin nematic films subject to competing surface interactions, and we find that the force is attractive at small distances and repulsive otherwise. The results provide a consistent interpretation of a recent study of spinodal dewetting of 5CB on a silicon wafer [F. Vandenbrouck *et al.*, Phys. Rev. Lett. **82**, 2693 (1999)], implying that this experiment can be regarded as the first observation of the pseudo-Casimir effect in liquid crystals.

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Recently, the number of experimental studies of spinodal dewetting—a spontaneous breakup of a liquid film into an array of droplets and dry patches—has grown very steeply. The effect has been observed in a variety of liquids such as liquid metals [1], polymers [2–5], protein solutions [6], and liquid crystals [7,8]. The interest in spinodal dewetting is undoubtedly fueled mainly by its relevance to the thin film technology (lubrication, drying, application of coatings, etc.) and this is why so much attention has been paid to its phenomenology, whereas the precise source of the instability is still largely unclear.

The underlying mechanism itself is transparent: if the force between the substrate/liquid interface and the liquid/air interface becomes less attractive with increasing distance, the capillary waves will destabilize the film [9]. However, the interaction involved is rarely discussed quantitatively although it is known that it comprises the van der Waals force and the structural force. The latter is particularly important in systems with long-range correlations such as liquid crystals because in this case the structural force is also long range. It is no surprise that the only quantitative analysis of the experimental data reported so far deals with spinodal dewetting in a nematic liquid crystal [8], and it explains the effect in terms of a mean-field elastic force. But this tentative interpretation seems to be inadequate and we propose an alternative scenario leading to nontrivial conclusions.

Our model relies on the fact that the structural force in liquid crystals does not consist solely of mean-field elastic force: at small distances, the force induced by director fluctuations is also important [10]. Moreover, in very thin films the fluctuation-induced force is dominant simply because the director field in such systems is uniform [11] so that the mean-field elastic force is absent. In this Letter, we analyze the fluctuation-induced interaction in a thin nematic film with conflicting boundary conditions, and we find that it is attractive at small thicknesses and repulsive otherwise. We show that the observed dewetting behavior [8] can be described consistently by a combination of fluctuation-induced and van der Waals forces, implying that the experiment discussed provides evidence of the pseudo-Casimir effect in nematic liquid crystals. As such, it represents one of the pioneering condensed-matter experimental studies that are intimately related to this interesting phenomenon.

Let us first briefly describe the experiment in question [8]. The sample consisted of a 5CB film spun cast on a silicon wafer bearing a natural 2 nm thick layer of silica. The dewetting was monitored using polarized optical microscopy, and one of the main conclusions of the study is that at room temperature spinodal dewetting occurs in thin films whereas thick ones are stable. The marginal thickness was found to be larger than 17 nm and smaller than 20 nm. Close to the clearing point, the marginal thickness increased and, in the isotropic phase, the film was unstable regardless of its thickness.

The existence of a marginal thickness d^* such that the dewetting occurs only for thicknesses smaller than d^* implies that the disjoining pressure Π (force between interfaces per unit area) must vary nonmonotonically with d: for $d < d^*$ $\partial\Pi/\partial d$ should be positive, and for $d > d^*$ it should be negative [9]. As we will show, both structural and van der Waals forces can exhibit this kind of behavior.

We start with the structural force which is predetermined by the competition between the homeotropic anchoring at the free surface and the planar anchoring at the substrate [8]. In a thick film the director field is distorted, thus minimizing the surface energy at the expense of the elastic energy. But in a thin enough film the elastic energy roughly proportional to d^{-1} exceeds the surface energy gained by satisfying the boundary conditions. In this case the equilibrium configuration is uniform rather than distorted (Fig. 1), the director being dictated by the strongest anchoring [11]. The mean-field free energy of the uniform state is given by the penalty for the violated boundary conditions at the weak interface, which does not depend on d. In other words, in the uniform state there is no mean-field force between the interfaces.

The structural force in the uniform configuration therefore relies entirely on the force induced by director fluctuations, and we analyze it using a model Hamiltonian based on the Frank elastic energy and on the Rapini-Papoular

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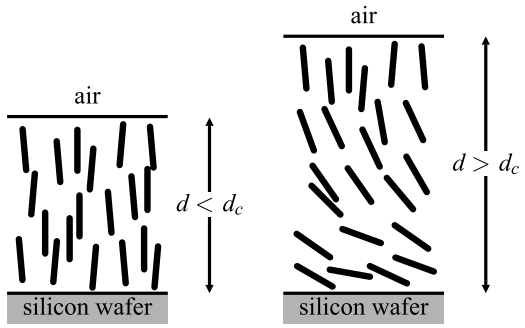

FIG. 1. Nematic film on solid substrate: homeotropic anchoring at the free surface is stronger than planar anchoring at the silicon wafer. If d is smaller than the critical thickness, the director field within the film is uniform rather than distorted.

type anchoring at the two interfaces,

$$H = \frac{1}{2}\left\{\int [K_{11}(\nabla\cdot\mathbf{n})^2 + K_{22}(\mathbf{n}\cdot\nabla\times\mathbf{n})^2 + K_{33}(\mathbf{n}\times\nabla\times\mathbf{n})^2]\,dV + W_P\int(\mathbf{n}\cdot\mathbf{k})^2\,dS_P - W_H\int(\mathbf{n}\cdot\mathbf{k})^2\,dS_H\right\}, \quad (1)$$

where $\mathbf{n} = \mathbf{n}(\mathbf{r})$ is the nematic director field, and K_{11}, K_{22}, and K_{33} are the splay, twist, and bend elastic constants [12]. W_P and W_H stand for the strength of the planar anchoring at the silicon substrate at $z = -d/2$ and the strength of the homeotropic anchoring at the free surface at $z = d/2$, respectively, and $\mathbf{k}$ is the normal to the two surfaces [13]. We assume that the homeotropic anchoring is stronger than the planar so that the mean-field director configuration, $\mathbf{n}_0$, is homeotropic as long as the film thickness d does not exceed the critical value,

$$d_c = \lambda_P - \lambda_H\,, \quad (2)$$

where $\lambda_P = K_{33}/W_P$ and $\lambda_H = K_{33}/W_H$ are the planar and the homeotropic extrapolation lengths [11].

Up to second order, the fluctuating director field is given by $\mathbf{n} = \mathbf{n}_0 + \delta\mathbf{n} \approx [n_x, n_y, 1 - (n_x^2 + n_y^2)/2]$. We Fourier transform n_x and n_y in the xy plane: $n_m(\mathbf{r}) = \sum_{\vec{q}}\tilde{n}_m(\vec{q},z)\exp[i(q_x x + q_y y)]$, where $m = x, y$, $\vec{q} = q_x\mathbf{i} + q_y\mathbf{j}$, and $\mathbf{i}$ and $\mathbf{j}$ are the in-plane members of the Cartesian orthonormal triad $(\mathbf{i},\mathbf{j},\mathbf{k})$. After diagonalizing the Hamiltonian by decomposing $\tilde{n}_x$ and $\tilde{n}_y$ into splay-bend and twist-bend modes $\tilde{n}_1 \parallel \vec{q}$ and $\tilde{n}_2 \perp \vec{q}$ [13], it can be integrated over x and y to yield

$$H = \frac{K_{33}S}{2}\sum_{\vec{q}}\sum_{m=1,2}\left[\int_{-d/2}^{d/2}\left(\frac{K_{mm}}{K_{33}}q^2\tilde{n}_m^2 + \tilde{n}_m'^2\right)dz - \lambda_P^{-1}\tilde{n}_{m,-}^2 + \lambda_H^{-1}\tilde{n}_{m,+}^2\right], \quad (3)$$

where S is the area of the film and $\tilde{n}_{m,\pm} = \tilde{n}_m(z = \pm d/2)$.

The free energy of fluctuations can be calculated in several ways. The approach we use is based on the formal analogy between the partition function of a planar statistical-mechanical system and the propagator of a quantum-mechanical system [14]. The details of the analysis will be published elsewhere; the final result is

$$F = \frac{kTS}{4\pi}\left(\frac{K_{33}}{K_{11}} + \frac{K_{33}}{K_{22}}\right)\int_0^\infty \times \ln\left(\frac{p^2 - \lambda_H^{-1}\lambda_P^{-1}}{p(\lambda_H^{-1} - \lambda_P^{-1})}\sinh(pd) + \cosh(pd)\right)p\,dp\,, \quad (4)$$

and the disjoining pressure $\Pi = -S^{-1}(\partial F/\partial d)_{S,V}$ reads

$$\Pi = \frac{kT}{2\pi}\left(\frac{K_{33}}{K_{11}} + \frac{K_{33}}{K_{22}}\right)\int_0^\infty \times \frac{p^2\,dp}{\frac{p-\lambda_P^{-1}}{p+\lambda_P^{-1}}\frac{p+\lambda_H^{-1}}{p-\lambda_H^{-1}}\exp(2pd) - 1}\,. \quad (5)$$

This integral cannot be computed analytically, and we present numerical results in Fig. 2. We scale the film thickness by the critical thickness d_c, which also determines the natural unit of the disjoining pressure, $\tilde{\Pi} = \frac{kT}{2}(\frac{K_{33}}{K_{11}} + \frac{K_{33}}{K_{22}})d_c^{-3}$, and leaves $\Lambda = \lambda_H/\lambda_P$ the only free parameter. A rather general feature of the disjoining pressure in the film—almost independent of the ratio of the extrapolation lengths—is its mixed character: at small distances Π is attractive whereas at large distances it becomes repulsive. The crossover from attraction to repulsion increases with Λ.

As surprising as it may seem at first, this behavior is perfectly reasonable. If the thickness of the film is smaller than both extrapolation lengths, both anchorings are effectively weak and the director field is free to fluctuate at the two surfaces. At small distances, the qualitative difference between the homeotropic anchoring, which damps the fluctuations, and the planar anchoring, which stimulates

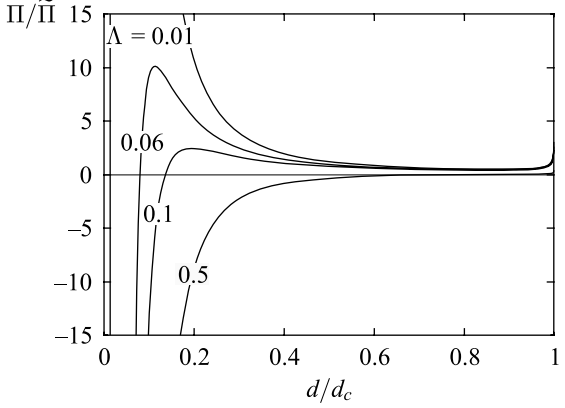

FIG. 2. Fluctuation-induced disjoining pressure vs reduced distance is attractive at small d/d_c's and repulsive at large d/d_c's. The crossover distance depends on $\Lambda = \lambda_H/\lambda_P$.

them, is not really important because both damping and stimulation are weak. This means that the system is qualitatively close to Neumann-Neumann boundary conditions, and the fluctuation-induced interaction between like walls is known to be attractive [10]. Indeed it can be shown that, for $d/d_c \to 0$, Π reduces to $-\frac{\zeta(3)}{4\pi}\tilde{\Pi}(d/d_c)^{-3}$, which coincides with the well-known result [10].

At somewhat larger distances, homeotropic anchoring becomes strong ($\lambda_H < d$) which suppresses the fluctuations at the free surface. Meanwhile, at the silicon substrate the fluctuations remain stimulated by the destabilizing action of planar anchoring. In this case, the boundary conditions experienced by the film are essentially mixed: quasi-Dirichlet at the free surface and quasi-Neumann at the substrate. This implies that the fluctuation-induced interaction is repulsive, and for Λ's small enough (so that the crossover from attraction to repulsion takes place at $d/d_c \ll 1$) and d/d_c's not too close to 1 (so that the pretransitional effects are not very pronounced) we recover the fluctuation-induced force in a strictly Dirichlet-Neumann geometry, $\frac{3\zeta(3)}{16\pi}\tilde{\Pi}(d/d_c)^{-3}$ [10].

Another interesting attribute of the structural force is its increase at the transition from a uniform to a distorted state. But this limiting behavior is really not crucial for the dewetting, and we will postpone a detailed and thorough discussion of this issue to a forthcoming study.

The nonmonotonicity of the structural force could itself explain the observed dewetting behavior. However, the van der Waals force must also be taken into account, and in case of a composite substrate it can be characterized by nontrivial dependence on the film thickness. The oxidized silicon wafer used in the study in question [8] is a composite substrate and the dielectric permittivities of silicon oxide and silicon are quite different. It is expected that for film thicknesses smaller than the thickness of the oxide layer—2 nm—the van der Waals force will be dictated by the dielectric properties of the oxide, whereas for films thicker than the oxide layer the force will depend primarily on the permittivity of the underlying silicon.

We have calculated the van der Waals interaction within the full Lifshitz theory [15,16]. The inputs of such an analysis are the dielectric permittivities of the media, which have been described by single-Lorentz-oscillator models. The parameters used are shown in Table I, and the absorption frequency of all materials has been estimated by 3×10^{15} s^{-1} [16]. As shown in Fig. 3, the van der Waals force is attractive at distances up to 2.3 nm [17] and repulsive at larger d's. This is in agreement with the rule-of-thumb estimates of the force [16] in 5CB on pure silica, which is attractive, and in 5CB on pure silicon, which is repulsive and not attractive as assumed in the original analysis of the experiment [8]. In absence of the structural force, dewetting would have occurred for d's up to 3.2 nm where the van der Waals repulsion is maximal, which is far smaller than the observed marginal thickness 17–20 nm. The structural force is obviously essential to the phenomenon.

TABLE I. Static relative permittivities and refractive indices of the media.

	Silicon	Silica	5CB	Air
ϵ	12	14	17	1
n	3.5	1.5	1.6	1.0

The structural disjoining pressure depends on the extrapolation lengths λ_P and λ_H, which must satisfy two conditions to ensure that the homeotropic state persists at thicknesses larger than d^*. Firstly, the planar anchoring is assumed to be weaker than the homeotropic anchoring, $\lambda_P > \lambda_H$, and, secondly, the difference between the extrapolation lengths should not be too small, say 30 nm at least. However, not all pairs of λ_P and λ_H that give the right value of d^* are equally acceptable, because anchoring at the free surface is known to be rather strong. The largest value of the homeotropic anchoring strength that explains the reported marginal thickness is $W_H = 56\ \mu\text{J/m}^2$ ($\lambda_H = 165$ nm) which agrees well with earlier measurements [18,19]. The corresponding planar anchoring is somewhat weaker: $W_P = 46\ \mu\text{J/m}^2$ ($\lambda_P = 200$ nm). Unfortunately, W_P of 5CB on an oxidized silicon wafer has not been determined independently, and in absence of a reference we note that our value is consistent with some [20] though not all estimates [21] of the anchoring strength of 5CB on obliquely evaporated silica.

To establish a closer contact with the experiment, we have also recalculated the growth rate and the wavelength of the instability [9]. We find that for $\lambda_P = 200$ nm and $\lambda_H = 165$ nm, the characteristic dewetting time of a 17 nm thick film is about 220 s and the characteristic length scale of the pattern is about 36 μm. These figures are perfectly consistent with the observed behavior [8].

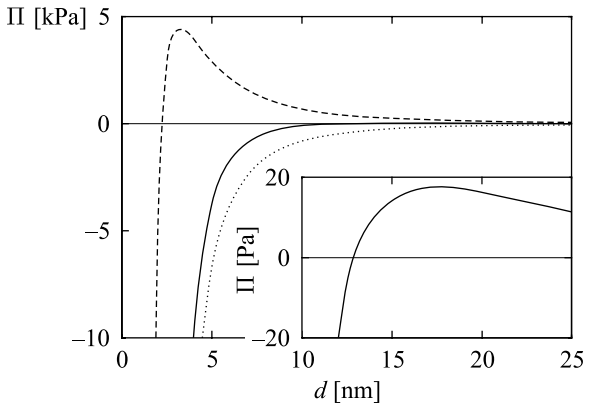

FIG. 3. Disjoining pressure in 5CB film on oxidized silicon wafer: van der Waals force (dashed line), structural force ($\lambda_P = 200$ nm, $\lambda_H = 165$ nm; dotted line), and their sum (solid line). In the inset, the behavior of the total force in the vicinity of the marginal thickness is shown in detail. Spinodal dewetting occurs at d's smaller than 17.6 nm.

In the experiment, the role of temperature in the dewetting process was also studied, and about 1 K below the clearing point spinodal dewetting was observed in a 42.8 nm thick film. This indicates that the marginal thickness increases on heating. Without an accurate estimate of d^* as a function of temperature, we are unable to address this point quantitatively. But it is clear that the van der Waals force cannot be responsible for the variation of d^* because the dielectric permittivities of the media do not change much with temperature. The effect could be attributed to the pretransitional increase of the extrapolation lengths often observed in liquid crystals [21,22] or to the attraction induced by fluctuations of the degree of orientational order, which becomes important in the vicinity of the clearing point [23]. Alternatively, the temperature variation could be caused by the short-range mean-field interaction due to the (partial) surface melting at the wafer/5CB interface, which accompanies the severe violation of the boundary condition.

In conclusion, we have reanalyzed the spinodal dewetting observed in nematic 5CB films on oxidized silicon wafers [8], and we have demonstrated that the phenomenon is driven by the attractive fluctuation-induced structural force. Although more detailed experimental as well as theoretical studies of dewetting are welcome if not necessary, we believe that this experiment can be considered the first indirect observation of the Casimir force in liquid crystals. Along with recently reported evidence of the phenomenon in binary fluid mixtures [24] and liquid helium [25], the spinodal dewetting experiment represents a long-sought for support of theoretical studies of the thermal Casimir effect in condensed matter.

In fact, spinodal dewetting may be an ideal probe of the fluctuation-induced force because the free surface of a spun cast film is really parallel to the substrate, which facilitates the analysis of the data, and because the dewetting process itself is a kind of pressure gauge. In principle, the phenomenon could be used to map the disjoining pressure in regions where $\partial\Pi/\partial d > 0$ by continuously varying the initial thickness of the film and measuring the growth rate and the periodicity of the instability. To make the experiment more sensitive to the structural force, one could even partly eliminate the van der Waals force by using a substrate such that its refractive index matches the refractive index of the liquid crystal.

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