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Molecular Theory of Orientational Fluctuations and Optical Kerr Effect in the Isotropic Phase of a Liquid Crystal

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(Received 28 February 1974)

By use of Kubo's statistical formalism, we show that the orientational fluctuations of interacting molecules are responsible for both the narrow central component and the broad Rayleigh-wing component in the light-scattering spectrum of a liquid crystalline material. The same formalism also describes the optical Kerr effect. We also point out the difference between the microscopic and the macroscopic order parameters.

The spectrum of light scattering from an isotropic nematic substance has a narrow central component presumably arising from fluctuations of the order parameter.[1] The order parameter here describes the orientational order of the long molecules in the medium.[2] On the other hand, a much broader central component was also observed in the spectrum.[3] Such a component always exists in ordinary liquids and is often called the Rayleigh-wing component.[4] It is well known that the Rayleigh-wing component comes from orientational fluctuations of molecules.[4] Thus, from the microscopic point of view, both components appear to be due to orientational fluctuations of molecules. It is then interesting to see how the orientational fluctuations can give rise to two very different components in the spectrum and how they are related. In this paper, we show from microscopic derivations that interaction between molecules is responsible for the observed results, and, in particular, the narrow central component appears because of the large mean-field modification on the orientational motion near a phase transition.

The orientational fluctuations are also directly related to the optical Kerr effect as a result of molecular reorientation.[5] From Kubo's fluctuation-dissipation theory,[6] we can express the birefringence induced by a linearly polarized optical field of sinusoidally varying intensity, $|E_0|^2(t) = |\mathcal{E}_0|_\Omega^2 \exp(-i\Omega t)$, in the isotropic phase as

$$\begin{aligned} &\delta n(\Omega) = (2\pi/n) F(\Omega) |\mathcal{E}_0|_\Omega^2, \\ &F(\Omega) = \delta\chi(\Omega)/|\mathcal{E}_0|_\Omega^2 = \beta\langle\delta\chi(0)\delta\chi(0)\rangle + i\Omega\beta\int_0^\infty \langle\delta\chi(0)\delta\chi(t)\rangle e^{-i\Omega t}\,dt, \end{aligned} \tag{1}$$

where $\beta \equiv 1/kT$, $\delta\chi(t)$ is the anisotropy in the susceptibility induced by the field, and the angular brackets indicate the ensemble average. On the other hand, the average induced anisotropy of the polarizability for each molecule is

$$\begin{aligned} &\delta\alpha(\Omega) = f(\Omega)|\mathcal{E}_0|_\Omega^2, \quad f(\Omega) = (\Delta\alpha) Q(\Omega)/|\mathcal{E}_0|_\Omega^2, \\ &Q(\Omega) = \left[\beta\langle S(0)S(0)\rangle + i\Omega\beta\int_0^\infty \langle S(0)S(t)\rangle e^{-i\Omega t}\,dt\right](2\Delta\alpha/3N)|\mathcal{E}_{1\mathrm{oc}}|_\Omega^2 = \gamma(\Omega)|\mathcal{E}_{1\mathrm{oc}}|_\Omega^2, \end{aligned} \tag{2}$$

where $\Delta\alpha = \alpha_\parallel - \alpha_\perp$ is the anisotropy of the molecular polarizability;

$$S = \sum_{i=1}^{N} s_i, \quad s_i = \tfrac{1}{2}(3\cos^2\theta_i - 1),$$

such that $Q = \langle S\rangle/N$ is the usual order parameter; N is the number of molecules per unit volume; and θ_i is the angle between $\vec{E}_0$ and the long axis of the ith molecule. $|\mathcal{E}_{1oc}|^2$ is the local field which is related to $|\mathcal{E}_0|^2$ by

$$\tfrac{2}{3}\Delta\alpha|\mathcal{E}_{1oc}|_\Omega{}^2 = V_0 Q(\Omega) + \tfrac{2}{3}\Delta\alpha|\mathcal{E}_0|_\Omega{}^2, \tag{3}$$

where $V_0Q(\Omega)$ is the local-field correction due to intermolecular interaction in the mean-field approximation.[2] We then obtain from Eq. (2)

$$f(\Omega) = (\Delta\alpha)\gamma(\Omega)[1 - \gamma(\Omega)V_0/\tfrac{2}{3}\Delta\alpha]^{-1}. \tag{4}$$

The relation between $F(\Omega)$ and $f(\Omega)$ is, from the Claussius-Mosotti equation,

$$F(\Omega) = Nf(\Omega)/(1 - \tfrac{4}{3}\pi N\alpha), \tag{5}$$

where α is the average polarizability.

Now that the spectrum of scattered radiation is given by

$$I(\Omega) = \mathrm{Re}[A\int_0^\infty \langle\delta\chi(0)\delta\chi(t)\rangle e^{-i\Omega t}\,dt], \tag{6}$$

where A is a proportional constant, we see immediately from Eq. (1) that

$$I(\Omega) = \mathrm{Re}\{[F(\Omega) - F(0)]A/i\omega\beta\}. \tag{7}$$

Then, in order to find $I(\Omega)$, we need only to find $\gamma(\Omega)$. We have calculated $\gamma(\Omega)$ after Zwanzig's approach.[7] We shall only sketch, in the following, the important steps of the calculations.

To find $\gamma(\Omega)$, we must first calculate the integral

$$(1/N)\int_0^\infty dt\, e^{-i\Omega t}\langle S(0)S(t)\rangle = (1/N)\int_0^\infty dt\, e^{-i\Omega t}\int d\hat{u}_0\, d\hat{u}\,\rho(\hat{u}_0)g(\hat{u}_0, \hat{u}, t)\sum_{i,j} s_i(0)s_j(t), \tag{8}$$

where $\hat{u}_0$ and $\hat{u}$ are the abbreviations indicating the orientations of the set of molecules initially and at time t, respectively, $\rho(\hat{u}_0)$ is the initial equilibrium distribution, and $g(\hat{u}_0, \hat{u}, t)$ is the probability of finding a specific set of orientations $\hat{u}$ at t when the initial set of orientations is $\hat{u}_0$. Thus, we have

$$\rho(\hat{u}_0) = e^{-\beta V}/\int d\hat{u}_0\, e^{-\beta V}, \tag{9}$$

where V is the intermolecular interaction potential. We shall use the simple form proposed by Maier and Saupe[2,8] for V:

$$V = \sum_i V_i = \sum_{i,j} C_{ij}s_i s_j, \quad i \neq j. \tag{10}$$

The function $g(\hat{u}_0, \hat{u}, t)$ obeys the rotational diffusion equation

$$\partial g/\partial t = \mathfrak{D}g, \tag{11}$$

where

$$\mathfrak{D}g = (1/\beta\zeta)\sum_n \vec{\Omega}_n\cdot[\vec{\Omega}_n g + \beta g\vec{\Omega}_n V], \quad \vec{\Omega}_n = \vec{r}_n \times \nabla_n,$$

and ζ is the frictional coefficient. The above equation, with the initial condition $g(t=0) = \delta(\hat{u}_0 - \hat{u}_0)$, gives

$$\int_0^\infty dt\, g(t)e^{i\Omega t} = -\delta(\hat{u} - \hat{u}_0)/(i\Omega + \mathfrak{D}). \tag{12}$$

Consequently, we can obtain from Eqs. (2) and (8)

$$\gamma(\Omega) = \gamma(0) + i\Omega\beta\frac{2\Delta\alpha}{3N}\int d\hat{u}\,(\sum_j s_j)\frac{-1}{i\Omega + \mathfrak{D}}\rho(\hat{u})\sum_i s_i, \quad \gamma(0) = \beta\frac{2\Delta\alpha}{3N}\int d\hat{u}\,\rho(\hat{u})\sum_{i,j} s_i s_j. \tag{13}$$

The evaluation of the above integrals is then carried out by perturbation expansion by assuming the intermolecular interaction potential V to be small compared with kT. This assumption is justified since, in the isotropic phase, we expect $\langle s_i s_j\rangle \ll 1$ and hence $\beta V_i \ll \beta\sum_j C_{ij} \approx 1$. The detailed calculations and the results are very similar to those in Zwanzig's case.[7] We find, to the second order,[9] that

$$\gamma(\Omega) \cong \tfrac{2}{15}\beta(\Delta\alpha)\left[\frac{1+18.4R}{1-4.4R-i\Omega\tau}+\frac{10R}{1-i\Omega\tau/2}+\frac{-4.2R}{1-i3\Omega\tau/13}\right], \tag{14}$$

where $\tau = \zeta/6kT$ and $R = (2/35)^2\beta^2\sum_{l,k} C_{lk}C_{kl}$. Then, from Eqs. (4) and (5), we obtain the expression

$$F(\Omega) = B\textstyle\sum_k C_k/(1-i\Omega\tau_k) \tag{15}$$

where

$$\begin{aligned} &B = [N/(1-\tfrac{4}{3}\pi N\alpha)]\tfrac{2}{75}(\Delta\alpha)^2;\\ &\tau_1 = \tau/[1-(T_c/T)+\theta(\beta^2C^2)], \quad \tau_2 = (\tau/2)[1+\theta(\beta^2C^2)], \quad \tau_3 = (3\tau/13)[1+\theta(\beta^2C^2)],\\ &C_1 = [1-(T_c/T)]^{-1}[1+28.6R/(1-T_c/T)][1+\theta(\beta^2C^2)],\\ &C_2 = 10[1+(T_c/T)]^{-2}R+\theta(\beta^3C^3), \quad C_3 = -4.2[1+(T_c/T)]^{-2}R+\theta(\beta^3C^3), \quad T_c = V_0/5k; \end{aligned} \tag{16}$$

$\theta(\beta^n C^n)$ is a term of the order of $\beta^n C^n$.

The spectrum of light scattering by orientational fluctuations can now be obtained by inserting Eq. (15) into Eq. (7). We see immediately that the spectrum is composed of several Lorentzian components with the intensity ratio given by $C_1:C_2:C_3$. The strongest component is C_1 and has a half-width $1/\tau_1$. We notice in Eq. (16) that if we neglect terms of $\theta(\beta^n C^n)$ with $n \geq 2$, then we can write

$$C_1 = T/(T-T_c), \quad \tau_1 = \zeta/6k(T-T_c), \tag{17}$$

which have the same forms as those derived for order-parameter fluctuations from the Landau-de Gennes theory.[10] T_c here is in fact identical to the second-order phase transition temperature derived from the mean-field theory by Maier and Saupe.[2] Consequently, we can say that the C_1 component is the same component known to be due to order-parameter fluctuations,[1,10] or, in our present language, it is due to orientational fluctuations of molecules under the influence of the mean field created by intermolecular interaction. Both the intensity and the inverse width of this component show the critical behavior which has been demonstrated experimentally in liquid crystalline materials.[1] In ordinary liquids, T_c is below the liquid-solid transition temperature and cannot be reached.

The other components in the spectrum arise from the correlated effect of intermolecular interaction. The fluctuating molecule modifies the dynamics of the orientational motion of neighboring molecules which, in turn, modify the dynamics of the orientational fluctuations of the original molecule. This case is analogous to the case of coupled damped harmonic oscillators. In both cases, new modes are created through coupling. Since $V_0 = \sum_k C_{ik}$ and hence $R = 4T_c/49T$, we find from Eq. (16) that C_2 and C_3 are about 10^4 times smaller than C_1. The corresponding half-widths $1/\tau_2$ and $1/\tau_3$ are characteristics of orientational fluctuations of a few molecules. Both components should not show critical behavior as $T \to T_c$.

The experimental results of Rayleigh-wing scattering in N-[p-methoxybenzylidine]-p-butylaniline (MBBA) indeed showed two broad Lorentzian components with no critical behavior.[3] Their integrated intensities were about 10^4 times smaller than that of the component due to order-parameter fluctuations studied by Stinson and Litster.[1] The variation of $1/\tau_2$ and $1/\tau_3$ with temperature is shown in Fig. 1 in comparison with theoretical predictions. For the theoretical curve, we have used $\zeta = a\eta(T)$, where a is an adjustable constant different for different components[1] and $\eta(T)$ is

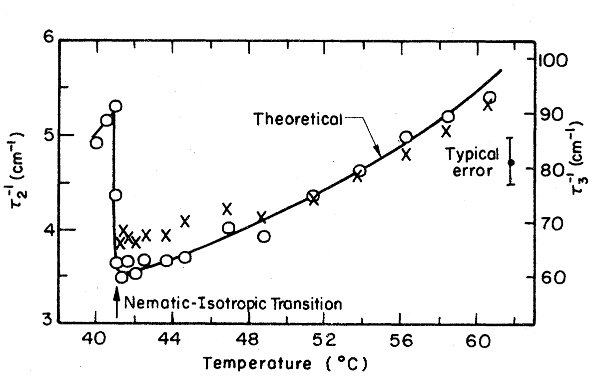

FIG. 1. Comparison of theoretical Rayleigh-wing linewidths in MBBA as a function of temperature with experimental data (circles for τ_2^{-1} and crosses for τ_3^{-1}) obtained by Amer, Lin, and Shen in Ref. 3.

the shear viscosity determined by Martinoty, Candau, and Debeauvais.[11] The agreement between theory and experiment is fairly good. We should, however, emphasize here that our theory is only meant to explain qualitatively the characteristic difference between the various components of light scattering due to molecular orientational fluctuations. Like other microscopic theories for liquids, because of the simplifying assumption on molecular interaction, it would not explain experimental results quantitatively. For example, we have not taken into account molecular collision which is believed to have strong influence on Rayleigh-wing scattering.[4]

From Eqs. (1) and (15), we can also find the time variation of the field-induced refractive index induced by a time-dependent field[6] $|\mathcal{E}_0|^2(t)$:

$$\delta n(t) = (2\pi/n)B\textstyle\sum_k (C_k/\tau_k)\int_{-\infty}^{t} |\mathcal{E}_0|^2(t') \exp[-(t-t')/\tau_k]dt'. \tag{18}$$

Again, the C_1 component dominates here. This equation applies to the optical Kerr effect. Such an effect in an isotropic nematic substance has recently been measured.[12]

Finally, we can obtain the equation of motion for $\delta n(t)$, or $\delta\chi(t) = n\delta n(t)/2\pi$, from Eq. (18):

$$(\partial/\partial t)\delta\chi(t) + A\textstyle\sum_k (C_k/\tau_k^2)\int_{-\infty}^{t} |\mathcal{E}_0|^2(t')\exp[-(t-t')/\tau_k]dt' = A\sum_k (C_k/\tau_k)|\mathcal{E}_0|^2(t). \tag{19}$$

If we retain only the C_1 terms in Eq. (19), we then find

$$(\partial/\partial t + \tau_1^{-1})\delta\chi(t) = A(C_1/\tau_1)|\mathcal{E}_0|^2. \tag{20}$$

de Gennes[10] has pointed out that $\delta\chi$ can be taken as the macroscopic order parameter. We recognize that Eq. (20) is in exactly the same form as the equation of motion for the macroscopic order parameter derived by de Gennes from thermodynamic consideration.[10] As seen from the above derivation, the macroscopic order parameter is different from the microscopic order parameter $Q = \langle\sum_i (3\cos^2\theta_i - 1)/2\rangle/N$. The two are related through the local field correction.

In conclusion, we have shown that the orientational fluctuations of molecules are responsible for both the narrow central component (known to be due to order parameter fluctuations) and the broad Rayleigh-wing component in the light-scattering spectrum of an isotropic liquid crystalline substance. The broad wing is due to coupling between fluctuating molecules through intermolecular interaction. We have also derived expressions for the optical Kerr response due to molecular reorientation and the equation of motion for the macroscopic order parameter. The theory is general. In particular, it also applies to solids such as the plastic crystals. Observations of light scattering by orientational fluctuations and the corresponding optical Kerr effect in a plastic crystal have recently been reported.[13,14]

One of us (Y.R.S.) thanks Dr. N. M. Amer for helpful discussions in formulating the problem. He also acknowledges the partial research support from the U. S. Atomic Energy Commission and the Guggenheim Memorial Foundation, and the hospitality of Professor J. Ducuing at the Laboratoire d'Optique Quantique.

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