Influence of long-range Van der Waals forces on the scattering of light in liquid crystals

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The long-range character of the Van der Waals forces leads to nonanalytic (in the scattering vector
q) increments to the scattering intensity I, with $1/q^2$ replaced by a formula of the type
$I \sim 1/(q^2 + \alpha|q|^3)$.

Scattering of light in liquid crystals has been diligently investigated recently both theoretically and experimentally. The scattering is determined principally by thermal fluctuations of the director n and has the character of critical opalescence in the entire range of existence of the liquid-crystal phase. The corresponding formula for the dependence of the intensity I on the vector q was obtained by de Gennes et al.[1]

$$ l_\alpha = \frac{T}{K_{33}q_z^2 + K_{\alpha\alpha}q_\perp^2}; \qquad \alpha = 1,2. \tag{1} $$

Here T is the temperature, K_{11}, K_{22}, and K_{33} are the elastic moduli of the liquid crystal, and the z axis is is chosen along the equilibrium direction of the director. The values $\alpha = 1$ and 2 correspond to two fluctuation modes (see[1]).

The latest progress in the experimental techniques[2] has made it reasonable to raise the question of calculating the next higher terms of the expansion in q in the denominator of (1) (McMillan[2] has in fact investigated the scattering of light at large q in the region of the

nematic—smectic A transition). It is clear that if the system contains only short-range forces, the next term of the expansion is of the fourth power in **q**. On the other hand, allowance for the Van der Waals long-range forces yields non-analytic terms cubic in $|q|$.

In fact, formula (1) corresponds to the usual expression of Oseen and Frank for the free energy of a liquid crystal[1]:

$$ \delta F_{OF} = \frac{1}{2}\int d^3q \sum_{\alpha=1,2} (K_{33}q_z^2 + K_{\alpha\alpha}q_\perp^2)\,|\,\nu_\alpha(q)\,|^2, \tag{2} $$

where ν_α are the independent components of the fluctuations of the direction of the director $n(n = n_0 + \nu;\; n_0 \cdot \nu = 0)$. Inasmuch as the molecules in liquid crystals have as a rule large effective dipole moments, it is necessary to add to (2) the Van der Waals interaction energy, a typical expression for which is (in the coordinate representation)

$$ \int d^3x\, d^3y\, \frac{(\,n(x)\,n(y)\,)^2}{|\,x-y\,|^6} . $$

Linearization of this expression and a transition to

Fourier components yield precisely an increment of the type $\int d^3q |\nu(\mathbf{q})|^2 |\mathbf{q}|^3$.

This increment can be determined exactly by using the general theory of Van der Waals forces.[3] The calculations are very similar to those of Kemoklidze and Pitaevskiĭ,[4] who obtained the cubic increments to the scattering intensity in an ordinary liquid. The details of the calculations will be published elsewhere, and we present here only the final results.

The Van der Waals energy is determined by the dielectric tensor of the liquid crystal

$$\epsilon_{ik} = \epsilon \delta_{ik} + \epsilon_a n_i n_k$$

for the imaginary frequencies $i\omega$ (see[3]): $\epsilon = \epsilon(i\omega)$, $\epsilon_\alpha = \epsilon_\alpha(i\omega)$. Since the anisotropic part ϵ_α in liquid crystals is as a rule small in comparison with the isotropic part ($\epsilon_\alpha \sim (0.1-0.01)\epsilon$), we confine ourselves to the highest-order term of the expansion in ϵ_α.

We have

$$l_1 \sim T/[K_{33}q_z^2 + K_{11}q_\perp^2 + 12Mq_z^2 q_\perp^2/q], \tag{3}$$

The constant M is expressed by an integral of ϵ and ϵ_α with respect to the imaginary frequency

$$M = \frac{\hbar}{2048\pi} \int_0^\infty \frac{\epsilon_a^2(i\omega)d\omega}{\epsilon^2(i\omega)}. \tag{4}$$

The principal values of the scattering tensors now take the form

$$l_2 \sim T/[K_{33}q_z^2 + K_{22}q_\perp^2 + 4Mqq_\perp^2]. \tag{5}$$

Theoretical estimates of the coefficient M by means of formula (4) are difficult, since they are very sensitive to the law that governs the decrease of the dielectric functions ϵ_α and ϵ with frequency. One can hope, however, that the Van der Waals forces are not too small in comparison with the Oseen—Frank energy. The latter can be estimated in general form at $\epsilon_0 q^2 \alpha^2$, where ϵ_0 is of the order of the atomic energy and α are interatomic distances. On the other hand, the Van der Waals energy is of the form $\epsilon_0 q^3 d^3$, where d is the "effective dipole length" and can be in principle much larger than α for liquid-crystal molecules.

The influence of the Van der Waals forces is particularly strong in smectic liquid crystals, where, as is well known, the modulus K_{11} is anomalously small ($K_{11} \sim 10^{-7}$ erg, whereas the moduli K_{22} and K_{33} retain the usual value $\sim 10^{-6}$ erg). In particular, we can expect appreciable anomalies in transverse ($q_z = 0$) scattering in the first mode

$$l_{1\perp} \sim \frac{T}{q_\perp^2(K_{11} + 2Mq_\perp)}.$$

[1]Groupe d'etude des cristaux liquides, J. Chem. Phys. 51, 816 (1968).

[2]W. L. McMillan, Phys. Rev. 7A, 1673 (1973).

[3]I. E. Dzyaloshinskiĭ, E. M. Lifshitz, and L. P. Pitaevskiĭ, Usp. Fiz. Nauk 73, 381 (1961) [Sov. Phys.-Usp. 4, 153 (1961)]; I. E. Dzyaloshinskiĭ, E. M. Lifshitz, and L. P. Pitaevskiĭ, Adv. Phys. 10, 165 (1961); A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, Metody kvantovoĭ teorii polya v statisticheskoĭ fizike (Quantum Field-Theoretical Methods in Statistical Physics), Moscow, 1962 [Pergamon, 1965].

[4]M. P. Kemoklidze and L. P. Pitaevskiĭ, Zh. Eksp. Teor. Fiz. 59, 2187 (1970) [Sov. Phys.-JETP 32, 1183 (1971)].