Wetting-Driven Casimir Force in Nematic Liquid Crystals

P. Ziherl, R. Podgornik, and S. Žumer

Department of Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia
and J. Stefan Institute, University of Ljubljana, Jamova 39, 1000 Ljubljana, Slovenia
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We study the fluctuation-mediated structural interaction between identical order-inducing substrates immersed in the isotropic phase of a liquid crystal. We show that because of the presence of substrate-stabilized nematic wetting layers, the force due to thermal fluctuations of nematic order is repulsive rather than attractive, which is in contrast with the standard pseudo-Casimir force between like walls. Contrary to expectations, this interaction is characterized by the same range as the mean-field attraction. [S0031-9007(99)08386-6]

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Nowadays, it is well established that the Casimir effect—the interaction between the walls of a container induced by either quantum or thermal fluctuations within the confined medium [1]—is ubiquitous. The phenomenon is especially important in systems with long-range correlations, where the force is also long range [2]. In soft matter physics, which covers easily deformable classical systems, long-range correlations occur in media with broken continuous symmetry and in critical systems.

Liquid crystals, which are characterized by orientational and in some phases also partial positional order of constituents, fall into both categories. The broken-symmetry long-range interaction results from fluctuations of the average molecular orientation, position of smectic layers, etc. [3,4]. Fluctuations of the degree of orientational order, amplitude of mass density wave, etc., however, induce a short-range force whose correlation length increases in the vicinity of the corresponding phase transition [5]. This in turn gives rise to an increase of the total Casimir interaction which is very prominent if the transition is continuous—and some of them are [6].

But even discontinuous phase transitions in liquid crystals are usually associated with rather small latent heat, and they can be made continuous by confining the sample by a substrate that promotes nucleation of one of the phases involved. The mechanism of such wetting-assisted phase transitions is quite different from the bulk one and is characterized by a phase boundary between the substrate-stabilized wetting layer and the bulk, which advances from the wall as the transition temperature is approached [7]. The corresponding soft mode represents fluctuations of position of the phase boundary [8].

In this Letter we analyze the wetting-driven pretransitional behavior of the fluctuation-induced force in liquid crystals, and we find that the force is repulsive and not attractive as in nonwetting geometries discussed earlier [5]. Its range is identical to the range of the mean-field attraction caused by the inhomogeneity of the ordering, which is also unusual: in nonwetting geometries the Casimir force decays more rapidly than the mean-field force. We also show that the phase boundary acts as an internal structural wall attracted to the nearby substrate.

The model system consists of isotropic phase bounded by parallel plates that induce homeotropic uniaxial nematic order, and the resulting paranematic phase is characterized by a nematic wetting layer and an isotropic core [7]. In this case, the natural representation of the orientational order parameter Q—an irreducible second rank tensor—is given by the tensorial base $\mathsf{T}_0 = (3\mathbf{n}\otimes\mathbf{n} - \mathsf{I})/\sqrt{6}$, $\mathsf{T}_1 = (\mathbf{e}_1\otimes\mathbf{e}_1 - \mathbf{e}_2\otimes\mathbf{e}_2)/\sqrt{2}$, $\mathsf{T}_{-1} = (\mathbf{e}_1\otimes\mathbf{e}_2 + \mathbf{e}_2\otimes\mathbf{e}_1)/\sqrt{2}$, $\mathsf{T}_2 = (\mathbf{e}_1\otimes\mathbf{n} + \mathbf{n}\otimes\mathbf{e}_1)/\sqrt{2}$, and $\mathsf{T}_{-2} = (\mathbf{e}_2\otimes\mathbf{n} + \mathbf{n}\otimes\mathbf{e}_2)/\sqrt{2}$, where $\mathbf{n}$ (the director), $\mathbf{e}_1$, and $\mathbf{e}_2$ form an orthonormal triad identified by $\mathbf{e}_z, \mathbf{e}_x, \mathbf{e}_y$, and I is the unit tensor [9]. The component of Q along T_0 is equal to the sum of the mean-field and fluctuating parts of the degree of order, and its projections onto $\mathsf{T}_{\pm1}$ and $\mathsf{T}_{\pm2}$ correspond to biaxial and director fluctuations.

By scaling the order parameter by the degree of order in the bulk nematic phase at the clearing point, the one-elastic-constant approximation of the Landau–de Gennes free energy density—the standard phenomenological model of the transition—can be cast into a concise form

$$f = \frac{L}{2}\{\xi_0^{-2}[\theta\,\mathrm{tr}\,\mathsf{Q}^2 - 2\sqrt{6}\,\mathrm{tr}\,\mathsf{Q}^3 + (\mathrm{tr}\,\mathsf{Q}^2)^2] + \nabla\mathsf{Q}\vdots\nabla\mathsf{Q}\}, \quad (1)$$

where L is the elastic constant, θ is the reduced temperature (equal to 0 at the supercooling limit and to 1 at the phase transition), and $\xi_0 \approx 10$ nm is the bare correlation length [8]. To make the model amenable to further analysis, the double-well Landau potential represented by the homogeneous part of f is replaced by a pair of parabolas corresponding to harmonic expansions of the free energy density at the two minima [10]. Within this approximation, the paranematic phase is regarded as being divided into a nematic and an isotropic region, each characterized by a set of bulk correlation lengths. In the nematic region, the correlation lengths of fluctuations of the degree of order, biaxiality, and director field are given

by

$$(\xi_{N,0}/\xi_0)^{-2} = \tfrac{9}{4}(1 + \sqrt{1 - 8\theta/9})\sqrt{1 - 8\theta/9}\,,$$
$$(\xi_{N,\pm1}/\xi_0)^{-2} = \tfrac{27}{4}(1 + \sqrt{1 - 8\theta/9})\,, \qquad (2)$$
$$\text{and} \quad (\xi_{N,\pm2}/\xi_0)^{-2} = 0\,,$$

where the subscripts refer to the tensorial base. In the isotropic region all five modes are degenerate: $(\xi_I/\xi_0)^{-2} = \theta$.

The equilibrium ordering consists of a mean-field part and of thermally excited fluctuations around it, $\mathsf{Q} = \mathsf{A} + \mathsf{B}$. The mean-field part, A, corresponds to the minimum of the free energy and describes the spatial variation of the nematic order within the sample consisting of an ordered wetting layer and a disordered core. A is determined by a single nontrivial scalar variable—the degree of order—whereas the other four coefficients in $\mathsf{A}(\mathbf{r}) = \sum_{i=-2}^{2} a_i(\mathbf{r})\mathsf{T}_i$ all vanish. Because of in-plane translational invariance of the system, a_0 depends on the transverse coordinate only, and as the walls located at $z = 0$ and $z = d$ are identical, it is symmetric and needs to be calculated in only half of the slab. The parabolic approximation of the homogeneous part of f thus reads

$$f_{h,PA} = \frac{L}{2}\{[\Phi + \xi_{N,0}^{-2}(a_0 - \tilde{a}_0)^2]H(l - z) + \xi_I^{-2}a_0^2 H(z - l)\}\,, \qquad (3)$$

where $L\Phi/2 = -(27L/256\xi_0^2)(1 - 4\theta/3 + \sqrt{1 - 8\theta/9})(1 + \sqrt{1 - 8\theta/9})^2$ and $\tilde{a}_0 = \frac{3}{4}(1 + \sqrt{1 - 8\theta/9})$ are the free energy density and the degree of order in the bulk nematic phase, and $H(z)$ is the Heaviside function. The position of the phase boundary, l, is determined by the condition that the equilibrium profile of a_0 be smooth.

The thermal fluctuations of the ordering, $\mathsf{B}(\mathbf{r}) = \sum_{i=-2}^{2} b_i(\mathbf{r})\mathsf{T}_i$, are governed by their Hamiltonian, which is diagonal in the tensorial base used here. Within the parabolic approximation, the homogeneous part of the density of the Hamiltonian for $0 < z < d/2$ is given by

$$h_{h,PA} = \frac{L}{2}\sum_{i=-2}^{2}[\xi_{N,i}^{-2}H(l - z) + \xi_I^{-2}H(z - l) + \Upsilon_i\delta(z - l)]b_i^2, \qquad (4)$$

$\Upsilon_i = \{\xi_{N,0}^{-2}[\tilde{a}_0 - a_0(l)] + \xi_I^{-2}a_0(l)\}[(da_0/dz)(l)]^{-1}\delta_{i0}$ being the discontinuity of the derivative of the scalar fluctuating field b_i at the phase boundary, which is, as implied by the Kronecker delta, nonzero only in the case of fluctuations of the degree of order.

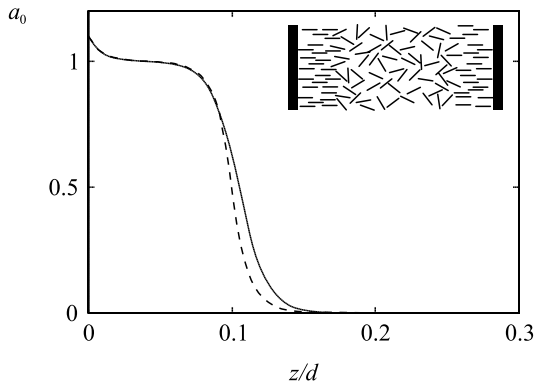

FIG. 1. Steplike mean-field profiles of the paranematic phase calculated within the full Landau–de Gennes expansion (solid line) and its parabolic approximation (dashed line). The substrate-prescribed degree of order equals 1.1 in reduced units; $\theta = 1 + 10^{-5}$, $d/\xi_0 = 100$. Inset: A schematic representation of the paranematic phase characterized by ordered wetting layers and a disordered core.

Let us compare the predictions of the Landau–de Gennes expansion and its parabolic approximation. As illustrated in Fig. 1, the agreement between the mean-field profiles of the ordering is very good in the whole range of applicability of the approximation (which is bounded by the clearing point, $\theta_{NI} = 1$, and the superheating limit, $\theta^{**} = 9/8$). Apart from the discontinuity of the derivative of b_0 at the phase boundary, the approximation also gives a fair description of the normal modes. Since the wetting-assisted critical behavior of the Casimir force is expected to be controlled by the slow modes [8], the quality of the approximation can be quantified by their relaxation rates. In the case of the strong-anchoring model of the surface interaction used here, the two slow modes—soft fluctuations of the position of phase boundary and director fluctuations within the wetting layer—are underestimated by $\approx 10\%$, which is quite satisfactory.

Having established the appropriateness of the parabolic approximation, we can calculate the interaction free energy of the fluctuations. With a piecewise homogeneous Hamiltonian, the partition function is reduced to a Gaussian functional integral, which can be evaluated by any of the standard methods. We use the Green function approach, based on the local formulation of the partition function and frequently encountered in the theory of van der Waals forces [11,12]. In the strong anchoring limit, the interaction free energy can be written as a sum over the five fluctuating degrees of freedom,

$$F_C = \frac{kTS}{4\pi}\sum_{i=-2}^{2}\int_0^\infty q\,dq\left\{\ln\left[1 - \Delta_{+,i}\exp\left(-\frac{2l}{\Xi_{N,i}}\right)\right]^2 + \ln\left[1 - D_i^2\exp\left(-\frac{2(d - 2l)}{\Xi_I}\right)\right]\right\}, \qquad (5)$$

where S is the area of each substrate, q is the in-plane wave vector of fluctuations, $\Xi_{N,i}^{-2}$ and Ξ_I^{-2} stand for $\xi_{N,i}^{-2} + q^2$ and $\xi_I^{-2} + q^2$, respectively, and $\Delta_{\pm,i} = \frac{U_i \pm V_i}{1 \pm V_i}$ and $D_i = \frac{1 - V_i}{1 + V_i}\frac{\Delta_{-,i} + \exp(-2l/\Xi_{N,i})}{1 - \Delta_{+,i}\exp(-2l/\Xi_{N,i})}$, where $U_i = \frac{\Xi_I^{-1} - \Xi_{N,i}^{-1}}{\Xi_I^{-1} + \Xi_{N,i}^{-1}}$ and $V_i = \frac{\Upsilon_i}{\Xi_I^{-1} + \Xi_{N,i}^{-1}}$.

Note that all information on the mean-field profile of the ordering is contained in l, the thickness of the wetting layer, and in Υ_i, the discontinuity of the derivative of the normal modes at the phase boundary.

According to its structure, the first term in Eq. (5) corresponds to the interaction between the wall and the phase boundary, and the second one represents the interaction between the two phase boundaries. The former is dominant for two reasons: (i) the distance between the wall and the phase boundary, l, is usually far smaller than the distance between the phase boundaries, $d - 2l$, and (ii) the nematic wetting layer is characterized by long-range correlations and long-range fluctuation-induced force, whereas correlations in the isotropic core are short ranged and so is the fluctuation-induced force [5].

There are three types of contributions to the interaction between the wall and the phase boundary, and they differ both in sign and in range. Let us first discuss the interaction induced by fluctuations of the degree of order, which are characterized by finite correlation lengths in both nematic and isotropic phases. Υ_0 is finite and negative, and $\Delta_{+,0}$ also turns out to be negative in the whole range of applicability of the parabolic approximation. This implies that the fluctuations of the degree of order give rise to a repulsion between the wall and the phase boundary, which can be estimated by

$$\frac{kTS}{4\pi\xi_{N,0}l}\,\frac{\xi_{N,0}^{-1} - \xi_I^{-1} - \Upsilon_0}{\xi_{N,0}^{-1} + \xi_I^{-1} + \Upsilon_0}\exp\left(-\frac{2l}{\xi_{N,0}}\right) \qquad (6)$$

and is short ranged. The sign of interaction can be understood by recognizing that the fluctuation-induced force between two objects that both impose either Dirichlet or Neumann boundary conditions is attractive, whereas in the case of Dirichlet boundary conditions at one object and Neumann at the other it is repulsive [3,4]. In the strong anchoring limit, fluctuations of the degree of order must vanish at the wall—a Dirichlet boundary condition. On the other hand, on crossing the phase boundary the derivative of the fluctuations must change discontinuously, which is qualitatively closer to a Neumann than to a Dirichlet condition; after all, the wetting-specific soft mode is localized at the phase boundary [8] so that the fluctuations are largest there. Therefore, the fluctuations of the degree of order within the wetting layer experience mixed boundary conditions, and that is why the resulting interaction is repulsive.

A similar argument applies to the interaction induced by biaxial fluctuations. Since $\xi_{N,\pm1} \ll \xi_I$, the lowest normal modes are restricted to the isotropic core: in the nematic wetting layer, they decay exponentially with the distance from the phase boundary. This means that within the wetting layer, the amplitude of biaxial fluctuations is largest at the phase boundary [8], so that the effect of the boundary condition that the fluctuations be smooth at $z = l$ is quite different from the strong anchoring imposed by the wall. The resulting repulsive interaction is approximately given by

$$\frac{kTS}{2\pi\xi_{N,\pm2}l}\,\frac{\xi_{N,\pm2}^{-1} - \xi_I^{-1}}{\xi_{N,\pm2}^{-1} + \xi_I^{-1}}\exp\left(-\frac{2l}{\xi_{N,\pm2}}\right) \qquad (7)$$

and is rather weak, because the correlation length of biaxial modes in the nematic phase is very short.

On the other hand, the correlation length of director fluctuations in the nematic phase is infinite, and the leading term of interaction induced by the two modes reads

$$-\frac{kTS\zeta(3)}{4\pi l^2}\,, \qquad (8)$$

where ζ is the Riemann zeta function. This long-range interaction is attractive, which can again be interpreted in terms of (dis)similarity of boundary conditions. In the isotropic phase, director fluctuations are very hard compared to the nematic phase, and the lowest normal modes are actually confined to the nematic layer and practically do not penetrate the isotropic core [8]. Thus the effective boundary condition at the phase boundary is very similar to strong anchoring at the solid substrate, and the force mediated by director fluctuations is attractive.

The force between the wall and the phase boundary, which is dominated by long-range director modes' attraction, is not directly measurable because the thickness of the wetting layer is not a free parameter. Its contribution to the total wall-to-wall force is determined by the functional dependence of l on sample thickness and reads

$$\mathcal{F}_C \approx -\frac{kTS\zeta(3)}{2\pi l^3}\,\frac{\partial l}{\partial d}\,. \qquad (9)$$

Now l is a decreasing function of d, because the nematic order in each wetting layer is stabilized both by nearby and distant walls, and the larger the distance between them, the thinner the wetting layers. This reverses the sign of interaction: attraction between the wall and the phase boundary results in repulsion between the walls. In the mean-field theory, $\partial l/\partial d \approx -\text{const} \times \exp(-d/\xi_I)$ for large d's [10], which means that the fluctuation-induced force is short ranged and characterized by the correlation length ξ_I. Let us stress that the subdominant attractive force caused by the interaction between the phase boundaries falls off twice as fast, i.e., as $\exp(-2d/\xi_I)$.

All in all, the pseudo-Casimir force in the paranematic phase is dominated by the repulsion originating in the long-range interaction between the substrate and the phase boundary. To establish its relevance for the total structural force it should be compared to the mean-field interaction resulting from the inhomogeneity of the ordering itself, which is attractive and decays asymptotically as $\exp(-d/\xi_I)$ [13]. This brings us to an important conclusion: the ranges of fluctuation-induced and mean-field forces in the paranematic phase are identical, which is quite unique. Their relative magnitude is primarily determined

by the ratio of their energy scales, $kT/S_{NI}^2 L\xi_0$, where S_{NI} is the unscaled value of the degree of order in the bulk nematic phase at the nematic-isotropic transition. In typical materials such as 5CB, this ratio is close to 1, so that in principle the two forces are comparable.

This rough estimate is confirmed by numerical analysis (Fig. 2). The fluctuation-induced force is indeed repulsive, and its magnitude typically ranges from 15% to 20% of the mean-field attraction. However, in the vicinity of the metastability limit of the paranematic phase—below which the system can exist only in the nematic state—the pseudo-Casimir force becomes attractive and even diverges at the very limit. It turns out that the crossover and the divergence are due to the attraction between the phase boundaries, which is not surprising: close to the metastability limit the wetting layers no longer occupy a small part of the total volume and the distance between the phase boundaries is comparable to the distance between the wall and the phase boundary.

How does the relative magnitude of pseudo-Casimir and mean-field force behave beyond the superheating limit $\theta^{**} = 9/8$, where the parabolic approximation is not applicable? On one hand, $\mathcal{F}_C/\mathcal{F}_{\mathrm{MF}}$ should increase on heating, because the phase boundary moves closer to the wall. But for $\theta \gg \theta_{NI} = 1$ the current model of the surface coupling is no longer relevant: the ordering power of real substrates is finite, so that the degree of order at the wall decreases with temperature. This suppresses both wetting-specific Casimir force and mean-field force, and far above the transition the total structural interaction reduces to the direct wall-to-wall Casimir attraction.

In conclusion, just above the clearing point the Casimir interaction between order-inducing substrates immersed into the isotropic phase is dominated by the repulsion resulting from the interaction between the wall and the phase boundary which separates the nematic wetting layer from the isotropic bulk. The wetting-driven fluctuation-induced repulsion is short ranged with the screening length identical to the range of the mean-field attraction, and the ratio of magnitudes of the fluctuation-induced and mean-field forces is typically 0.15–0.2.

The effect must be observable. We have shown that in wetting geometry, the fluctuation-induced force represents a considerable part of the total structural force, and structural force in liquid crystals has already been studied by the surface force apparatus [14]. The error of the reported measurements is well below 10%, so that the setup is sensitive enough to detect the Casimir force provided that the temperature resolution of the experiment is ~10 mK. This level of thermal stability is achievable [14], and our results can readily be put to the test.

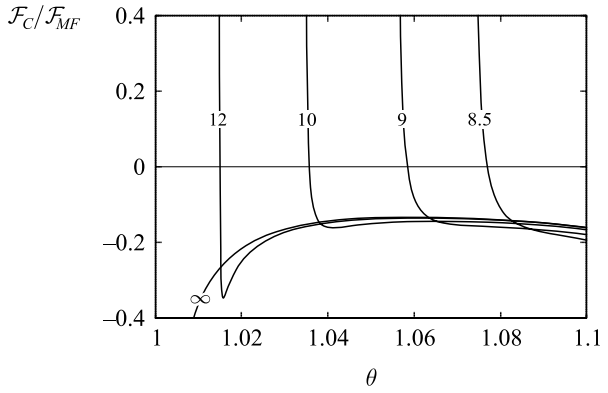

FIG. 2. Ratio of the fluctuation-induced and the mean-field forces as a function of temperature for $d/\xi_0 = 8.5, 9, 10, 12$, and ∞. The relative magnitude of the Casimir interaction typically ranges between -0.15 and -0.2 except in the vicinity of the metastability limit of the paranematic phase, where it becomes positive and eventually diverges at the very limit.

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