Long-range Casimir interactions between impurities in nematic liquid crystals and the collapse of polymer chains in such solvents

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(received 27 July 1999; accepted in final form 14 January 2000)

PACS. 61.30.-v – Liquid crystals.
PACS. 36.20.-r – Macromolecules and polymer molecules.
PACS. 83.70.Hq – Heterogeneous liquids: suspensions, dispersions, emulsions, pastes, slurries, foams, block copolymers, etc.

Abstract. – The elastic interactions between objects embedded in a nematic liquid crystal are usually caused by the average distortion—rather than by the fluctuations—of the nematic orientational field. We argue that for sufficiently small particles, the nematic-mediated interaction originates purely from the fluctuations of the nematic director. This Casimir interaction decays as $d^{-6}$, $d$ being the distance between the particles, and it dominates van der Waals interactions close to the isotropic-to-nematic transition. Considering the nematic as a polymer solvent, we show that the onset of this Casimir interaction at the isotropic-to-nematic transition can discontinuously induce the collapse of a flexible polymer chain from the swollen state to the globular state, without crossing the Θ-point.

In 1948, Casimir originally showed that the interplay between electromagnetic quantum fluctuations and boundary conditions generates long-range interactions between uncharged conducting walls [1]. The corresponding energy density per unit area falls off as $d^{-3}$, where $d$ is the distance between the two walls. Similar effects can also arise in liquid crystals [2, 3]. Nematic liquid crystals are fluid mesophases composed of rod-like molecules exhibiting a broken rotational symmetry along a nonpolar direction, which is characterized by a unit vector $\mathbf{n}$ called the nematic director [4]. Although a nematic material placed between two walls imposing identical orientational boundary conditions does not store any elastic energy, and hence does not give rise to any mean-field force between the walls, it was shown that the interplay between the director’s thermal fluctuations and the boundary conditions induces a “Casimir” long-range interaction falling off as $d^{-2}$ [3]. Note that Casimir-like interactions have been reviewed recently in [5].

Such Casimir interactions should exist without any distortion of the average director orientation, which makes them so intriguing. However, they have not yet been experimentally brought to the fore. Indeed, in most studied systems, e.g., macroscopic colloidal particles immersed in nematic liquid crystals [6, 7], the interactions mediated by the nematic phase
are dominated by the energy of the mean-field elastic distortions of the director field, which decays as $d^{-3}$ or $d^{-5}$ depending on the symmetries of the inclusions [6,8,9]. We argue here that inclusions of size smaller than the molecules orientational correlation length $\xi$ should experience pure Casimir interactions. We argue here that inclusions of size smaller than the molecules orientational correlation length $\xi$ should experience pure Casimir interactions. The latter are found to decay as $d^{-6}$, and should dominate van der Waals interactions in the vicinity of the nematic-to-isotropic transition. Then, considering a single flexible polymer chain in a nematic solvent [10], we show that this Casimir interaction can induce the collapse of the chain at the isotropic-to-nematic transition.

In a nematic liquid crystal, the constituent molecules are locally oriented on the average parallel to some direction $n$. Close to the isotropic transition, although the macroscopic degree of order can be very weak, the molecular orientations are correlated over “swarms” of size $\xi$, which can be as large as 10 to 20 times the molecular dimensions [4]. On length scales larger than $\xi$, these essentially uncorrelated swarms fluctuate about their common orientation $n$, the fluctuations being all the more important than the degree of order is small. To construct the nematic order-parameter $Q$ —a traceless tensor describing the amount of uniaxial anisotropy of the nematic phase [4]—one can average over a small volume the microscopic quantity $q = \frac{3}{2} (m m - \frac{1}{3} I)$ made from the molecular orientation $m$ and the identity tensor $I$. However, it follows from the previous discussion that the averaging volume must be of dimension larger than $\xi$ for this average to be representative of the macroscopic degree of order. One actually defines the director $n$ and the amount of order $S$ by writing the average of $q$ in the form $Q = \frac{3}{2} S (n n - \frac{1}{3} I)$. Hence, both $S$ and $n$ are only defined on length scales larger than the cutoff $\xi$.

Let us now consider a microscopic (neutral) impurity of size less than $\xi$, embedded in the nematic phase. On the range of molecular forces (a few molecular lengths), it will directly affect the orientation of the nematic molecules, either reducing or enhancing their parallelism (see fig. 1). Due to the orientational correlations of the nematic molecules, this direct influence will spread over $\xi$. However, the nematic director—which is only defined at length scales larger than $\xi$—will not be affected by the presence of the particle. This is because the orientational correlations essentially vanish beyond $\xi$ [11]. Such a microscopic impurity cannot therefore induce any mean-field distortion of $n$, as a macroscopic colloidal particle would (the difference being that the latter is physically correlated on a macroscopic scale). Nevertheless, a microscopic impurity should affect the local degree of order $S$, because the swarms around it are strongly disoriented. Hence, within the macroscopic Landau-de Gennes description of nematics—which is naturally coarse-grained over $\xi$—molecular impurities are simply represented by point-like variations of the degree of order $S$. Moreover, since the Frank elastic constants [12] associated with the distortions of the director field are proportional to $S^2$ [4], such impurities should be modelled as point-like variations of the Frank elastic constants.

To simplify, we describe the nematic elasticity in the one constant approximation [4], and we assume that the director undergoes only small deviations with respect to $e_z$. Setting $n \simeq (n_x, n_y, 1)$ and considering a spatially varying elastic constant

$$K(r) = K + \delta k_1 \delta(r - r_1) + \delta k_2 \delta(r - r_2),$$

which models two molecular impurities located at $r_1$ and $r_2$, the system’s free energy takes the form

$$\mathcal{H} = \int dr \frac{1}{2} K(r) \left[ (\nabla n_x)^2 + (\nabla n_y)^2 \right].$$

Throughout the paper, all the energies are expressed in units of $k_B T$. The minimum of (2) corresponds to the uniform state $n_x = n_y = 0$. Therefore the inclusions do not experience any mean-field interaction. The total free energy of the system, however, which takes into account
The nematic molecules under the direct influence of the impurity are drawn in dark gray. The correlation “swarms”, of size $\xi$, indirectly influenced by the impurity are drawn in light gray. Note that the orientational fluctuations within the swarm have been diminished for the sake of clarity. The director $n$, which is only defined by spatial averages over distances larger than $\xi$, is not influenced by the impurity. In particular, the above $+1/2$ and $-1/2$ disclinations of the molecular orientation are irrelevant, since their separation compares with $\xi$. However, after coarse-graining on a scale larger than $\xi$, the impurity is seen to reduce the nematic degree of order $S$, thereby inducing a point-like reduction of the Frank elastic constants.

The fluctuations of the director field, depends in a non-trivial way on $r = |r_2 - r_1|$. Because $n_x$ and $n_y$ are decoupled and play a symmetric role, the partition function $Z$, and hence the total free energy, can be expressed as a functional integration over $n_x$ only. By performing a Hubbard-Stratonovich transformation [13], we obtain

$$Z^{1/2} = \int \mathcal{D}[n_x] \exp \left[ -\int dr \left( \frac{1}{2} K (\nabla n_x)^2 + \frac{1}{2} \sum_{j=1,2} \delta k_j \delta(r - r_j) (\nabla n_x)^2 \right) \right]$$

$$= \int dh_1 dh_2 e^{-\frac{h_1^2}{2\delta k_1} - \frac{h_2^2}{2\delta k_2}} \int \mathcal{D}[n_x] \exp \left[ -\int dr \left( \frac{1}{2} K (\nabla n_x)^2 + i \sum_{j=1,2} h_j \cdot \nabla n_x \delta(r - r_j) \right) \right].$$

Then, calculating all the Gaussians integrals yields

$$Z(r) \propto \det^{-1} \begin{pmatrix} \frac{I}{\delta k_1} - \nabla \nabla G(0) & -\nabla \nabla G(r) \\ -\nabla \nabla G(r) & \frac{I}{\delta k_2} - \nabla \nabla G(0) \end{pmatrix},$$

in which the above $6 \times 6$ matrix, made of four $3 \times 3$ blocks, involves the identity tensor $I$, and the tensor $\nabla \nabla G(r)$. Here, $G(r)$ is the Green function of the operator $-K \nabla^2$. The total free energy of the system, consisting of the nematic liquid and of the two impurities, can then be calculated as $F(r) = -\ln Z(r)$. This total free energy can be decomposed as the sum of the free energies of individual impurities in the nematic solvent (which we call the
ground-state free energy, and of the interaction free energy between the two impurities. In the following, we consider only the latter, which we denote by \( F_C(r) \) and which goes to zero when the separation of the particles goes to infinity. The ground-state free energy appears as a constant that we drop.

To calculate the interaction free energy \( F_C(r) \), one has to introduce a short-distance cutoff \( \Lambda^{-1} \). Note that this cutoff is arbitrary [14], however it cannot be smaller than the correlation length \( \xi \) of the nematicsolvent, since the free energy (2) is not defined below shorter distances. After regularization involving the cutoff \( \Lambda \) in the reciprocal space, we obtain (in units of \( k_B T \))

\[
F_C(r) = -\frac{27}{8\pi^2} \frac{\delta K_1(\Lambda) \delta K_2(\Lambda)}{[3K + \delta K_1(\Lambda)] [3K + \delta K_2(\Lambda)]} \left( \frac{\Lambda^{-1}}{r} \right)^6 + O(r^{-12}),
\]

(5)

with \( \delta K_i(\Lambda) = (2\pi)^3 \Lambda^{-3} \delta k_i(\Lambda) \). The perturbations \( \delta k_i(\Lambda) \) depend on the cutoff; this dependence may be determined from the property that the interaction free energy, however, should not depend on the cutoff. Anyhow, when \( \Lambda^{-1} \) is chosen to be of order \( \xi \), the perturbation of the nematic order due to the impurity is expected to be of the same order as the nematic order itself. Thus, from now on, we set \( \Lambda = 2\pi/\xi \) and we assume \( |\delta K_i| \lesssim K \).

We find that the Casimir interaction is attractive when the two inclusions are of the same nature, i.e. when \( \delta K_1 \delta K_2 > 0 \), and repulsive otherwise. Let us compare it with the van der Waals interaction, which decays with the same power law. With \( F_{vdW}(r) = -A/\pi \rho^3 r^6 \), in which \( A \) is the Hamaker constant and \( \rho \) the inverse of the molecular volume of the impurities [15], we obtain

\[
\frac{F_C}{F_{vdW}} = \frac{27}{8\pi A} \left( \frac{\delta K}{3K + \delta K} \right)^2 (\rho \xi^3)^2 \equiv \mu (\rho \xi^3)^2.
\]

(6)

With typically \( A \simeq 1 \) (in units of \( k_B T \)) and \( |\delta K| \lesssim K \), we expect \( \mu \) in the range \( 10^{-2} - 0.25 \) (the latter value corresponding to \( \delta K \simeq -K \)). Deep in the nematic phase, where \( \rho \xi^3 \simeq 10 \), the Casimir and van der Waals interactions should therefore be comparable. However, in the vicinity of the nematic-to-isotropic transition, where \( \rho \xi^3 \simeq 10^3 \), the Casimir interaction should be the leading one. There can be dramatic consequences to this fact, as we argue now by considering a flexible polymer embedded in a liquid crystal solvent [16,17].

For flexible polymers, the persistence length corresponds to one monomer length and is about 5 Å, which is smaller than the correlation length \( \xi \) of the nematic liquid crystal. Thus, as discussed above, the polymer cannot induce director gradients on the scale of one persistence length (as a particle larger than \( \xi \) would, e.g., by means of anchoring interactions). Beyond the chain persistence length, the monomers orientations are uncorrelated, or, if they are correlated [18], this correlation is induced by the surrounding nematic field, and cannot therefore induce any director gradient. We conclude that the presence of a non-collapsed flexible polymer in a nematic liquid does not give rise to Frank elasticity. In the following, we shall neglect the possible large-scale anisotropy of the Gaussian conformation of the polymer induced by the nematic solvent.

We suppose that the liquid crystal in its isotropic phase is a good solvent for the considered flexible polymer. This property is characterised by a positive excluded-volume parameter \( v_0 \), which takes into account the short-range microscopic monomer-monomer, nematogen-monomer, and nematogen-nematogen interactions. The Flory theory predicts a collapse of the polymer chains when the excluded volume is negative. In the particular case \( v_0 = 0 \), called the \( \Theta \)-point [19], the conformation of the chain is essentially Gaussian. For positive values of the excluded volume, chains are swollen as compared to the Gaussian random walk,
and for chains long enough, the end-to-end distance of the polymer is given, in the Flory picture, by [19]

$\langle R^2 \rangle^{1/2} \sim b^{2/5} v_0^{1/5} N^{3/5}$, \hspace{1cm} (7)

where $b$ is the monomer length and $N$ is the degree of polymerization of the chain.

The issue we address now is the effect of the isotropic-to-nematic transition on the chain conformation, in the case of a flexible chain with persistence length $b < \xi$. In the nematic phase, the effective interaction between monomers results now from a bare excluded volume $v_b$ that takes into account the short-range interactions, plus the long-range Casimir interaction calculated previously. Since at length scales smaller than $\xi$, the nematic and the isotropic phases are essentially indistinguishable from the point of view of the local molecular organisation (as argued above), we do not expect the isotropic-to-nematic transition to shift the value of the bare excluded volume: thus we take $v_b \equiv v_0$. The Casimir interaction, however, is defined only on length scales larger than $\xi$. Hence, to compare the bare excluded volume and the Casimir interaction, one must coarse-grain the polymer in order that the monomer length becomes $\xi[20]$. This coarse-graining of the chain imposes to rescale the bare excluded volume $v_0$. Thus, we redefine the monomer according to

$N \rightarrow N/\lambda \equiv N', \hspace{1cm} b \rightarrow b \lambda^{\nu} \equiv b'$, \hspace{1cm} (8)

while the end-to-end distance, which is unchanged, is now given by

$\langle R^2 \rangle^{1/2} \sim b'^{2/5} v_0'^{1/5} N'^{3/5}$, \hspace{1cm} (9)

where $v_0'$ is the rescaled excluded volume. Thus, one has

$v_0' = v_0 \lambda^{\gamma}$, \hspace{1cm} (10)

with $\gamma = 9/5$ if we take for $\nu$ the Flory exponent $\nu = 3/5$, or $\gamma = 2$ if we assume that the chain has a Gaussian structure at small scale, which corresponds to $\nu = 1/2$. Note that rederiving the end-to-end distance by the Flory argument—i.e. calculating a Gaussian entropy for the chain, neglecting correlations to calculate the excluded-volume interaction, and balancing both contributions—yields the result $\gamma = 2$. Considering now monomers of size $b' = \xi$, we take $\lambda = (\xi/b)^{2/5}$, and thus the rescaled excluded volume is

$v_0' = v_0 \left( \frac{\xi}{b} \right)^{2/5}$, \hspace{1cm} (11)

with $\gamma/\nu = 3$ when assuming a swollen state at small scale, or $\gamma/\nu = 4$ when assuming a Gaussian conformation at small scale. If one considers chains not far from the $\Theta$-point, since $\xi$ is not order of magnitudes larger than $b$, we can assume a Gaussian behaviour at scales smaller than $\xi$ [19]. A rescaling exponent 4 is thus more reasonable than 3, and will be retained for the discussion below.

The chain can now be seen as an ensemble of monomers of size $\xi$, submitted to the bare rescaled excluded-volume interaction $v_0'$, and to a long-range Casimir interaction characterized in our model by $\delta K \simeq K$. Note that the Casimir effect is pairwise additive at lowest order. The effective excluded-volume interaction is $v_{\text{eff}} = v_0' + v_C$, with

$v_C = \int_{r > \xi} d\mathbf{r} F_C(r) = -\frac{9}{2\pi} \left( \frac{\delta K}{3K + \delta K} \right)^2 \xi^3 \equiv -\alpha \xi^3$.

This Casimir contribution is indeed attractive, and its effect is to reduce the quality of the solvent. Adding the two contributions, we obtain

$v_{\text{eff}} = v_0 \left( \frac{\xi}{b} \right)^4 - \alpha \xi^3$, \hspace{1cm} (13)
with $\alpha \sim 0.1$ for $\delta K \simeq K$. The collapse condition $v_{\text{eff}} < 0$ can be written as

$$\frac{v_0}{b^3} \lesssim \frac{a}{\xi}.$$  \hspace{1cm} (14)

Assuming $b/\xi \sim 0.1$, we find that an abrupt collapse may be induced by the isotropic-to-nematic transition, provided the isotropic phase is not too far from the $\Theta$-point. For instance, with $v_0/b^3 \sim 10^{-2}$, chains with degree of polymerization $N > 10^4$, which are thus swollen in the isotropic phase [19], should effectively collapse at the transition. Note that the transition from the swollen to the collapse state occurs without crossing the $\Theta$-point: this is a consequence of the first-order nature of the isotropic-to-nematic transition, which induces a discontinuous change of the interactions between the monomers. One could not expect this effect with a continuous second-order phase transition.

In conclusion, we have shown that small impurities in nematic solvents undergo long-range Casimir interactions decaying as $d^{-6}$. For such inclusions, elastic interactions are absent, while Casimir interactions dominate over the van der Waals interactions. These Casimir forces are attractive for identical particles and can lead to the collapse of flexible polymer chains. They could thus be measured by determining the phase diagram of various flexible polymers close to the isotropic-nematic transition.

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We thank A. AJDARI and L. PELITI for useful discussions.

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