Van der Waals forces and light scattering in liquid crystals

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The part of the energy of a liquid crystal that is associated with the long-range character of the van der Waals forces is calculated. In a substantial region this energy is found, roughly speaking, to be cubic in the derivatives, in contrast to the Oseen–Frank energy which is quadratic in the derivatives. The corresponding corrections (cubic in the momentum transfer) to the scattered-light intensity are given.

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1. INTRODUCTION

The recent experiments performed by McMillan[1] on light scattering by liquid crystals have shown important deviations from the law previously predicted theoretically[2] for the intensity ($J \sim 1/q^2$ where q is the momentum transfer). One of the reasons for such deviations may be the influence of the Van der Waals interaction between the molecules at distances of the order of 1/q. By virtue of the power-law rather than exponential fall-off, the contribution of the Van der Waals (VdW) forces can be appreciable: actually (see below), the law for the scattering intensity will acquire the form

$$J\sim 1/(q^2+\text{const}\cdot|q|^3).$$

The influence of VdW forces on light scattering near the critical point in an ordinary liquid was first taken into account by Kemoklidze and Pitaevskiĭ[3]. They calculated the VdW interaction between the density fluctuations and showed that the usual Ornstein-Zernike formula $J \sim 1/(a + bq^2)$ is replaced by the law $J \sim 1/(a + bq^2 + c|q|^3)$. The difference between light scattering in an isotropic liquid and in liquid crystals is connected with the fact that, in the latter, the scattering occurs principally not at density fluctuations but at fluctuations of the direction of the optical axis—fluctuations $\delta\mathbf{n}$ of the director. Therefore, in liquid crystals critical opalescence always occurs[2].

Thus, besides the Oseen-Frank energy

$$F_{O.F}={}^1/_2\int dV\{K_{11}(\operatorname{div}\mathbf{n})^2+K_{22}(\mathbf{n}\operatorname{rot}\mathbf{n})^2+K_{33}[\mathbf{n}\times\operatorname{rot}\mathbf{n}]^2\}, \tag{1}$$

corresponding to a nonuniform distribution of the director $\mathbf{n}(\mathbf{r})$, our purpose is to take into account the VdW interaction energy of molecules that are differently oriented at different points in space. For this we shall make use of the general theory of VdW forces in condensed—solid or liquid—media[4] (cf. also[5]), according to which the VdW energy in a nonuniform condensed system is equal to the change in energy of the fluctuational electromagnetic field due to the appearance of the nonuniformity. If the nonuniformities are macroscopic, the fluctuational field is determined by the local value of the dielectric permittivity $\epsilon_{ik}(\omega, \mathbf{r})$. In an isotropic liquid $\epsilon_{ik} = \epsilon\delta_{ik}$ and all the nonuniformities reduce essentially to a nonuniform density $\rho(\mathbf{r})$ only: $\epsilon(\omega, \mathbf{r}) = \epsilon(\omega, \rho(\mathbf{r}))$. In a liquid crystal ϵ_{ik} is the important tensor

$$\varepsilon_{ik}(\omega,\mathbf{r})=\varepsilon(\omega)\delta_{ik}+\varepsilon_a(\omega)n_i(\mathbf{r})n_k(\mathbf{r}), \tag{2}$$

where $\epsilon \equiv \epsilon_\perp$ is the permittivity transverse to the optical axis, and $\epsilon_a = \epsilon_\parallel - \epsilon_\perp$ is the difference between the longitudinal and transverse permittivities. We shall not take into account possible nonuniformities in the functions ϵ, ϵ_a, as was done for the isotropic case by Kemoklidze and Pitaevskiĭ[3], but shall confine ourselves only to the case characteristic for liquid crystal, i.e., the case of substantial nonuniformity of the director $\mathbf{n}(\mathbf{r})$.

The corresponding calculations are carried through in Sec. 2. In Sec. 3 formulas for the scattered-light intensity are written out. Finally, in Sec. 4 arguments are given which indicate that, if VdW forces are dominant, a liquid crystal may in general lose its uniformity and be transformed from the initial nematic into a cholesteric (without natural optical activity!) or a smectic-C.

2. VdW INTERACTION ENERGY IN A LIQUID CRYSTAL

Thus, we shall calculate the energy of the fluctuational electromagnetic field. This is completely determined by the temperature Green function $\mathscr{D}_{ik}(\mathbf{r}, \mathbf{r}'; \omega)$ of the electric field (cf., e.g.,[4,5]). This function satisfies the equation[4,5]

$$[\varepsilon_{il}(\mathbf{r}, i|\omega|)\omega^2+(\operatorname{rot}^2)_{il}]\mathfrak{D}_{lk}(\mathbf{r},\mathbf{r}';\omega)=4\pi\omega^2\delta(\mathbf{r}-\mathbf{r}')\delta_{ik}, \tag{3}$$

in which the dielectric permittivity ϵ_{ik} appears with an imaginary ("Matsubara") value of the frequency: $\epsilon_{ik} \equiv \epsilon_{ik}(i|\omega|)$. Here and below, unless otherwise stated, we shall use the system of units with $\hbar = c = 1$.

To solve the equation for $\mathscr{D}$ with an arbitrary distribution of the director $\mathbf{n}(\mathbf{r})$ in formula (2) for ϵ_{ik} is, of course, impossible. We shall therefore make use of the fact that the dielectric anisotropy ϵ_a is small in real liquid crystals (usually, $\epsilon_a/\epsilon \approx 0.1$–$0.01$) and shall seek the Green function and energy of the fluctuation field in the form of an expansion in powers of ϵ_a. In this case, for the energy we can immediately make use of the expression for its first variation with respect to $\delta\epsilon_{ik}$[4,5]:

$$\delta F=\frac{1}{8\pi^2}\int_0^\infty d\omega\int d\mathbf{r}\,\mathfrak{D}_{ik}(\mathbf{r},\mathbf{r};\omega)\,\delta\varepsilon_{ik}(\mathbf{r},i\omega), \tag{4}$$

where, in our case of small ϵ_a,

$$\delta\varepsilon_{ik}=\varepsilon_a(i|\omega|)n_i(\mathbf{r})n_k(\mathbf{r}). \tag{5}$$

We note that formula (4) takes into account only the quantum fluctuations and in fact corresponds to not too high temperatures. It is certainly valid at room temperatures (for more detail, cf.[3-5]).

Confining ourselves to quadratic terms in ϵ_a in the energy, it is sufficient to find $\mathscr{D}$ to terms linear in ϵ_a. We have

$$\mathfrak{D}_{ik}(\mathbf{r},\mathbf{r}')=\mathfrak{D}_{ik}^{(0)}(\mathbf{r}-\mathbf{r}')-\frac{1}{4\pi}\omega^2\int d\mathbf{r}''\mathfrak{D}_{il}^{(0)}(\mathbf{r}-\mathbf{r}'')\mathfrak{D}_{mk}^{(0)}(\mathbf{r}''-\mathbf{r}')\delta\varepsilon_{lm}(\mathbf{r}''), \quad (6)$$

where $\mathscr{D}^{(0)}$ is the solution of Eq. (3) for $\epsilon_a = 0$, i.e., the Green function of the radiation in uniform space with permittivity $\epsilon\delta_{ik}$. In Fourier components,

$$\mathfrak{D}_{ik}^{(0)}(\mathbf{q},\omega)=\frac{4\pi\omega^2}{\varepsilon(i|\omega|)\omega^2+q^2}\left(\delta_{ik}+\frac{q_iq_k}{\varepsilon(i|\omega|)\omega^2}\right). \quad (7)$$

Substitution of the first term in (6) into the formula for the energy gives, in principle, the term linear in ϵ_a. It cannot be of interest to us, however, inasmuch as the space integral in it has the structure $\int \mathscr{D}_{ik}^{(0)}(\mathbf{r}-\mathbf{r}\equiv 0;\omega)n_i(\mathbf{r})n_k(\mathbf{r})d\mathbf{r}$ and obviously describes the energy of a uniform distribution of the director. Using the concrete form (7), it is straightforward to show that all the nonuniformity effects reduce only to surface integrals.

The contribution quadratic in ϵ_a is the required VdW energy of attraction. It has the form

$$F_{\mathrm{vdw}}=-\frac{1}{16\pi^2}\frac{1}{(2\pi)^7}\int_0 \omega^4 d\omega\int d\mathbf{p}\,d\mathbf{q}\,\mathfrak{D}_{ik}^{(0)}\left(\mathbf{p}+\frac{\mathbf{q}}{2}\right)\cdot$$
$$\cdot\mathfrak{D}_{ml}^{(0)}\left(\mathbf{p}-\frac{\mathbf{q}}{2}\right)\delta\varepsilon_{im}(-\mathbf{q})\delta\varepsilon_{kl}(\mathbf{q}). \quad (8)$$

Here $\delta\epsilon_{ik}(\mathbf{q})$ is the Fourier component of $\epsilon_a n_i(\mathbf{r}) n_k(\mathbf{r})$:

$$\delta\varepsilon_{ik}(\mathbf{q})=\varepsilon_a(i|\omega|)N_{ik}(\mathbf{q}),\quad N_{ik}(\mathbf{r})=n_i(\mathbf{r})n_k(\mathbf{r}). \quad (9)$$

The integration over p in formula (8) with $\mathscr{D}^{(0)}$ from (7) leads, in the general form, to cumbersome formulas. Simple expressions are obtained in the limits of large and small q. These limits correspond respectively to short and large distances in the theory of VdW forces (cf.[4,5]). The criterion, as always, in a certain characteristic wavelength λ_0 in the absorption spectrum of the substance (for a more precise definition of it, see below). The calculations repeat, practically completely, the corresponding calculations in the article by Kemoklidze and Pitaevskiĭ[3], and therefore we shall give the corresponding results without derivation.

At large distances $R \gg \lambda_0$, corresponding to $q\lambda_0 \ll 1$, the principal role is played by the retarded part of the VdW interaction. The corresponding energy is quadratic in q and (in the usual system of units) has the form

$$F_{\mathrm{vdw}}=\frac{L}{(2\pi)^3}\int d\mathbf{q}\{4q_kq_lN_{il}(\mathbf{q})N_{ki}^*(\mathbf{q})-q^2N_{il}(\mathbf{q})N_{il}^*(\mathbf{q})\}, \quad (10)$$

$$L=\frac{\hbar}{192\pi^2c}\int_0^\infty\frac{\varepsilon_a^2(i\omega)}{\varepsilon^{3/2}(i\omega)}\omega\,d\omega. \quad (11)$$

In the coordinate representation, when (9) is taken into account (10) has the form of the Oseen-Frank energy:

$$F_{\mathrm{vdw}}={}^1/{}_2\int dV\{8L(\operatorname{div}\mathbf{n})^2-8L(\mathbf{n}\operatorname{rot}\mathbf{n})^2+8L[\mathbf{n}\operatorname{rot}\mathbf{n}]^2\} \quad (12)$$

and thus implies a renormalization of the original moduli K in the energy (1). It is interesting to note that the VdW forces tend to decrease K_{22} and increase K_{11} and K_{33}; this correctly reflects the situation in real liquid crystals, in which, in all experimentally-known examples, $K_{22} < K_{11}, K_{33}$. Extreme manifestations of this tendency will be considered in Sec. 4.

Short distances $R \ll \lambda_0$ ($q\lambda_0 \gg 1$) are the region of action of ordinary VdW forces. The corresponding energy is cubic in $|\mathbf{q}|$ and has the form

$$F_{\mathrm{vdW}}=\frac{M}{(2\pi)^3}\int d\mathbf{q}\Big\{2|\mathbf{q}|^3N_{ik}(\mathbf{q})N_{ik}^*(\mathbf{q})-4|\mathbf{q}|q_iq_kN_{il}(\mathbf{q})N_{kl}^*(\mathbf{q})$$
$$+3\frac{q_iq_kq_lq_m}{|\mathbf{q}|}N_{il}(\mathbf{q})N_{km}^*(\mathbf{q})\Big\}, \quad (13)$$

$$M=\frac{\hbar}{2048\pi}\int_0^\infty\frac{\varepsilon_a^2(i\omega)}{\varepsilon^2(i\omega)}d\omega. \quad (14)$$

It is easily verified that, unlike (10), the energy (13) is positive-definite (see below-Sec. 4). In the coordinate representation the energy (13) is nonlocal and is given by the formula

$$F_{\mathrm{vdw}}=\frac{M}{2\pi^2}\int d\mathbf{r}\,d\mathbf{r}'\Big\{24\frac{(\mathbf{n}(\mathbf{r})\mathbf{n}(\mathbf{r}'))^2}{|\mathbf{r}-\mathbf{r}'|^6}+$$
$$+\frac{8}{|\mathbf{r}-\mathbf{r}'|^4}\frac{\partial}{\partial x_i}(n_i(\mathbf{r})n_l(\mathbf{r}))\frac{\partial}{\partial x_k'}(n_k(\mathbf{r}')n_l(\mathbf{r}'))$$
$$-\frac{3}{|\mathbf{r}-\mathbf{r}'|^2}\frac{\partial^2n_i(\mathbf{r})n_l(\mathbf{r})}{\partial x_i\partial x_l}\frac{\partial^2n_k(\mathbf{r}')n_m(\mathbf{r}')}{\partial x_k'\partial x_m'}\Big\}. \quad (15)$$

The numerical estimation of the coefficients L and M is extremely difficult, since for this it is necessary to know $\epsilon(i\omega)$ and $\epsilon_a(i\omega)$ in a broad range of frequencies. For this it is necessary, in practice, to know[4] the dispersion and the anisotropy of the absorption in the whole spectral range. A qualitative comparison of the expressions (10) and (13) enables us to find the above-mentioned wavelength λ_0. Putting $q \sim 1/\lambda_0$ and $L/\lambda_0^2 \sim M/\lambda_0^3$, we find $\lambda_0 \sim c/\omega_0$,

$$\omega_0\sim\int_0^\infty\frac{\varepsilon_a^2(i\omega)}{\varepsilon^{3/2}(i\omega)}\omega\,d\omega\Big/\int_0^\infty\frac{\varepsilon_a^2(i\omega)}{\varepsilon^2(i\omega)}d\omega.$$

Thus, ω_0 is the frequency at which dispersion of the anisotropy ϵ_a of the dielectric permittivity begins to be important (we recall that as $\omega \to \infty$ the permittivity ϵ tends to unity while ϵ_a goes to zero no more slowly that ω^{-2}).

3. LIGHT SCATTERING

The expressions (13), (15) for the energy can lead in principle to a whole series of new qualitative effects. These effects will be especially pronounced if the renormalization of the moduli K in the quadratic region, i.e., the quantity L, is of the same order as the moduli K themselves. Such a situation is a priori perfectly possible, since the quantities L and M are determined entirely by the optical properties of the liquid crystal and are independent, at least at first sight, of the unrenormalized moduli K, which are determined by the interaction of neighboring molecules. Evidence in favor of the assumption of a large value of L is the above-mentioned smallness of the modulus K_{22}.

In the case of large L, for sufficiently small distances $R \lesssim \lambda_0$ and correspondingly large $q\lambda_0 \gtrsim 1$, the VdW energy will exceed the Oseen-Frank energy. Correspondingly, the distribution of the director n in thin ($d \lesssim \lambda_0$) films of liquid crystals, and their behavior in sufficiently strong magnetic fields H, will change. In particular, the dependence of the coherence length ξ_H introduced by de Gennes will change from the law $\xi_H \sim H^{-1}$ in weak fields to the law $\xi_H \sim H^{-2/3}$ in strong fields.

Here we shall consider only the influence of the VdW forces on the scattering of light by thermal fluctuations of the orientation of the director about the constant equilibrium value n_0. Introducing the small deviations ν:

$$\mathbf{n}(\mathbf{r})=\mathbf{n}_0+\boldsymbol{\nu}(\mathbf{r}),\quad \mathbf{n}_0\boldsymbol{\nu}(\mathbf{r})=0,$$

we shall write out the energy of the fluctuations to terms quadratic in ν.

For small $q\lambda_0 \ll 1$ the energy is principally given by the Oseen-Frank expression (1) with the renormalized values of the moduli:

$$K_{11}\to K_{11}+8L,\quad K_{22}\to K_{22}-8L,\quad K_{33}\to K_{33}+8L.$$

The corrections to this are found to be of fourth order in q (in fact, they are proportional to $q^4 \ln q$; cf.[3]) and can be discarded. For the Fourier components $\nu(\mathbf{q})$, we introduce, as usual, a coordinate system $(\nu_1 \nu_2 \nu_z)$ with the z-axis along n_0, i.e., $\nu_z = 0$, with the 2-axis (unit vector $e_2(\mathbf{q})$) perpendicular to $\mathbf{q}$ and n_0, and with the 1-axis (unit vector $e_1(\mathbf{q})$) orthogonal to n_0 and the 2-axis. In these components the energy of the fluctuations has the form[2]

$$F_{O\cdot F} = {}^1/_2 \int d\mathbf{q} \{(K_{33} q_z^2 + K_{11} q_\perp^2) |\nu_1(\mathbf{q})|^2 + (K_{33} q_z^2 + K_{22} q_\perp^2) |\nu_2(\mathbf{q})|^2\}. \quad (16)$$

For large $q\lambda_0 \gg 1$ the contribution of the Oseen-Frank energy will be given by the same formula (16), but with the "bare" values of the moduli K, i.e., with $K_{11} - 8L$, $K_{22} + 8L$, $K_{33} - 8L$, in place of K_{11}, K_{22}, K_{33}. To this is added the VdW energy, obtained by linearizing the expression (13). In the same axes (1, 2, z), we have[1)]

$$F_{VdW} = \frac{4M}{(2\pi)^3} \int d\mathbf{q} \left\{ q q_\perp^2 |\nu_2(\mathbf{q})|^2 + 3 \frac{q_\perp^2 q_z^2}{q} |\nu_1(\mathbf{q})|^2 \right\}. \quad (17)$$

We shall now give formulas for the total intensity of the scattered light[2]. Let **i** and **f** be the polarization vectors of the incident and scattered light and let **q** be the momentum transfer. The scattering in unit solid angle (the extinction coefficient dh) is given by the sum of the scatterings by the director fluctuations $\nu_1(\mathbf{q})$, $\nu_2(\mathbf{q})$ along the axes e_1 and e_2 (the z-axis is along n_0):

$$\frac{dh}{d\Omega} = \frac{\omega^4}{16\pi^2 c^4} |\varepsilon_a(\omega)|^2 \{J_1(\mathbf{q}) (f_z i_1 + f_1 i_z)^2 + J_2(\mathbf{q}) (f_z i_2 + f_2 i_z)^2\}. \quad (18)$$

We emphasize that here, in contrast to all the other formulas, the anisotropy $\epsilon_a(\omega)$ of the dielectric permittivity appears at a real (!) frequency ω—the frequency of the incident and scattered light.

For small $q\lambda_0 \ll 1$ the de Gennes formula[2] is conserved:

$$J_1(\mathbf{q}) = \frac{T}{K_{33} q_z^2 + K_{11} q_\perp^2}, \quad J_2(\mathbf{q}) = \frac{T}{K_{33} q_z^2 + K_{22} q_\perp^2}. \quad (19)$$

For large $q\lambda_0 \gtrsim 1$ we must take the VdW energy into account. Taking into account also the renormalization of the moduli K, we have, with L from (11) and M from (14),

$$J_1(\mathbf{q}) = \frac{T}{(K_{33} - 8L) q_z^2 + (K_{11} - 8L) q_\perp^2 + 12M q_z^2 q_\perp^2 / q},$$

$$J_2(\mathbf{q}) = \frac{T}{(K_{33} - 8L) q_z^2 + (K_{22} + 8L) q_\perp^2 + 4M q q_\perp^2}. \quad (20)$$

In the intermediate region $q \sim 1/\lambda_0$, the expressions for the intensity are cumbersome and are given by the integrals in formula (8).

Unfortunately, a direct comparison of formulas (19), (20) with experiment is as yet impossible, since, on the one hand, the experiments of McMillan[1] were carried out near the nematic-smectic-A transition point and, on the other, it is not easy to obtain numerical values of the coefficients L and M.

4. CHOLESTERIC CRYSTAL WITHOUT OPTICAL ACTIVITY

We shall discuss, finally, the possibility, conceivable in principle, that the contribution of the long-range VdW forces (in the limit of small $q\lambda_0 \ll 1$) substantially exceeds the contribution of the other, short-range forces which are the source of the Oseen-Frank energy. In this case, the energy of the crystal will be described by formula (12), which signifies the instability of the uniform nematic state.

On the other hand, "perturbations" with too large q will not be able to develop, since for $q\lambda_0 \gg 1$ the energy of the crystal will again be described by the positive-definite expression (13). It is clear also that the true structure will be composed principally of perturbations with values $q \sim 1/\lambda_0$ that are determined by the important wavelengths in the dispersion of the optical anisotropy.

To find the structure of a liquid crystal in practice, it is necessary to know the VdW energy for $q \sim 1/\lambda_0$, i.e., to investigate accurately the cumbersome expressions (8). However, the form of the energy in the limit $q \to 0$ (formula (12)) gives a basis for highly plausible conclusions. It can be seen from (12) that the "maximally stable" structure is that satisfying the equations $\operatorname{div} \mathbf{n} = 0$, $\mathbf{n} \times \operatorname{curl} \mathbf{n} = 0$, i.e., the well-known cholesteric spiral. If we assume that this spiral will remain the true structure of the liquid crystal, its period will be equal in order of magnitude to the same wavelength λ_0.

At present there are insufficient experimental data to estimate the wavelength λ_0. It may well amount to thousands of Angstroms or more, and this means that the reason for the existence of a cholesteric phase is not necessarily natural optical activity; a spiral arises because of the long-range character of the VdW forces. On the other hand, λ_0 may be no greater than hundreds of Angstroms, i.e., than the sizes of the molecules themselves. In this latter case we must rather regard the phase as a smectic-C.

Thus, the Van der Waals long-range character can in principle be responsible for the formation of cholesteric and smectic phases.

[1)] In our preliminary communication [6], the formula for the VdW energy and the corresponding expressions for the intensity are incorrect.

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248