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VAN DER WAALS FORCES IN NON-ISOTROPIC SYSTEMS

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Non-isotropic systems are considered on the basis of the general theory of Van der Waals forces developed in[2]. The torque tending to rotate two isotropic crystals separated by an air layer relative to each other is calculated, as is the quasiperiodic increment to the interaction force of isotropic bodies separated by a cholesteric liquid crystal. The obtained anisotropic increments lie within the limits of experimental accuracy.

1. Most results for Van der Waals forces in isotropic systems were first obtained by E. M. Lifshitz[1] without using the methods of quantum field theory. Although it is usually perfectly permissible to neglect the anisotropy of the dielectric constant, even a small anisotropy of the bodies leads to a number of specific phenomena. Dzyaloshinskiĭ, Lifshitz, and Pitaevskiĭ[2] noted the appearance of a torque that tends to rotate two anisotropic crystals relative to each other. In the present paper we calculate this torque and, in addition, consider the anisotropic addition to the force of interaction of isotropic bodies separated by a cholesteric liquid crystal. The analysis is by the methods of quantum field theory. Although physically the problems considered by us are quite different, they have something in common, for, as will be shown later, the anisotropic parts of the forces result from the same property of the equations for the temperature Green's function of the photon. Therefore for both cases there are similar dependences on the distance between the bodies (different from the dependences of the isotropic parts). It should also be noted that the quasiperiodic addition to the force, resulting from the cholesteric layer, is due to the torque acting on the pitch of the cholesteric helix. It is precisely for these reasons that both problems are considered in this paper jointly. With respect to the second problem, it should be stated that if the axis of the cholesteric helix is not perpendicular to the planes of the attracting bodies, then besides the calculated force there appears also a torque due to the Van der Waals interaction. There are in this case, however, also torques connected with the short-range orientation forces, and in some cases the Van der Waals contribution may be the main one. Leaving this question for a separate analysis, we assume in the present paper that the axis of the cholesteric helix is perpendicular to the planes of the interacting bodies.

2. In order to obtain an expression for the stress tensor in the anisotropic case, it is necessary to recognize that the polarization operator is connected with the dielectric tensor by the following relation:

$$\Pi_{ik}(\mathbf{r}_1, \mathbf{r}_2; \xi_n) = \frac{\varepsilon_{ik}(\mathbf{r}_1, i|\xi_n|) - \delta_{ik}}{4\pi}\xi_n^2\delta(\mathbf{r}_1 - \mathbf{r}_2). \tag{1}$$

This formula is obtained from the Dyson equation[2] in perfect analogy with the isotropic case. Here ϵ_{ik} is the dielectric tensor, $\xi_n = 2\pi nT$. Using this expression for the polarization operator, we can write in the usual manner[2] the contribution of the Van der Waals forces to the free energy of the system and then find the stress tensor. We present immediately the final expression for the stress tensor after subtracting the constant uniform pressure:

$$\sigma_{ik} = -\frac{T}{2\pi}\sideset{}{'}\sum_{n=0}^{\infty}\{\varepsilon_{im}D_{mk}{}^E(\mathbf{r}, \mathbf{r}) - {}^1/_2\delta_{ik}\varepsilon_{lm}D_{ml}{}^E(\mathbf{r}, \mathbf{r}) + D_{ik}{}^H(\mathbf{r}, \mathbf{r}) - {}^1/_2\delta_{ik}D_{ll}(\mathbf{r}, \mathbf{r})\}. \tag{2}$$

The prime at the summation sign denotes that the zero term has a half weight,

$$D_{ik}{}^E(\mathbf{r}, \mathbf{r}'; \xi_n) = -\xi_n^2 D_{ik}(\mathbf{r}, \mathbf{r}'; \xi_n), \tag{3}$$

$$D_{ik}{}^H(\mathbf{r}, \mathbf{r}'; \xi_n) = +\operatorname{rot}_{il}\operatorname{rot}_{km}{}' D_{ml}(\mathbf{r}, \mathbf{r}'; \xi_n), \tag{4}$$

$D_{ik}(\mathbf{r}, \mathbf{r}'; \xi_n)$ is the temperature Green's function of the radiation.

From formula (2) we readily obtain the acting force

$$F_i = \partial\sigma_{ik}/\partial x_k. \tag{5}$$

Thus, the problem reduces to a solution of equations for the Green's function in the anisotropic case:

$$[\varepsilon_{il}(\mathbf{r}, i\xi_n)\xi_n^2 + \operatorname{rot}_{im}\operatorname{rot}_{ml}]D_{lk}(\mathbf{r}, \mathbf{r}'; \xi_n) = -4\pi\delta(\mathbf{r} - \mathbf{r}')\delta_{ik}. \tag{6}$$

We consider first the problem of two anisotropic crystals (regions 1 and 2), separated by an air layer (region 3) of width l; let the x axis be perpendicular to the surfaces of the crystals (the planes x = 0 and x = l). We refer the dielectric tensor of one of the crystals (say, the second) to the principal axes:

$$\varepsilon^{(2)} = \begin{Bmatrix} \varepsilon_1^{(2)} & 0 & 0 \\ 0 & \varepsilon_2^{(2)} & 0 \\ 0 & 0 & \varepsilon_3^{(2)} \end{Bmatrix}.$$

The dielectric constant of the first crystal is obtained by applying the matrix of rotation through an angle θ (the angle of rotation of the principal axes in the (y, z) plane):

$$\varepsilon_{ik}^{(1)} = A_{im}A_{kl}\varepsilon_{ml},$$

$$A_{ik} = \begin{Bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{Bmatrix}.$$

We ultimately obtain the following components of the dielectric tensor of the first crystal:

$$\varepsilon_{11} = \varepsilon_1^{(1)}, \quad \varepsilon_{22} = \varepsilon(1 - \delta\cos 2\theta), \quad \varepsilon_{33} = \varepsilon(1 + \delta\cos 2\theta),$$
$$\varepsilon_{32} = \varepsilon_{23} = \varepsilon\delta\sin 2\theta, \quad \varepsilon_{12} = \varepsilon_{21} = \varepsilon_{13} = \varepsilon_{31} = 0. \tag{7}$$

We have introduced here the notation

$$\varepsilon = {}^1/_2(\varepsilon_2^{(1)} + \varepsilon_3^{(1)}), \quad \delta = (\varepsilon_2^{(1)} - \varepsilon_3^{(1)})/(\varepsilon_2^{(1)} + \varepsilon_3^{(1)}). \tag{8}$$

The Green's function that enters in (6) depends only on the coordinate difference $y - y'$ and $z - z'$. We can therefore take the Fourier transforms with respect to these coordinates. For convenience we choose the wave vector q parallel to the y axis. Then all the derivatives with respect to z vanish. We also assume (without loss of generality) that $0 < x' < l$. Then, for example, we have for the function $D_{zz}(x, x', q; \xi_n)$ the following system of equations:

for $x > l$

$$(\varepsilon_3^{(2)}\xi_n^2 + q^2 - d^2/dx^2)D_{zz} = 0, \tag{9a}$$

for $0 < x < l$

$$(\xi_n^2 + q^2 - d^2/dx^2)D_{zz} = -4\pi\delta(x - x'), \tag{9b}$$

for $x < 0$

$$\left(\varepsilon_{33}\xi_n^2 + q^2 - \frac{d^2}{dx^2}\right)D_{zz} + \varepsilon_{32}\xi_n^2 D_{yz} = 0,$$

$$\left(\varepsilon_{22}\xi_n^2 - \frac{\varepsilon_{11}\xi_n^2}{\varepsilon_{11}\xi_n^2 + q^2}\frac{d^2}{dx^2}\right)D_{yz} + \varepsilon_{32}\xi_n^2 D_{zz} = 0. \tag{9c}$$

There are homogeneous equations for D_{yz} in the first two regions, where this function vanishes. The solutions for $x > l$ and for $0 < x < l$ can be found readily (they are the same as in the isotropic case):

$$D_{zz} = Ae^{-w_2 x},$$

$$D_{zz} = C_1 e^{-w_3 x} + C_2 e^{w_3 x} - \frac{2\pi}{w_3}\exp\{-w_3|x - x'|\}. \tag{10}$$

Here

$$w_2 = \sqrt{\varepsilon_3^{(2)}\xi_n^2 + q^2}, \quad w_3 = \sqrt{\xi_n^2 + q^2}.$$

For $x < 0$ we seek solutions in the form

$$D_{zz} = A_+ e^{sx}, \quad D_{yz} = B_+ e^{sx}. \tag{11}$$

Substituting (11) in (9), we obtain from the compatibility condition a biquadratic secular equation for the determination of s. Its positive roots yield

$$s_{1,2} = \left\{\frac{\varepsilon_{22}\xi_n^2 - \varepsilon_{11}\xi_n^2}{2} \pm \left[\frac{(\varepsilon_{22}\xi_n^2 - \varepsilon_{11}\xi_n^2)^2}{4} - \varepsilon_{11}\varepsilon_{22}\xi_n^4 + \varepsilon_{32}^2\xi_n^4\frac{\varepsilon_{11}\xi_n^2}{\varepsilon_{11}\xi_n^2 + q^2}\right]^{1/2}\right\}^{1/2}, \tag{12}$$

$$\frac{A_{\pm}}{B_+} = f_{1,2} = \frac{\varepsilon_{32}\xi_n^2}{\varepsilon_{33}\xi_n^2 + q^2 - s^2_{1,2}}. \tag{13}$$

In writing down formulas (13) and (12) it was assumed for simplicity that the crystals are uniaxial, i.e., $\epsilon_3^{(1)} = \epsilon_1^{(1)}$, $\epsilon_1^{(2)} = \epsilon_3^{(2)}$. The arbitrary case does not introduce anything new in principle, but the calculations for a uniaxial crystal are much simpler. To determine the constants A, C_1, C_2, $A_+^{(1,2)}$ and $B_+^{(1,2)}$ it is necessary to satisfy the boundary conditions of continuity of the function $D_{zz}(x)$ and its derivative at $x = 0$ and $x = l$. After straightforward but rather cumbersome calculations and after subtracting the terms corresponding to the homogeneous case, we obtain ultimately

$$D_{zz}(l, l) = \frac{2\pi}{w_3}\frac{(w_3 - w_2)(w_3 r - p)}{(w_3 - w_2)(w_3 r - p) - e^{2w_3 l}(w_3 r + p)(w_3 + w_2)}. \tag{14}$$

Here

$$r = 1 - f_2/f_1, \quad p = s_2 - s_1 f_2/f_1. \tag{15}$$

Analogous calculations for the remaining components of the Green's function of the photon yield expressions for the moment of the forces acting on a unit area at a distance between bodies l and a disorientation angle of the principal axes θ:

$$M(l, \theta) = -\frac{\partial}{\partial\theta}\int_l^\infty dl\left\{\frac{T}{2\pi}\sum_{n=0}^{\infty}{}'\int_0^\infty q\,dq\,w_3\right.$$
$$\times\left[\frac{(w_3 - w_2)(w_3 r - p)}{(w_3 - w_2)(w_3 r - p) - e^{2w_3 l}(w_3 + w_2)}(w_3 r + p)\right.$$
$$\left.\left.+\frac{(w_3\varepsilon_2^{(2)} - w_2)(\varepsilon_{22}w_3 r - p)}{(w_3\varepsilon_2^{(2)} - w_2)(\varepsilon_{22}w_3 r - p) - e^{2w_3 l}(w_3\varepsilon_2^{(2)} + w_2)(\varepsilon_{22}w_3 r + p)}\right]\right\}. \tag{16}$$

The general case is quite difficult to visualize, and we therefore confine ourselves to low anisotropy and low disorientation. In addition, we assume the temperature to be sufficiently low to be able to replace the summation over the frequencies by integration[2]. Then for $l < \lambda_0$ (where λ_0 is the wavelength characteristic of the absorption spectra of the given bodies), we get

$$M(l, \theta) = -\frac{3}{16\pi^2}\frac{\delta\sin 2\theta}{l^2}\bar{\omega}, \tag{17}$$

$$\bar{\omega} = \int_0^\infty \frac{\varepsilon_2(i\xi) - 1}{\varepsilon_2(i\xi) + 1}\left(\frac{\varepsilon(i\xi) - 1}{\varepsilon(i\xi) + 1}\right)^2\sqrt{\varepsilon(i\xi)}\,d\xi. \tag{18}$$

The quantity $\bar{\omega}$ plays the role of the characteristic frequency of the absorption spectra of the given bodies. The dielectric constant of the imaginary frequency is connected in the usual manner with the imaginary part of the dielectric constant at real frequencies[3].

For $l \gg \lambda_0$, when retardation is significant, we have

$$M = \delta l^{-3}\sin 2\theta. \tag{17'}$$

3. We now consider the problem of two isotropic bodies separated by a layer of cholesteric liquid. The respective dielectric-constant tensors are now given by

$$\hat{\varepsilon}^{(1)} = \begin{Bmatrix}\varepsilon_1 & 0 & 0\\ 0 & \varepsilon_1 & 0\\ 0 & 0 & \varepsilon_1\end{Bmatrix}, \quad \hat{\varepsilon}^{(2)} = \begin{Bmatrix}\varepsilon_2 & 0 & 0\\ 0 & \varepsilon_2 & 0\\ 0 & 0 & \varepsilon_2\end{Bmatrix}, \quad \hat{\varepsilon}^{(3)} = \begin{Bmatrix}\varepsilon_3 & 0 & 0\\ 0 & \varepsilon_{22} & \varepsilon_{23}\\ 0 & \varepsilon_{32} & \varepsilon_{33}\end{Bmatrix}, \tag{19}$$

where (see, for example,[4])

$$\varepsilon_{22} = \varepsilon(1 - \delta\cos 2\alpha x), \quad \varepsilon_{32} = \varepsilon_{23} = \varepsilon\delta\sin 2\alpha x,$$
$$\varepsilon_{33} = \varepsilon(1 + \delta\cos 2\alpha x),$$

$\omega = 2\pi/h$, and h is the pitch of the cholesteric helix.

Substituting expressions (19) in Eqs. (6) for the temperature Green's function, we obtain for the function D_{zz}, for example, the following system ($0 < x < l$):

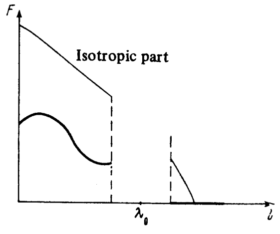
$$\left(\varepsilon\xi_n^2 - \frac{d^2}{dx^2} + q^2\right)D_{zz} + \varepsilon\delta\xi_n^2\cos 2\alpha x\,D_{zz} + \varepsilon\delta\xi_n^2\sin 2\alpha x\,D_{yz} = 0,$$

$$\left(\varepsilon\xi_n^2 - \frac{\varepsilon(1+\delta)\xi_n^2}{\varepsilon(1+\delta)\xi_n^2 + q^2}\frac{d^2}{dx^2}\right)D_{yz} - \varepsilon\delta\xi_n^2\cos 2\alpha x\,D_{yz} + \varepsilon\delta\xi_n^2\sin 2\alpha x\,D_{zz} = 0. \tag{20}$$

At other values of x, the equations are the same as in the isotropic case ($D_{yz} = 0$).

Unlike (9), the system (20) cannot be solved exactly. However, as before[4], we can find solutions in a "resonant" region ($\sqrt{\epsilon\xi_n^2 + q^2} \sim \alpha$) and in the region of applicability of perturbation theory in δ ($\delta < 1$; in real cholesteric media $\delta \sim 0.01$). By matching with the isotropic solutions, we obtain, in analogy with the foregoing, for $l < \lambda_0$

$$F(l) = \frac{\delta\alpha}{4\pi^2}\frac{\cos 2\alpha l}{l^2}\omega^r, \tag{21}$$



where ω^r is the characteristic "resonant" frequency (the factor $\delta\alpha$ corresponds to the width of the "resonant" region). On the other hand, the region $l \gg \lambda_0$ for real cholesteric media corresponds to $l \gg 1/\alpha$, since $\alpha \sim 0.5 \times 10^5$ and the quasiperiodic increment vanishes because of the rapid oscillations.

We note one more essential difference between formula (21) and the isotropic contribution to the force F. This difference is connected with the fact that usually the Van der Waals forces depend very little on the temperature (at low temperatures). The pitch of the cholesteric helix, to the contrary, and consequently the "period" of the anisotropic increment are very sensitive to the influence of the temperature. Therefore the increment to the force (21), unlike the main term, also has a strong temperature dependence, which can be separated experimentally. We present also an expression for the resonance frequency in formula (21):

$$\omega^r = \bar{\xi}\frac{(\varepsilon_1(i\bar{\xi}) - \alpha^2/\bar{\xi}^2)(\varepsilon_2(i\bar{\xi}) - \alpha^2/\bar{\xi}^2)}{(\varepsilon_1(i\bar{\xi}) + \alpha^2/\bar{\xi}^2)(\varepsilon_2(i\bar{\xi}) + \alpha^2/\bar{\xi}^2)}$$

where ξ is the "resonant" frequency in Eqs. (20). The figure shows the schematic dependence of the quasiperiodic increment F on the distance between the bodies (the period 10^{-5} and the characteristic wavelength λ_0 are of the same order of magnitude). The same figure shows (not to scale) the isotropic contribution to the force.

In conclusion we note that it is possible to solve other non-isotropic problems in similar fashion, for example, the attraction of non-isotropic particles dissolved in a liquid to a solid surface. The necessary formulas are obtained by slightly modifying those given above. However, for actual utilization of these formulas it is necessary to compare the Van der Waals contribution with the short-range forces exerted on the liquid by the wall. To this end it is necessary to calculate the second variation of the free energy and to compare it with the short-range contribution ($\sim \beta k^2$, where k is the momentum and β is a certain coefficient). The corresponding estimates show that the Van der Waals contribution, generally speaking, is of the same order as the short-range one and may exceed it at not too small momenta. This is precisely why in the present paper we were interested only in problems in which the short-range forces are insignificant ($l \gg$ a, where a is the characteristic interatomic distance in the liquid).

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