

"Pseudo-Casimir" effect in liquid crystals

A. Ajdari, Bertrand Duplantier, D. Hone, L. Peliti, Jacques Prost

► To cite this version:

A. Ajdari, Bertrand Duplantier, D. Hone, L. Peliti, Jacques Prost. "Pseudo-Casimir" effect in liquid crystals. Journal de Physique II, 1992, 2 (3), pp.487-501. 10.1051/jp2:1992145. jpa-00247645

HAL Id: jpa-00247645 https://hal.science/jpa-00247645

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés. Classification Physics Abstracts 61.30B — 68.45

"Pseudo-Casimir" effect in liquid crystals

A. Ajdari(1), B. Duplantier(2,*), D. Hone(3), L. Peliti(4,**) and J. Prost(1)

- (¹) Laboratoire de Physico-Chimie Théorique (***), ESPCI, 10 rue Vauquelin, F-75231 Paris Cedex 05, France
- (²) Service de Physique Théorique, CE Saclay, Institut de Recherche Fondamentale, F-91191 Gif-sur-Yvette Cedex, France
- (³) Department of Physics, University of California, Santa Barbara CA 93106, U.S.A.
- (⁴) Dipartimento di Scienze Fisiche and Unità INFM, Mostra d'Oltremare, Pad. 19, I-80125 Napoli, Italy

(Received 29 August 1991, accepted 15 November 1991)

Abstract. — We show that the boundary conditions imposed on the director fluctuations in nematics by the presence of rigid walls give rise to long-range forces analogous to the Casimir effect in electrodynamics. We discuss different calculational schemes for the derivation of this result. We derive the spatial behavior of this interaction for smectics and columnar phases in different geometries.

1. Introduction.

The fluctuations of the electromagnetic field generate long-range forces between macroscopic objects such as conducting bodies. These fluctuations may be of quantum or of thermal origin. To each eigenmode of angular frequency ω of the classical electromagnetic field corresponds a quantum zero-point energy equal to $\hbar\omega/2$. Casimir [1] first remarked that, although the total zero-point energy of the electromagnetic field contained in a cavity bounded by conducting walls is divergent, its variation due to a displacement of the boundaries is finite and corresponds to a weak, but measurable attraction between the walls. In the case of two parallel, conducting plates separated by a distance d, Casimir showed that the interaction energy density per unit area is given by:

$$E(d) = -\frac{\pi^2}{720} \frac{\hbar c}{d^3}.$$
 (1.1)

The presence of \hbar witnesses the quantum origin of the fluctuations.

(***) URA 1382.

^(*) Physique Théorique CNRS.

^(**) Associato INFN, Sezione di Napoli.

At high temperature, the same effect shows up in the classical regime, where fluctuations are of thermal origin. It produces long-range interactions, akin to van der Waals interactions. In this regime $(k_{\rm B}Td \gg \hbar c)$, the energy density between two parallel conducting walls is given by

$$E(d) = -\frac{k_{\rm B}T}{d^2} \frac{\zeta_{\rm R}(3)}{8\pi},\tag{1.2}$$

where $\zeta_{\mathbf{R}}$ is Riemann's zeta function.

An analogous effect takes place in anisotropic mesophases [2], when immersed bodies constrain thermal orientational fluctuations, through the boundary conditions they impose on the surface. This is the case, for example, for nematic liquid crystalline phases, which is the main subject of this paper, but also of smectic and columnar phases, which we shall touch upon briefly. There is however an important difference with the electromagnetic case: if the geometry of the immersed bodies imposes a distortion on the *average* director field, the repulsion resulting from the corresponding energetical cost will in general dominate the fluctuation-induced interaction. Such a mean-field interaction does not exist for the case of uncharged bodies in the vacuum.

In the present paper, we shall only consider the simplest geometry: namely, the case of two parallel plates, immersed in a nematic solvent, with normal boundary conditions on the nematic director ("strong homeotropic anchoring"). In this situation the average director field is normal to the wall and uniform in space, producing thereby no interaction. We shall show how the fluctuation-induced interaction may be calculated by adapting to the present case several techniques developed for the Casimir effect. In the regime where anisotropic mesophases are stable, thermal fluctuations dominate over quantum effects. We shall only be concerned, therefore, with the analogue to the high-temperature limit of the Casimir effect (Eq. (1.2)).

The model and notation are introduced in section 2, where we show that longitudinal and transverse degrees of freedom contribute separately to the effect. In section 3, we introduce a transfer-matrix technique and we compute the free energy by exploiting the analogy with the one-dimensional quantum oscillator. A dynamic approach is expounded in section 4: we introduce a formal dynamics by means of a Langevin equation, which allows to calculate directly the correlation functions of the director and the stress exerted on the plates. Section 5 contains the discussion: similarities and differences with the Casimir effect are pointed out, extensions to other mesophases are described, and a few cases where the effect we have described may be experimentally relevant are reviewed. The splitting of longitudinal and transverse modes is discussed in more detail in Appendix 1, whereas an approach based on the direct counting of fluctuating modes and on the zeta regularization technique is reported in Appendix 2.

2. Model.

We consider a nematic slab of thickness d, placed between two flat, parallel walls situated on the planes z=0 and z=d respectively (Fig. 1). We denote by \vec{n} the nematic director, and by \vec{i} , \vec{j} , \vec{k} the unit vectors parallel to the x, y and z axes. The energy of the system is the sum of a bulk term \mathcal{H}_{b} , and of the surface contribution \mathcal{H}_{s} , describing the anchoring of the nematic ordering on the walls. The bulk term is given by [3]:

$$\mathcal{H}_{\rm b} = \int \mathrm{d}x \mathrm{d}y \int_0^d \mathrm{d}z \left[\frac{1}{2} \kappa_1 (\operatorname{div} \vec{n})^2 + \frac{1}{2} \kappa_2 (\vec{n} \cdot \operatorname{rot} \vec{n})^2 + \frac{1}{2} \kappa_3 (\vec{n} \times \operatorname{rot} \vec{n})^2 \right].$$
(2.1)

The surface contribution is given by

$$\mathcal{H}_{\rm s} = \int \mathrm{d}x \mathrm{d}y \left(-\frac{\lambda}{2}\right) (\vec{k} \cdot \vec{n})^2, \qquad (2.2)$$



Fig. 1. — Schematic drawing of the "Casimir" geometry for the nematic case.

where the integral extends to both walls. If $\lambda > 0$, the nematic director tends to align along the normal to the surface. On the other hand, if $\lambda < 0$, the director tends to lie parallel to the surface. The situation is made more complicated, in this case, by the unavoidable presence of anisotropy fields which tend to align \vec{n} along preferred directions in the plane. We shall only consider the first case, and take the strong anchoring limit, corresponding to $\lambda \to \infty$.

In the state of lowest energy the director \vec{n} is uniform and parallel to \vec{k} . If we consider only small fluctuations around this state, we have

$$\vec{n} \simeq (n_x, n_y, 1) = (\mathbf{n}, 1).$$
 (2.3)

We shall denote by v a two-dimensional vector and by \vec{v} a three-dimensional one. In the harmonic approximation one obtains the following expressions for \mathcal{H}_b and \mathcal{H}_s :

$$\mathcal{H}_{\rm b} = \int \mathrm{d}x \mathrm{d}y \int_0^d \mathrm{d}z \left[\frac{1}{2} \kappa_1 (\nabla \cdot \mathbf{n})^2 + \frac{1}{2} \kappa_2 (\nabla \times \mathbf{n})^2 + \frac{1}{2} \kappa_3 (\partial_z \mathbf{n})^2 \right], \tag{2.4}$$

$$\mathcal{H}_{s} = \int \mathrm{d}x \mathrm{d}y \left(\frac{\lambda}{2}\right) \left[\mathbf{n}^{2}(x, y, z=0) + \mathbf{n}^{2}(x, y, z=d)\right].$$
(2.5)

Here ∇ is the two-dimensional nabla operator. The field **n** may be split into its longitudinal and transverse components:

$$\mathbf{n} = \mathbf{n}_{\ell} + \mathbf{n}_{t},\tag{2.6}$$

such that

$$\nabla \times \mathbf{n}_{\ell} = 0; \qquad \nabla \cdot \mathbf{n}_{t} = 0. \tag{2.7}$$

By applying this decomposition to (2.4) we obtain:

$$\mathcal{H}_{\rm b} = \mathcal{H}_{\ell}[\mathbf{n}_{\ell}] + \mathcal{H}_{\rm t}[\mathbf{n}_{\rm t}], \qquad (2.8)$$

where

$$\mathcal{H}_{\ell}[\mathbf{n}_{\ell}] = \int \mathrm{d}x \mathrm{d}y \int_{0}^{d} \mathrm{d}z \left[\frac{1}{2} \kappa_{1} (\nabla \cdot \mathbf{n}_{\ell})^{2} + \frac{1}{2} \kappa_{3} (\partial_{z} \mathbf{n}_{\ell})^{2} \right]; \qquad (2.9)$$

$$\mathcal{H}_{t}[\mathbf{n}_{t}] = \int \mathrm{d}x \mathrm{d}y \int_{0}^{d} \mathrm{d}z \left[\frac{1}{2} \kappa_{2} (\nabla \times \mathbf{n}_{t})^{2} + \frac{1}{2} \kappa_{3} (\partial_{z} \mathbf{n}_{t})^{2} \right].$$
(2.10)

The surface contribution (2.5) splits into two terms of the same form, one involving the longitudinal field n_{ℓ} and the other the transverse one n_t . Therefore one may consider the longitudinal and transverse fluctuations separately.

3. Partition function.

We now calculate, in the harmonic approximation, the partition function of nematic fluctuations in the slab. Due to the separation of longitudinal and transverse modes, we can first consider only the longitudinal field n_{ℓ} , treating it as a *scalar* field ϕ . This procedure can be justified by the projection operator technique discussed in Appendix 1. We obtain therefore:

$$Z_{\ell} = \int \mathcal{D}\phi \, \exp\left\{-\frac{1}{k_{\rm B}T} \left(\mathcal{H}_{\ell}[\phi] + \mathcal{H}_{\rm s}[\phi]\right)\right\}.$$
(3.1)

Due to translation invariance in the (x, y) plane, Z_{ℓ} factors into independent contributions $Z_{\ell}(\mathbf{q})$, one for each independent wavevector \mathbf{q} parallel to the (x, y) plane.

One has:

$$Z_{\ell}(\mathbf{q}) = \int \mathrm{D}\phi(\mathbf{q}, z) \exp\left\{-\frac{\tilde{\lambda}}{2} \left(\phi^{2}(\mathbf{q}, z=0) + \phi^{2}(\mathbf{q}, z=d)\right)\right\} \exp\left(-\tilde{\mathcal{H}}_{\mathbf{q}}\right), \quad (3.2)$$

where $\phi(\mathbf{q}, z)$ is the Fourier transform of $\phi(x, y, z)$ along the (x, y) plane, and we have defined

$$\tilde{\mathcal{H}}_q = \int_0^d \mathrm{d}z \, \left[\frac{1}{2} \tilde{\kappa}_1 q^2 \phi^2 + \frac{1}{2} \tilde{\kappa}_3 (\partial_z \phi)^2 \right]. \tag{3.3}$$

The elastic parameters have been rescaled by $k_{\rm B}T$:

$$\tilde{\lambda} = \lambda/k_{\rm B}T;$$
 $\tilde{\kappa}_i = \kappa_i/k_{\rm B}T, \quad i = 1, 2, 3.$ (3.4)

Equation (3.2) may be cast in the form

$$Z_{\ell}(\mathbf{q}) = \int \mathrm{d}\phi_0 \mathrm{d}\phi_1 \exp\left\{-\frac{\tilde{\lambda}}{2} \left(\phi_0^2 + \phi_1^2\right)\right\} K_d(\phi_1, \phi_0), \qquad (3.5)$$

where

$$K_d(\phi_1, \phi_0) = \int_{\phi(0)=\phi_0}^{\phi(d)=\phi_1} \mathrm{D}\phi(z) \exp\left\{-\int_0^d \mathrm{d}z \,\left[\frac{1}{2}\tilde{\kappa}_1 q^2 \phi^2 + \frac{1}{2}\tilde{\kappa}_3 (\partial_z \phi)^2\right]\right\}.$$
 (3.6)

The kernel $K_d(\phi, \phi_0)$ satisfies the equation

$$\frac{\partial}{\partial d}K_d(\phi,\phi_0) = \left[\frac{1}{2\tilde{\kappa}_3}\frac{\partial^2}{\partial\phi^2} - \frac{1}{2}\tilde{\kappa}_1 q^2 \phi^2\right]K_d(\phi,\phi_0),\tag{3.7}$$

analogous to the Schrödinger equation for the one-dimensional oscillator. The initial condition reads:

$$K_0(\phi, \phi_0) = \delta(\phi - \phi_0). \tag{3.8}$$

Therefore $K_d(\phi, \phi_0)$ may be expanded in the form

$$K_d(\phi,\phi_0) = \sum_{p=0}^{\infty} e^{-\omega_q(p+1/2)d} \psi_p(\phi) \psi_p^*(\phi_0), \qquad (3.9)$$

where

$$\omega_{\mathbf{q}} = \left(\frac{\tilde{\kappa}_1}{\tilde{\kappa}_3}\right)^{\frac{1}{2}} q = \left(\frac{\kappa_1}{\kappa_3}\right)^{\frac{1}{2}} q, \qquad (3.10)$$

and where the ψ_p 's are eigenfunctions of the quantum harmonic oscillator. They are given by

$$\psi_p(\phi) = \frac{1}{\sqrt{2^p p!}} \left(\frac{\beta_\mathbf{q}}{\pi}\right)^{\frac{1}{4}} e^{-\beta_\mathbf{q} \phi^2/2} H_p(\sqrt{\beta_\mathbf{q}}\phi), \tag{3.11}$$

where

$$\beta_{\mathbf{q}} = (\tilde{\kappa}_1 \tilde{\kappa}_3)^{\frac{1}{2}} q, \qquad (3.12)$$

and $H_p(x)$ is the p-th Hermite polynomial.

Equation (3.5) now takes the form

$$Z_{\ell}(\mathbf{q}) = \sum_{p=0}^{\infty} e^{-\omega_{\mathbf{q}}(p+1/2)d} \left(\int d\phi_0 e^{-\tilde{\lambda}\phi_0^2/2} \psi_p(\phi_0) \right) \left(\int d\phi_1 e^{-\tilde{\lambda}\phi_1^2/2} \psi_p(\phi_1) \right).$$
(3.13)

The integrals can be evaluated (Ref. [4], formula (7.373.2) p.837) and give

$$Z_{\ell}(\mathbf{q}) = e^{-\omega_{\mathbf{q}}d/2} \left(\frac{\beta_{\mathbf{q}}}{\pi}\right)^{\frac{1}{2}} \left(\frac{2\pi}{\beta_{\mathbf{q}} + \tilde{\lambda}}\right) \sum_{p=0}^{\infty} \frac{(2p-1)!!}{(2p)!!} \left[e^{-2\omega_{\mathbf{q}}d} \left(\frac{\beta_{\mathbf{q}} - \tilde{\lambda}}{\beta_{\mathbf{q}} + \tilde{\lambda}}\right)^{2}\right]^{p}$$
(3.14)

Performing the sum we obtain

$$Z_{\ell}(\mathbf{q}) = \mathrm{e}^{-\omega_{\mathbf{q}}d/2} \left(\frac{\beta_{\mathbf{q}}}{\pi}\right)^{\frac{1}{2}} \left(\frac{2\pi}{\beta_{\mathbf{q}} + \tilde{\lambda}}\right) \left[1 - \left(\frac{\beta_{\mathbf{q}} - \tilde{\lambda}}{\beta_{\mathbf{q}} + \tilde{\lambda}}\right)^2 \mathrm{e}^{-2\omega_{\mathbf{q}}d}\right]^{-\frac{1}{2}}$$
(3.15)

The contribution of the longitudinal modes to the free energy per unit area of the nematic slab is therefore given by

$$\frac{\mathcal{F}}{L^{2}} = -k_{\mathrm{B}}T \int \frac{\mathrm{d}^{2}\mathbf{q}}{(2\pi)^{2}} \ln Z_{\ell}(\mathbf{q})$$

$$= \frac{k_{\mathrm{B}}T}{2} d \int \frac{\mathrm{d}^{2}\mathbf{q}}{(2\pi)^{2}} \omega_{\mathbf{q}} - k_{\mathrm{B}}T \int \frac{\mathrm{d}^{2}\mathbf{q}}{(2\pi)^{2}} \ln \left[\left(\frac{\beta_{\mathbf{q}}}{\pi} \right)^{\frac{1}{2}} \left(\frac{2\pi}{\beta_{\mathbf{q}} + \tilde{\lambda}} \right) \right] \qquad (3.16)$$

$$+ \frac{k_{B}T}{2} \int \frac{\mathrm{d}^{2}\mathbf{q}}{(2\pi)^{2}} \ln \left[1 - \left(\frac{\beta_{\mathbf{q}} - \tilde{\lambda}}{\beta_{\mathbf{q}} + \tilde{\lambda}} \right)^{2} \mathrm{e}^{-2\omega_{\mathbf{q}}d} \right].$$

Taking now the strong anchoring limit $(\lambda \rightarrow \infty)$ we obtain

$$\frac{\mathcal{F}_{t}}{L^{2}} = \frac{k_{\mathrm{B}}T}{2} d\int \frac{\mathrm{d}^{2}\mathbf{q}}{(2\pi)^{2}} \omega_{\mathbf{q}} + k_{\mathrm{B}}T \int \frac{\mathrm{d}^{2}\mathbf{q}}{(2\pi)^{2}} \left[\ln\left(\frac{\tilde{\lambda}}{2\pi}\right) - \frac{1}{2}\ln(\beta_{\mathbf{q}}) \right] \\
+ \frac{k_{\mathrm{B}}T}{2} \int \frac{\mathrm{d}^{2}\mathbf{q}}{(2\pi)^{2}} \ln\left(1 - \mathrm{e}^{-2\omega_{\mathbf{q}}d}\right).$$
(3.17)

The first term is a bulk contribution to the free energy density of the system. The second term, independent of d, is a contribution to the surface tension between the nematic and the walls. Both terms are divergent for $|\mathbf{q}| \to \infty$. We shall discuss below how to cope with this problem. We are interested in the third term, which is finite, and represents the fluctuation-induced interaction between the walls. It may be explicitly evaluated to yield

$$\frac{\delta \mathcal{F}_{\ell}}{L^2} = \frac{k_{\rm B}T}{4\pi} \int_0^\infty q \,\mathrm{d}q \,\ln\left\{1 - \exp\left[-2\left(\frac{\kappa_1}{\kappa_3}\right)^{\frac{1}{2}}qd\right]\right\}$$
$$= -\frac{k_{\rm B}T}{16\pi} \left(\frac{\kappa_3}{\kappa_1}\right) \zeta_{\rm R}(3)\frac{1}{d^2},$$
(3.18)

where $\zeta_{\mathbf{R}}(3) = 1.202$. and, since the integral is convergent, we have moved the upper integration limit to infinity.

The contribution of the transverse modes to the elastic energy is analogous to that of the longitudinal ones, up to the substitution of κ_1 with κ_2 . The result is therefore analogous to equation (3.18), with κ_2 instead of κ_1 . Thus, the total contribution of the nematic modes to the attraction between the walls is given by

$$\frac{\delta \mathcal{F}}{L^2} = -\frac{k_{\rm B}T}{16\pi} \left(\frac{\kappa_3}{\kappa_1} + \frac{\kappa_2}{\kappa_1}\right) \zeta_R(3) \frac{1}{d^2}.$$
(3.19)

The interaction thus obtained is obviously attractive.

The divergence of the first two terms of equation (3.17) is removed by the introduction of an upper cutoff Λ in the integral over \mathbf{q} . This cutoff corresponds to the shortest wavelength of fluctuations in the directions parallel to the wall, and is of the order of the inverse molecular size. It has therefore an explicit physical interpretation. On the other hand, no such cutoff has been imposed, in our calculation, on the wavelength of fluctuations in the z direction. We do not expect this slight inconsistency to modify our final result (3.19).

The analogy that we have highlighted between the phenomenon we have described and the Casimir effect in quantum electrodynamics [1] suggests to analyze the present problem by methods developed for the Casimir effect [5, 6]. The authors of reference [6] distinguish two broad classes of approaches: the mode-summation method, based on the direct evaluation of infinite sums over energy eigenvalues of the zero-point modes, and local formulations, in which one examines the constrained propagation of virtual field quanta and considers the vacuum stress tensor, which can be expressed in terms of propagators. The method we have just discussed is close in philosophy to the mode-summation methods. We have also attempted a direct evaluation of the mode sum, taking advantage of the zeta regularization technique. This calculation is reported in Appendix 2.

We discuss in the next section a method based on the direct evaluation of the stress tensor.

4. Dynamic approach.

We discuss in this section the definition of the stress exerted on the walls by the nematic present between them, and show how it can be directly calculated by an approach based on a Langevin equation, similar to the method originally used by Lifshitz [7] to discuss van der Waals forces.

Let us consider a fluid, enclosed in a volume V, whose local ordering is described by a scalar field φ (e.g., either the longitudinal or the transverse component of the nematic field **n**). The corresponding free energy reads:

$$\mathcal{F} = \int_{V} d\vec{r} F(\vec{\nabla}\varphi). \tag{4.1}$$

Here $\vec{\nabla}$ is the *three dimensional* nabla operator. We shall suppose to have "strong anchoring" boundary conditions, $\varphi = 0$.

Let us consider the effect of a virtual expansion of V due to a displacement $\delta \ell$ of each surface element dS of the boundary ∂V of V. The variation of \mathcal{F} may be written:

$$\delta \mathcal{F} = \int \mathrm{d}\vec{r} \frac{\partial F}{\partial(\vec{\nabla}\varphi)} \cdot \delta(\vec{\nabla}\varphi) + \int_{S=\partial V} \mathrm{d}\vec{S} \cdot \delta\vec{\ell} F(\vec{\nabla}\varphi)$$

$$= -\int_{V} \mathrm{d}\vec{r} \vec{\nabla} \cdot \frac{\partial F}{\partial(\vec{\nabla}\varphi)} \delta\varphi + \int_{S=\partial V} \mathrm{d}\vec{S} \cdot \frac{\partial F}{\partial(\vec{\nabla}\varphi)} \delta\varphi + \int_{S=\partial V} \mathrm{d}\vec{S} \cdot \delta\vec{\ell} F(\vec{\nabla}\varphi).$$
(4.2)

The first term vanishes because the equilibrium state is a minimum of the elastic free energy. On the other hand, φ does no more vanish on the actual surface S, whereas it vanishes on the virtual surface $\partial V + \delta(\partial V)$. Therefore, $\delta \varphi$ can be approximated on the actual surface by:

$$\delta \varphi + \vec{\nabla} \varphi \cdot \delta \vec{\ell} = 0. \tag{4.3}$$

Therefore

$$\delta \mathcal{F} = -\int_{S} \mathrm{d}\vec{S} \cdot \frac{\partial F}{\partial(\vec{\nabla}\varphi)} \delta \vec{\ell} \cdot \vec{\nabla}\varphi + \int_{S} \mathrm{d}\vec{S} \cdot \delta \vec{\ell} F.$$
(4.4)

Defining the stress τ by

$$\delta \mathcal{F} = \int_{S} (d\vec{S} \cdot \tau \cdot \delta \vec{\ell}), \tag{4.5}$$

we have therefore

$$\tau_{\alpha\beta} = -\nabla_{\alpha}\varphi \frac{\partial F}{\partial(\nabla_{\beta}\varphi)} + \delta_{\alpha\beta} F.$$
(4.6)

The first term on the right hand side corresponds to the part described by de Gennes [3] for incompressible nematics.

This description is well adapted to our problem, in which the walls are immersed in a nematic bath, implying that an increase in d leads to an increase in the quantity of nematic contained between the walls.

We shall now relate the above expression to the correlation functions of the scalar degree of freedom φ . By changing the scale in the z direction we may write:

$$\mathcal{H} = \frac{1}{2}\kappa \int \mathrm{d}x \mathrm{d}y \int_0^h \mathrm{d}z \left[(\nabla \varphi)^2 + (\partial_z \varphi)^2 \right], \qquad (4.7)$$

where $\kappa = \sqrt{\kappa_i \kappa_3}$, i = 1 (2) for longitudinal (transverse) modes, ∇ is the two-dimensional nabla operator, and

$$h = \left(\frac{\kappa_i}{\kappa_3}\right)^{1/2} d. \tag{4.8}$$

The stress on the wall at z = h reads

$$\tau_{zz} = \left\langle \kappa (\partial_z \varphi)^2 \right\rangle - \left\langle \frac{1}{2} \kappa \left[(\partial_z \varphi)^2 + (\nabla \varphi)^2 \right] \right\rangle, \tag{4.9}$$

where we have taken the average with respect to the thermal fluctuations.

The thermal averages appearing in this formula can be simply calculated within a dynamic approach. Although the introduction of a dynamic equation is strictly speaking unnecessary, it simplifies considerably the calculations, and it has a physical appeal, since it clarifies the fact that the stress we are computing originates in the thermal fluctuations of the director. We thus introduce a Langevin equation describing a model dynamics of our system:

$$\gamma \frac{\partial \varphi}{\partial t} - \kappa \vec{\nabla}^2 \varphi = \eta(\vec{r}, t), \qquad (4.10)$$

where $\eta(\vec{r}, t)$ is a Gaussian white noise, satisfying

$$\langle \eta(\vec{r},t) \rangle = 0; \qquad \left\langle \eta(\vec{r},t)\eta(\vec{r'},t') \right\rangle = 2\gamma k_{\rm B} T \delta(t-t') \delta(\vec{r}-\vec{r'}).$$
(4.11)

The dynamics we have just defined does not necessarily describe the actual dynamical behavior of the system, but the above relations are sufficient to ensure that the equilibrium properties of the model (in which we are interested) are the ones we have so far considered.

The $\varphi(\vec{r},t)$ field is then given by

$$\varphi(\vec{r},t) = \int d\vec{r'} dt' G(\vec{r},t;\vec{r'},t') \eta(\vec{r'},t'), \qquad (4.12)$$

where $G(\vec{r},t;\vec{r'},t')$ is the Green's function of the evolution equation (4.10) and satisfies:

$$\gamma \frac{\partial G}{\partial t} - \kappa \vec{\nabla}^2 G = \delta(\vec{r} - \vec{r'}) \delta(t - t'), \qquad (4.13)$$

with the boundary conditions

$$G(x, y, z = 0, t; \vec{r'}, t') = G(x, y, z = h, t; \vec{r'}, t') = 0.$$
(4.14)

A Fourier transformation with respect to x, y and t yields:

$$(i\omega\gamma + \kappa q^2)G_{\mathbf{q}\omega} - \kappa \frac{\partial^2}{\partial z^2}G_{\mathbf{q}\omega} = \delta(z - z');$$

$$G_{\mathbf{q}\omega}(z=0,z') = G_{\mathbf{q}\omega}(z=h,z') = 0; \quad \forall (z',\omega,\mathbf{q}).$$
(4.15)

The solution of this system of equations reads:

$$G_{\mathbf{q}\omega}(z,z') = \begin{cases} -[\alpha\kappa\sinh(\alpha h)]^{-1}\sinh\left[\alpha(z'-h)\right]\sinh(\alpha z), & \text{if } z < z';\\ -[\alpha\kappa\sinh(\alpha h)]^{-1}\sinh\left[\alpha(z-h)\right]\sinh(\alpha z'), & \text{if } z > z'; \end{cases}$$
(4.16)

where

$$\alpha = \left(\frac{i\omega\gamma}{\kappa} + q^2\right)^{\frac{1}{2}} \tag{4.17}$$

We can now evaluate the stress on the z = h plane, using equation (4.9) and taking into account that the last term vanishes because of the boundary conditions (4.14):

$$\tau_{zz} = \left\langle \frac{1}{2} \kappa (\partial_z \varphi)^2 \right\rangle$$

= $\kappa \gamma k_{\rm B} T \int_{\mathbf{q}} \int \frac{\mathrm{d}\omega}{2\pi} \int_0^h \mathrm{d}z' \left. \frac{\partial}{\partial z} G_{\mathbf{q}\omega}(z,z') \right|_{z=h} \left. \frac{\partial}{\partial z} G_{-\mathbf{q}-\omega}(z,z') \right|_{z=h}$ (4.18)

Taking now into account the explicit form (4.16) of G, and integrating over z', we obtain:

$$\tau_{zz} = \frac{\gamma k_{\rm B} T}{\kappa} \int_{\mathbf{q}} \int \frac{\mathrm{d}\omega}{2\pi} \left[\frac{2\alpha^+}{(\alpha^+)^2 - (\alpha^-)^2} \coth(\alpha^+ h) - \frac{2\alpha^-}{(\alpha^+)^2 - (\alpha^-)^2} \coth(\alpha^- h) \right], \quad (4.19)$$

where $\alpha^{\pm} = \alpha(\pm \mathbf{q}; \pm \omega)$.

In order to obtain the stress for a finite value of h, we subtract the corresponding value for an infinite distance: $\Delta \tau_{zz} = \tau_{zz} - \tau_{zz}^{\infty}$. We thus obtain, after some algebra,

$$\Delta \tau_{zz} = -\frac{1}{8\pi} \frac{k_{\rm B}T}{h^3} \zeta_{\rm R}(3). \tag{4.20}$$

Going back to the original length scale, and taking into account that $\Delta \tau_{zz}$ must also be rescaled, we obtain

$$\Delta \tau_{zz} = -\frac{1}{8\pi} \left(\frac{\kappa_3}{\kappa}\right) \zeta_{\rm R}(3) \frac{k_{\rm B}T}{d^3},\tag{4.21}$$

corresponding to equation (3.18) or to the analogous one for the transverse modes.

5. Discussion.

The phenomenon we have discussed in this paper is obviously analogous to the Casimir effect, if one observes that in the isotropic case ($\kappa_1 = \kappa_2 = \kappa_3$) the Frank elastic energy is identical to the electromagnetic energy, with \vec{n}_{ℓ} (\vec{n}_t) playing the role of the electric (magnetic) field. The boundary conditions correspond to a field constrained between grounded conducting plates. It is therefore no surprise that in the isotropic case equation (3.19) coincides with equation (1.2).

It might then appear totally superfluous to derive the same expression with three different techniques. However, while in the electromagnetic problem there is no small scale (ultraviolet) cutoff, there is one obvious one in the spectrum of nematic fluctuations: molecular size. As a consequence, ultraviolet divergent terms, which must be dropped altogether in the electromagnetic problem (in the spirit of renormalization theory), have a definite physical meaning in nematics. For example, the first term of equation (3.17) corresponds to a bulk free energy, and the second to a surface tension. They scale like $k_{\rm B}Tq_{\rm c}^2 d$ and $k_{\rm B}Tq_{\rm c}^2$ respectively, where $q_{\rm c}$ is of the order of an inverse molecular size. Since the Casimir-like interaction scales like $k_{\rm B}Td^{-2}$, one may wonder if there is any $k_{\rm B}Tq_{\rm c}d^{-1}$ term. Although the zeta regularization would be unable to reveal its existence, the Euler-MacLaurin summation or the dynamical approach could. Therefore it is important to attack the problem with different techniques. The advantage of the dynamical approach is to allow us to evaluate directly the force applied on the boundaries. It involves only one cutoff-dependent term τ_{zz}^{∞} , which expresses the pressure due to short-scale

fluctuations. It is worth noting that the surface tension term is numerically sizable, since it is of order $k_{\rm B}Tq_{\rm c}^2$. It will also contribute to surface anisotropy and anchoring energy, essentially via the cutoff anisotropy. To our knowledge, this source of anchoring energy has never been considered before: it should always be large on a smooth surface; reported small anchoring energies should be the effect of inhomogeneities.

We can now try to understand why there is no term mixing short and long scales. The simplest picture that we can give is borrowed from colloid physics: the interaction mediated by the fluctuations can be thought of as a depletion force. The harmonically fluctuating field may be seen as a collection of ideal gas particles, whose size is equal to their wavelength. The particles of size larger that the gap between the plates are excluded from it, and the walls feel the outer ideal gas pressure which tends to bring the walls closer together:

$$p = nk_{\rm B}T = -\Delta\tau_{zz}.\tag{5.1}$$

Here *n* is the number density of excluded "particles". Since each particle has an extension proportional to *d* in each direction, their number density scales like d^{-3} This expression is equivalent to (4.21), up to a numerical factor.

Actually the same argument provides some hunches on the numerical factor too. Indeed, if the particle has a size d along z, it must have a linear size $(\kappa_1/\kappa_3)^{1/2}d$ for the longitudinal and $(\kappa_2/\kappa_3)^{1/2}d$ for the transverse fields, in the (x, y) plane. We have therefore, with obvious notations:

$$n_{\ell} + n_{\rm t} \propto \frac{1}{d^3} \left(\frac{\kappa_3}{\kappa_1} + \frac{\kappa_3}{\kappa_2} \right).$$
 (5.2)

In this interpretation, there is no room for the interplay of short and long scales.

The correct d dependence has been obtained in equation (5.1) by retaining only the smallest excluded "particle" size, but one can trace down the occurrence of the Riemann $\zeta_{\rm R}$ function to the exclusion of a spectrum of particles of larger size. Indeed, if we accept that the gap quantizes the modes, it is clear that all multiple integers of d are also excluded: one then has

$$n \propto \frac{1}{d^3} \sum_{k=1}^{\infty} \frac{1}{k^3} \propto \frac{\zeta_{\mathbf{R}}(3)}{d^3}$$
(5.3)

This simplified picture allows us to consider at the same time other liquid crystals such as smectics and columnar phases in the geometries of figure 2. Their common feature is the simultaneous existence of first and second order elasticities:

$$\mathcal{H}_{s} = \frac{B}{2} \int \mathrm{d}^{3} \vec{r} \left[\left(\frac{\partial u}{\partial z} \right)^{2} + \lambda_{1}^{2} \left(\nabla^{2} u \right)^{2} \right]; \qquad (5.4)$$

$$\mathcal{H}_{c} = \frac{B}{2} \int d^{3}\vec{r} \left[\left(\nabla \cdot \mathbf{u} \right)^{2} + \mu \left(\nabla \mathbf{u} - \frac{\left(\nabla \cdot \mathbf{u} \right)}{2} \mathbf{I} \right)^{2} + \lambda_{3}^{2} \left(\frac{\partial^{2} \mathbf{u}}{\partial z^{2}} \right)^{2} \right].$$
(5.5)

Here u is the displacement of the layers along the normal direction z; and the two-dimensional vectors u and ∇ are perpendicular to the column axis z. The two lengths λ_1 and λ_3 compare pression to curvature. The "excluded particles" must now have a very anisotropic shape, since in the smectic q_z scales like $\lambda_1 q^2$, and in columnar phases like $(q/\lambda_3)^{1/2}$ One thus finds:

$$\Delta \tau_{zz} \propto \begin{cases} -k_{\rm B}T/(\lambda_1 d^2), & \text{case a}; \\ -(\lambda_1 k_{\rm B}T)/(d^4), & \text{case b}; \\ -(k_{\rm B}T)/(\lambda_3^{1/2} d^{5/2}), & \text{case c}; \\ -(\lambda_3^2 k_{\rm B}T)/(d^5), & \text{case d}. \end{cases}$$
(5.6)



Fig. 2. — Schematic drawing of the relevant geometries for smectic-A (a and b) and columnar phases (c and d).

The determination of the prefactor is beyond the scope of this analysis, but the argument leading to (5.4) suggests that $\zeta_{\rm R}(2)$, $\zeta_{\rm R}(4)$, $\zeta_{\rm R}(5/2)$ and $\zeta_{\rm R}(5)$ should respectively come into play. We have checked by explicit calculations that this is indeed true for cases a) and c). These are the most interesting geometries, since they lead to forces stronger than van der Waals. For smectics we obtain indeed:

$$\Delta \tau_{zz} = -\frac{1}{8\pi} \frac{k_{\rm B}T}{\lambda_1 d^2} \zeta_{\rm R}(2). \tag{5.7}$$

Since λ_1 is a measurable quantity, this prediction could be tested experimentally without any adjustable parameters. Force measurement apparatuses [8] are well suited in principle for this purpose, and experiments in smectics have indeed been performed [9]. However, the geometry of the experiment involves curved boundaries, which imply the existence of dislocation loops. Creation (upon compression) or annihilation (upon dilation) of these loops gives rise to oscillatory forces, whose minimum sits on an attractive background. It is not clear whether this background corresponds to the long-range attraction discussed in this paper. The analysis of this problem requires consideration of the modification of the fluctuation spectrum due to the non-uniform distribution of the order parameter induced by dislocations.

An interesting consequence of fluctuation-induced forces concerns wetting. Wetting of surfaces by smectic layers has been observed at the isotropic-air interface of some mesogenic compounds [10]. In the case of a disjoining pressure arising from van der Waals forces the growth of the wetting layer is known to follow a $(T - T_c)^{-1/3}$ law, where T_c is the bulk transition temperature. With suitable boundary conditions (e.g., strong (weak) anchoring at the smectic-air (smectic-isotropic) interface), the growth should follow a $(T - T_c)^{-1/2}$ law. Indeed, the energy density per unit area of the smectic layer reads in such a case

$$\mathcal{F} = fd + \frac{k_{\rm B}T\kappa}{\lambda d},\tag{5.8}$$

where $\kappa = \zeta_{\rm R}(2)/32\pi$, and $f \propto (T - T_{\rm c})$ is the difference in the bulk free energy between the isotropic and smectic phases. This result gives the proposed law for *d* upon minimization. It is worth noting that symmetric boundary conditions are also possible (e.g., rigid boundary conditions require the anisotropic part of the interfacial tension to be larger than $\sqrt{\kappa B}$): in this case the behavior is qualitatively changed. The wetting layer is finite at the transition temperature, since the attraction due to the smectic fluctuations can be compensated by the van der Waals disjoining pressure. This could explain the finite value of smectic layers at the isotropic-air interface close to the smectic-isotropic phase transition.

Acknowledgements.

DH gratefully acknowledges the hospitality and financial support provided by ESPCI during his visit, and the financial support of the National Science Fundation under grant number DMR-8906783. LP thanks the Laboratoire de Physico-Chimie Théorique of the ESPCI for a most kind hospitality and a pleasant working atmosphere.

Appendix 1. Splitting of longitudinal and transverse modes.

We discuss here with some more care the splitting of the fluctuating field **n** into its longitudinal and transverse components. Let us introduce the longitudinal and parallel projectors P_{ℓ} and P_{t} by means of:

$$\mathbf{n}_{\ell} = P_{\ell} \mathbf{n}; \qquad \mathbf{n}_{t} = P_{t} \mathbf{n}. \tag{A1.1}$$

They are defined by:

$$(P_{\ell})_{\alpha\beta} = \nabla^{-2} \partial_{\alpha} \partial_{\beta}; \qquad (P_{t})_{\alpha\beta} = \delta_{\alpha\beta} - \nabla^{-2} \partial_{\alpha} \partial_{\beta}, \qquad (A1.2)$$

where α , $\beta = 1, 2$. The Hamiltonian (bulk plus surface) can then be written in the form

$$\mathcal{H}_{\mathbf{b}} = \int \mathrm{d}x \mathrm{d}y \int_{0}^{d} \mathrm{d}z \left[\frac{1}{2} (P_{\ell} \mathbf{n}) A_{\ell} (P_{\ell} \mathbf{n}) + \frac{1}{2} (P_{\mathrm{t}} \mathbf{n}) A_{\mathrm{t}} (P_{\mathrm{t}} \mathbf{n}) \right], \qquad (A1.3)$$

where A_{ℓ} and A_{t} are suitable operators, and, say, periodic boundary conditions are imposed on the fluctuating field **n**.

By performing the functional integral, and exploiting the property $P^2 = P$ of the projectors, we obtain the following expression for the free energy:

$$\mathcal{F} = k_{\rm B} T \frac{1}{2} \operatorname{Tr} \ln \left(P_{\ell} A_{\ell} P_{\ell} + P_{\rm t} A_{\rm t} P_{\rm t} \right). \tag{A1.4}$$

By taking the Fourier transform in the (x, y) plane, we obtain

$$\mathcal{F} = k_{\rm B} T \frac{L^2}{2} \int_{\mathbf{q}} \sum_{n} \left(\ln \omega_{\mathbf{q}n}^t + \ln \omega_{\mathbf{q}n}^t \right), \qquad (A1.5)$$

where ω_{qn}^{ℓ} and ω_{qn}^{t} are the eigenvalues of A_{ℓ} and A_{t} . Since they are both scalar operators, and $\operatorname{Tr} P_{\ell} = \operatorname{Tr} P_{t} = 1$, this is the same result one would obtain if there were two independent scalar fields, one subject to the Hamiltonian \mathcal{H}_{ℓ} , and one to the Hamiltonian \mathcal{H}_{t} , and with the same surface term \mathcal{H}_{s} .

Appendix 2. Zeta regularization.

We discuss in this appendix a method based on the direct summation over fluctuating modes, regularized by means of the zeta regularization technique, already known in the context of the Casimir effect [5, 6, 11]. For simplicity, let us first consider a scalar field φ , subject to vanishing boundary conditions on the two parallel plates situated at z = 0 and z = d:

$$\varphi(0) = \varphi(d) = 0. \tag{A2.1}$$

We assume the Hamiltonian to be given by

$$\mathcal{H}[\varphi] = \int \mathrm{d}x \mathrm{d}y \int_0^d \mathrm{d}z \left[\frac{1}{2} \kappa (\nabla \varphi)^2 + \frac{1}{2} \kappa_3 (\partial_z \varphi)^2 \right], \qquad (A2.2)$$

where $\kappa = \kappa_1$ (= κ_2) for longitudinal (transverse) modes. We can take the Fourier transform along the (x, y) plane and expand in eigenmodes along the z direction, obtaining the following expression for the energy:

$$\mathcal{H} = L^2 d \sum_{n=1}^{\infty} \int \frac{\mathrm{d}^2 \mathbf{q}}{(2\pi)^2} \left[\kappa q^2 |\varphi_{\mathbf{q}n}|^2 + \kappa_3 \left(\frac{n\pi}{d}\right)^2 |\varphi_{\mathbf{q}n}|^2 \right].$$
(A2.3)

The free energy is given by:

$$\mathcal{F} = -k_{\rm B}T \ln \int \mathrm{D}\varphi \,\mathrm{e}^{-\mathcal{H}/k_{\rm B}T} \tag{A2.4}$$

If the functional integral is formally performed, we obtain

$$\mathcal{F} = k_{\rm B} T \frac{L^2}{2} \int_{\mathbf{q}} \sum_{n} \ln \epsilon_{\mathbf{q}n}, \qquad (A2.5)$$

where we have introduced the shorthand notation

$$\int_{\mathbf{q}} = \int \frac{\mathrm{d}^2 \mathbf{q}}{(2\pi)^2},\tag{A2.6}$$

$$\epsilon_{\mathbf{q}n} = \tilde{\kappa} q^2 + \tilde{\kappa}_3 \left(\frac{n\pi}{d}\right)^2, \qquad (A2.7)$$

with rescaled Frank constants (Eq. (3.4)), and where a constant contribution has been dropped by normalization. We are therefore proceeding to a direct summation over the fluctuating modes, identified by the quantum numbers q and n.

The sum (A2.5) is divergent and may be regularized by setting

$$\zeta(s) = \int_{\mathbf{q}} \sum_{n=1}^{\infty} (\epsilon_{\mathbf{q}n})^{-s}, \qquad (A2.8)$$

where the real part of s is sufficiently large so that the sum converges. Then $\zeta(s)$ is analytically continued to the whole (finite) complex plane. One then sets

$$\int_{\mathbf{q}} \sum_{n} \ln \epsilon_{\mathbf{q}n} = -\left. \frac{\mathrm{d}}{\mathrm{d}s} \zeta(s) \right|_{s=0}, \qquad (A2.9)$$

Nº3

where $\zeta(s)$ is the analytically continued function. We have:

$$\begin{aligned} \zeta(s) &= \tilde{\kappa}^{-2s} \int_{\mathbf{q}} \sum_{n} \left[q^2 + \frac{\kappa_3}{\kappa} \left(\frac{n\pi}{d} \right)^2 \right]^{-s} = \frac{\tilde{\kappa}^{-2s}}{4\pi(s-1)} \sum_{n} \left(\sqrt{\frac{\kappa_3}{\kappa}} \frac{n\pi}{d} \right)^{-2(s-1)} \\ &= \frac{\tilde{\kappa}^{-2s}}{4\pi(s-1)} \left(\sqrt{\frac{\kappa_3}{\kappa}} \frac{\pi}{d} \right)^{2-2s} \zeta_{\mathbf{R}}(2s-2). \end{aligned}$$
(A2.10)

In this form $\zeta(s)$ may be analytically continued to the complex plane. Let us remark that the Riemann zeta function $\zeta_{\rm R}(z)$ has a simple pole at z = 1 and vanishes for z = -2n, where n is a positive integer. Therefore, if we are interested in differentiating $\zeta(s)$ at s = 0, we need only differentiate the Riemann zeta function factor. For this purpose it is convenient to use the representation (Ref. [4], formula (9.513.3), p. 1072)

$$\zeta_{\rm R}(z) = \frac{\pi^{z/2}}{\Gamma(z/2)} \left\{ \frac{1}{z(z-1)} + \int_1^\infty {\rm d}t \left[t^{(1-z)/2} + t^{z/2} \right] \frac{1}{t} \sum_{k=1}^\infty {\rm e}^{-k^2 \pi t} \right\},\tag{A2.11}$$

which vanishes explicitly for z = -2n because $\Gamma(-n) = \infty$. The expression between braces in the above equation is symmetric in the interchange $z \leftrightarrow 1-z$. We are interested in z = -2, but the expression is the same for z = +3. Then

$$\frac{\mathrm{d}}{\mathrm{d}s}\zeta_{\mathrm{R}}(2s-2)\Big|_{s=0} = -\frac{1}{\pi} \frac{\Gamma(3/2)}{\pi^{3/2}} \zeta_{\mathrm{R}}(3) = -\frac{1}{2\pi^2} \zeta_{\mathrm{R}}(3).$$
(A2.12)

Substituting this result into equation (A2.10) yields

$$\left. \frac{\mathrm{d}\zeta(s)}{\mathrm{d}s} \right|_{s=0} = \frac{1}{8\pi} \left(\frac{\kappa_3}{\kappa} \right) \zeta_{\mathrm{R}}(3) \frac{1}{d^2},\tag{A2.13}$$

corresponding to equation (3.18) or to the analogous one for the transverse modes.

The interesting property of this approach is that no explicit cutoff has been imposed, neither on \mathbf{q} nor on the z quantum number n. The asymmetry that we have discussed at the end of section 3 does not appear. In reference [11] it is shown that the zeta regularization method yields the same result as a method in which the sum over the *discrete* quantum number n is regularized by the imposition of an exponential cutoff. Indeed, it may be seen that all such regularization method yield equivalent results, once it is realized that the physics of the problem imposes to subtract the free energy of unconstrained fluctuations in a region having the same volume and the same plate area.

The same result may be obtained by a method close to the original method used for the Casimir effect in electrodynamics, namely, by means of the Euler-MacLaurin summation formula. In this case the expressions are regularized by the introduction of a cutoff at large values of $|\mathbf{q}|$, which is let to infinity at the end of the calculation. We shall not discuss this method, since it is algebraically more involved than the one we have just expounded, and since the asymmetry in the cutoff procedure is more difficult to circumvent.

Note added in proof:

We learn that the case of smectics in the geometry of figure 2a has been worked out for arbitrary surface tension in: Mikheev L.V., Zh. Eksp. Theor. Phys. 96 (1989) 632 [Sov. Phys. JETP 69 (1989) 358].

References

- [1] Casimir H. B. G., Proc. Kon. Ned. Akad. Wet. 51 (1948) 793.
- [2] Ajdari A., Peliti L. and Prost J., Phys. Rev. Lett. 66 (1991) 1481.
- [3] de Gennes P.-G., The Physics of Liquid Crystals (Oxford: Oxford Univ. Press, 1974).
- [4] Gradshteyn I. S. and Ryzhik I. M., Tables of Integrals, Series and Products (San Diego: Academic Press, 1987).
- [5] Reuter M. and Dittrich W., Eur. J. Phys. 6 (1985) 33.
- [6] Plunien G., Müller B. and Greiner W., Phys. Reps. 134 (1986) 87.
- [7] Lifshitz E. M., Sov. Phys. JETP 2 (1956) 73.
- [8] Parker J. L., Christenson H. K. and Ninham B. W., Rev. Sci. Instrum. 60 (1989) 3135.
- [9] Richetti P., Kékicheff P., Parker J. L. and Ninham B. W., Nature 346 (1990) 252.
- [10] Ocko B. M., Braslau A., Pershan P. J., Als-Nielsen G. and Deutsch M., Phys. Rev. Lett. 57 (1986) 94.
- [11] Svaiter N. F. and Svaiter B. F., J. Math. Phys. 32 (1991) 175.

501