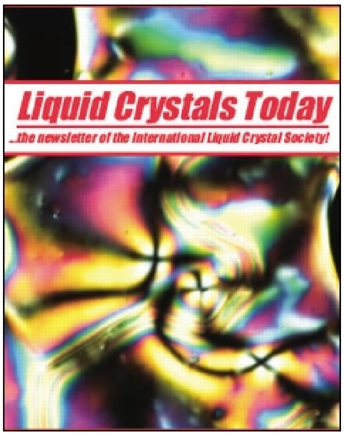

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P. Ziherl

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Fluctuation-induced forces in liquid crystals: stability of thin nematic films and fine nematic colloidal dispersions

P. ZIHERL

Department of Physics, University of Ljubljana, Slovenia and J. Stefan Institute, Slovenia

In traditional liquid-crystalline systems such as the now-ubiquitous twisted nematic cells, the interaction that is induced between the substrates by the liquid crystal is virtually irrelevant because the supporting frame is both very rigid and very heavy compared to the liquid crystal. The frame does not respond to pressure within the cell, and that is why the force mediated by the liquid crystal is usually neglected. But in the past decade, several liquid-crystalline composites with a less sturdy chassis have been introduced or identified. Examples include filled aerogels, liquid crystals stabilized with a polymer network, colloids dispersed in a liquid crystal, as well as a number of structures *in vivo*. The limited mechanical rigidity of these materials is much more susceptible to structural forces. In some cases, e.g., in liquid-crystal-colloid composites characterized by liquid-crystalline droplets encapsulated in a colloidal bubble-like structure [1], they could even be responsible for the self-assembly of the system. Another system where these forces are crucial are thin liquid-crystalline films: the structural interaction—sometimes called the disjoining pressure—can be blamed for their wetting properties.

The importance of a detailed insight into the behaviour of the structural force in the self-organizing systems of all kinds can hardly be overemphasized. In the era of nano-technology, the typical size of the building blocks of the various composite materials has decreased considerably, and thus it is necessary to understand the behaviour of the force even at the smallest separations, down to the nanometer scale. At such small separations, the structural interaction may include some less intuitive effects.

The most common notion of the structural force† in liquid crystals is linked to the existence of a certain director structure, such as the bent director field in a hybrid nematic cell (figure 1). If the director structure changes with the separation, there will be some inter-

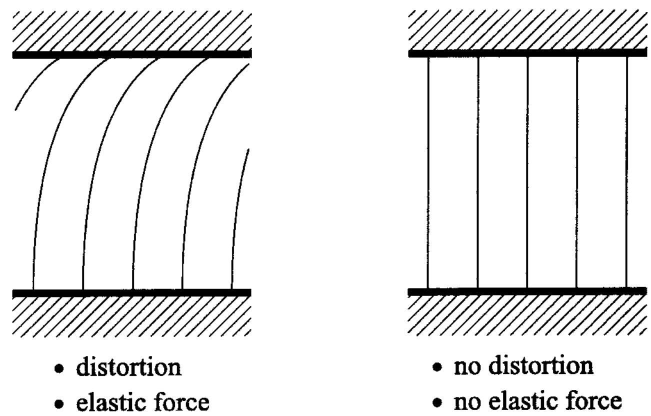

Figure 1. A distorted director profile gives rise to an elastic mean-field repulsion (left). In a uniform director field, the elastic force is absent (right) but the fluctuation-induced force is still there.

action between the confining surfaces. This is the mean-field elastic contribution which is dominant at large distances. However, it may happen that the mean-field structure does not depend on separation. Think of the usual symmetric nematic cell with homeotropic anchoring: the director will be homeotropic regardless of thickness. In this case, there will be no elastic force and one is tempted to conclude that the structural interaction will be absent—but that is incorrect.

The structure of emptiness

The first person to realize that the structural forces are present even in systems with no obvious structure was the Dutch physicist H. G. B. Casimir. He predicted that the walls of an evacuated metallic box should experience an attractive force brought about by the fluctuations of the electromagnetic field. The ground state of this system appears to be quite boring at first sight because both $\langle E \rangle$ and $\langle B \rangle$ must vanish throughout the cavity to satisfy the boundary conditions at the wall. Nevertheless, the electromagnetic vacuum has a non-trivial structure because the spectrum of both quantum and thermal fluctuations changes with separation. This gives rise to the so-called Casimir force.

† When speaking of structural force, we refer to forces induced directly by the liquid-crystalline structure, e.g., the director field. Forces like the van der Waals and the electrostatic force, which depend on the director structure indirectly, are not included in this definition.

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The simplest liquid-crystalline analog of Casimir's evacuated metallic box is an ordinary nematic cell with identical substrates. The uniform director profile plays the role of the electromagnetic vacuum and the interaction between the walls is induced by the thermally driven director fluctuations. As in the electrodynamic case, the fluctuations are subject to boundary conditions, here due to anchoring, and the boundary conditions discretize the spectrum of the normal modes. As a result, the free energy of the confined liquid crystal is different from its bulk counterpart and this generates the force.

The similarities between the thermal electrodynamic Casimir effect and its nematic analog are, in fact, fairly deep. In a nematic cell bounded by identical substrates of area A and separated by h, the fluctuation-induced force is attractive

$$\mathscr{F} = -\frac{\zeta(3)k_BTA}{8\pi h^3}\left(\frac{K_{33}}{K_{11}} + \frac{K_{33}}{K_{22}}\right) \qquad (1)$$

(where $\zeta(n)$ is the Riemann zeta function and $\zeta(3) = 1.202$) and it differs from the thermal electrodynamic force only by the factor that accounts for the elastic anisotropy of the liquid crystal [2]. Apart from the numerical constants, this result can be derived by dimensional arguments, and it describes the interaction both in the strong and the vanishingly weak anchoring limit. This seemingly strange fact is no longer surprising as soon as we realize that although the two limits differ in the symmetry of the normal modes, their spectra are identical.

Unfortunately, an intuitive explanation of where this interaction comes from is not readily available. It is tempting to believe that it originates in the absence of the low-energy, long-wavelength modes which are forbidden by the boundary conditions, making the free energy of the confined region larger than its bulk counterpart. This explanation seems plausible, and it appears to support the fact that the attraction becomes stronger with the decreasing separation between the plates. However, it fails to explain the *repulsive* force in a system with infinitely strong anchoring at one plate and infinitely weak anchoring at the other plate. In this case, the long-wavelength modes are also absent, and following the above argument, this should result in an attractive force. But mixed boundary conditions are known to give rise to a fluctuation-induced repulsion, which indicates that the collective effect of the different modes cannot be interpreted in a straightforward manner.

Understanding boundary conditions

The above simple formula reveals an important feature of the fluctuation-induced force in nematics—its long range. However, it only applies to a very idealized situation where the anchoring is either infinitely strong or infinitely weak. In practice, these conditions are very rarely met at separations where the fluctuation-induced forces are expected to be important. For example, several force-measurement techniques are sensitive enough to detect the fluctuation-induced interaction at distances ranging from some 10 to a few 100 nm (this is also the characteristic size of many microconfined liquid crystals), and these distances are comparable to typical extrapolation lengths (λ). As a rule of thumb, we should expect the effect of anchoring to be most important when $h \approx \lambda$, right between the weak anchoring regime ($h \ll \lambda$) and the strong anchoring regime ($h \gg \lambda$). In both limiting regimes, the force is inversely proportional to h^3 as described by the above formula, but in between it should deviate from this power law. The main questions here are (i) how strong is this deviation and (ii) what is the range of separations where the deviation is significant.

In principle, the two anchoring strengths need not be identical. In this more general case, there exists an intermediate regime in between the strong ($h \gg \lambda_1, \lambda_2$) and weak anchoring ($h \ll \lambda_1, \lambda_2$). The intermediate regime corresponds to the range of separations such that $h < \lambda_1$ but $h > \lambda_2$. If the anchoring strengths are very different, we can have the strong anchoring regime at one plate and the weak anchoring regime at the other (figure 2). This limit can be worked out analytically, and the result is a long-range repulsive force given by $3\zeta(3)k_BTA/8\pi h^3$ (here we have assumed the one-constant approximation).

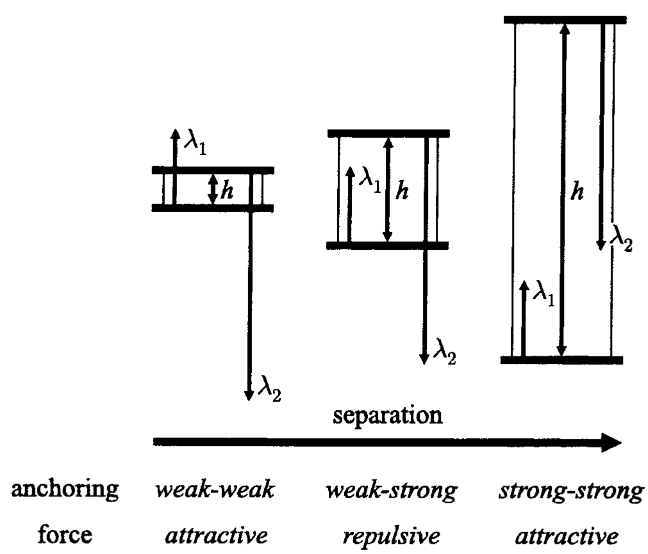

Figure 2. At small separations, both anchorings are effectively weak and the fluctuation-induced interaction is attractive. At intermediate h's, the anchoring is strong at one plate and weak at the other one and the interaction is repulsive. At large separations, anchoring is strong at both plates, which gives rise to a fluctuation-induced attraction.

The different force profiles are illustrated in figure 3 where the anchoring strengths were chosen in order to emphasize the variety of the different behaviours. The force can be either monotonic or non-monotonic, attractive or repulsive... but it is always attractive at small enough and large enough separations. Whatever happens in between, depends on the interplay of the different lengthscales involved, and the character of the force often changes with separation.

For a more quantitative representation of the force [3], it is convenient to scale it with respect to the strong-strong (or, equivalently, weak-weak) limit given in (1). In other words, we plot its reduced magnitude defined as

$$\rho = \frac{\mathscr{F}(h, \lambda_1, \lambda_2)}{\mathscr{F}(h, \lambda_1 = \lambda_2 = 0)}. \tag{2}$$

The curves in figure 4 correspond to several relative strengths of the anchorings. If the extrapolation lengths are very different, then the intermediate repulsive regime is well-developed and ρ closely approaches $-3/4$ over a few decades, indicating a h^{-3} repulsion. But as λ_1/λ_2 becomes smaller, the intermediate regime is less and less pronounced and the plateau gradually vanishes altogether. For λ_1/λ_2 ranging from about 3.5 to 1, the transition from the weak-weak to strong-strong regime no longer includes the repulsive section, the only remaining sign of the transition between the weak-weak and strong-strong anchoring regimes being the dip in the reduced magnitude. Even so, one should note that the dip is fairly deep in the sense that it corresponds to at least 10-fold decrease of the magnitude of the force, and this dip occurs over a range of separations about two decades wide and centred around its minimum. This implies that

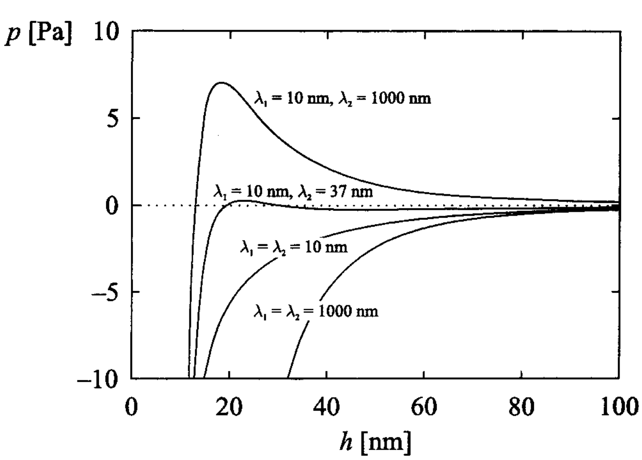

Figure 3. A few force profiles in a homeotropic cell with $\lambda_1 \neq \lambda_2$. The curves labelled by λ_1 and λ_2 were chosen so as to illustrate the multifaceted behaviour of the fluctuation-induced force in this system. Note the oscillatory force profile for $\lambda_1 = 10$ nm, $\lambda_2 = 37$ nm.

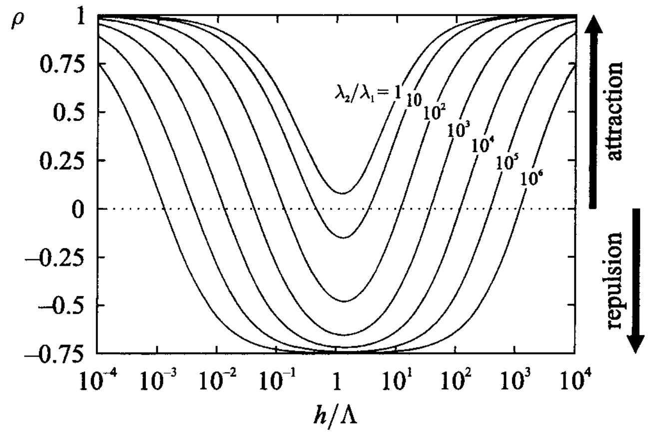

Figure 4. Reduced magnitude as a function of separation for various relative anchoring strengths. If the ratio of the anchoring strengths is larger than about 3.5, the force is repulsive at separations comparable to $\Lambda = \sqrt{\lambda_1 \lambda_2}$.

at $0.1\Lambda < h < \Lambda$ (where $\Lambda = \sqrt{\lambda_1 \lambda_2}$), the effective force profile is actually quite close to h^{-4} law, whereas at $\Lambda < h < 10\Lambda$ it appears to obey the h^{-2} law. Since the force measurements rarely span more than 2 orders of magnitude ranging from a few nm to a few 100 nm, these apparent power laws may well describe a large part of what is seen in experiments, provided that the anchoring is not too weak.

The main message of this discussion is that even in very simple real systems, the fluctuation-induced force has many faces. Depending on the three lengths involved, it may be either attractive or repulsive, monotonic or nonmonotonic, it may and may not follow an apparent power law, but most importantly, it should not conform to the h^{-3} law. This convoluted behaviour is a result of the broad transitions between the limiting regimes and the fact that most real systems fall right in the middle of these transitions.

Can it be measured?

Once the effect of the anchoring is analysed, one starts to wonder where the fluctuation-induced force should be most easily observable. It is not hard to see that the planar geometry has several advantages over the various curved geometries. The main reason for this is that in curved geometries, such as the crossed cylinders arrangement of the surface force apparatus [4] and the sphere-plate geometry of the atomic force microscope [5], the fluctuation-induced interaction is usually masked by the mean-field interaction due to the non-uniform director field. On the other hand, the mean-field force is always absent in thin planar cells: even if the boundary conditions are mismatched, the director field is uniform at small enough separations. The second reason in favor of planar geometry is that in this case the theoretical analysis as well as the interpretation of the experimental data is more straightforward than in curved geometries.

However, it is virtually impossible to ensure that the plates of a classical nematic cell be parallel at small enough separations. Presently, it appears that the only truly planar nematic system of thickness ranging from say 10 nm to a few 100 nm is a thin film deposited on a solid substrate by, e.g., spin casting. But this eliminates the possibility of a direct measurement of the force between the solid-liquid crystal and the liquid crystal-air interface, and so the force must be probed indirectly. Although this path has not been explored systematically yet, an indirect measurement of the structural force was performed a few years ago by Vandenbrouck *et al.* [6] who studied spinodal dewetting of a thin 5CB film on a silicon wafer.

They observed that the 5CB films spontaneously disintegrated into an array of droplets if they were thinner than about 20 nm, whereas the thicker films were stable. Theoretically, the film is unstable if the spatial derivative of the force between the interfaces is positive, which roughly speaking means that the force itself should be attractive. The first thing that comes to one's mind is that the process could be driven by the van der Waals force, but it turns out to be repulsive in the relevant range of separations. If it were present, the elastic structural force due to director distortion would also be repulsive. This leaves very few possibilities for the source of instability; it seems that the fluctuation-induced attraction is the only one. Indeed, a careful analysis of the structural interaction in this system showed that the above scenario is more than reasonable [7], implying that the spinodal dewetting experiment is one of the few studies where the fluctuation-induced interaction was observed in the material world.

In principle, this experiment could be redone to reconstruct the force profile from the measured dewetting time and the droplet size as a function of the initial film thickness. This may not be a very easy experiment to carry out and analyse, but presently it appears that the best possibility is to focus on an indirect measurement where the structural force would manifest itself on a macroscopic scale via a secondary mechanism such as spinodal dewetting.

As an aside, let us note that the imbalance of the experimental and the theoretical studies of the effect is not limited only to liquid crystals and soft matter. The electrodynamic Casimir effect itself has been predicted well before the first reasonably convincing experimental studies. It took about 50 years to carry out the force measurement accurately enough to confirm Casimir's prediction [8] and in the meantime, the theoretical understanding of the effect has advanced considerably.

Fluctuation-induced interaction at work

During the past 5 years, we have witnessed a rapid development of experiments related to the electrodynamic Casimir effect. Initially, the main issue was how to build a device sensitive enough to detect the fluctuation-induced interaction [8] but recently the question seems to be somewhat reformulated: How important is the effect in modern technology? In 2001, it has been demonstrated that the behaviour of a microelectromechanical system (MEMS)—a 500 μm polysilicon seesaw—can be controlled by the Casimir force [9]. Until now, such effects were not considered essential in MEMSs and in nanotechnology but apparently they are important. In a similar way, the interaction induced by thermal fluctuations in a correlated fluid such as liquid crystal could affect the operation of a microfluidic or nanofluidic device used for processing tiny amounts of fluids. Presently, the diameter of channels in microfluidic devices ranges from tens to hundreds of micrometers, which is still somewhat too big for the pseudo-Casimir effect to play a dominant role, but the miniaturization is by no means over yet.

An already viable field where the fluctuation-induced interactions in liquid crystals are important is the self-assembly of complex 2D and 3D systems. The most representative 2D example is a thin liquid film whose stability is determined by both structural and van der Waals forces. As discussed above, the film may undergo one of the dewetting processes, e.g., spinodal dewetting. In some applications, it is desirable for the film to remain stable, and in others the objective is controlled dewetting. The latter was suggested as a method of preparation of patterned substrates with a given topology and size of the liquid patches [10, 11]. In this context, a detailed insight into the anchoring-related issues is absolutely vital because the two interfaces are necessarily unidentical. As a result, the fluctuation-induced structural interaction can be either attractive or repulsive, depending on the anchoring strengths and the relevant range of film thickness.

As far as the 3D self-assembled systems are concerned, it appears that the pseudo-Casimir force could play an significant role in stabilization of small colloidal particles in liquid-crystalline solvents. Such composite materials have been studied already [1] and they may exhibit additional phase-separated superstructures on top of the usual colloidal phases. To this date, most colloids dissolved in a liquid crystal were based on relatively big particles so that the structural interaction between them was controlled by the mean-field elastic force [12] but this should not be the case in particles no larger than a few tens of nanometers where the fluctuation-induced force is expected to become dominant [3]. Depending on the parameters of the system, the fluctuation-induced force can act either as a cohesive or a disjoining force.

An important and unresolved question related to these self-assembled systems is the behaviour of the fluctuation-induced interaction curved geometry, say in a sphere-sphere configuration. While we can expect that in the dense colloidal phases the plate-plate force profile can be used to describe the interaction between two spheres in terms of the Derjaguin approximation, a more accurate model is needed whenever the typical interparticle separation is comparable or larger than the particle size.

It must be pointed out that the fluctuation-induced structural interaction is by no means the only force in nematic systems discussed above. Other contributions include van der Waals interaction, presmectic interaction due to partial positional order of molecules at the wall, elastic interaction due to distorted director field, electrostatic interaction, and so on. However, the force induced by director fluctuations is an omnipresent phenomenon, like the van der Waals and the presmectic force. It may be subdominant in some systems, but it is always there.

A few more ideas

We hope that we have shown that the fluctuation-induced forces are not just a mere scientific curiosity but an interesting and a potentially technologically important phenomenon. With this note, we have not even scratched the surface of the current insight into the fluctuation-induced interaction in liquid-crystalline mesophases. As far as the nematic phase is concerned, issues that have been studied include interaction between point-like inclusions [13], the effects of external and internal fields [14, 15], etc. A neat idea suggested recently is that an azimuthally anisotropic anchoring should result in a fluctuation-induced torque [16]. In smectic and columnar phases, the main characteristics of the fluctuation-induced interaction have been worked out in the groundbreaking study by Ajdari *et al.* [2]. Also studied were the effects of presmectic fluctuations in the isotropic phase [17], which may be related to certain experiments on lyotropic phases. From a more general soft-matter perspective, a very promising development is a recent theoretical study of the effect in prelamellar systems where an unusually strong and long-range force was predicted [18]. Finally, the fluctuation-induced interactions also appear in the various systems of reduced dimensionality, such as membranes, and they are affected by the roughness of the confining surfaces [19]. Along with the renewed interest in the experimental studies of the phenomenon, this all proves that the fluctuation-induced interaction has become a well-defined and active area of liquid crystal research.

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