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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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FEBRUARY 1974

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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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ABSTRACT

Using 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 due to 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, $|E_o|^2(t) = |\mathcal{E}_o|^2_\Omega \exp(-i\Omega t)$, in the isotropic phase as

$$\delta n(\Omega) = (2\pi/n)F(\Omega)|\mathcal{E}_o|^2_\Omega$$

$$F(\Omega) = \delta\chi(\Omega)/|\mathcal{E}_o|^2_\Omega$$

$$= \beta < \delta\chi(0)\ \delta\chi(0) > + i\Omega\beta\int_o^\infty < \delta\chi(0)\delta\chi(t) > e^{-i\Omega t}dt \qquad (1)$$

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

$$\delta\alpha(\Omega) = f(\Omega)|\mathcal{E}_o|^2_\Omega$$

$$f(\Omega) = (\Delta\alpha)\ Q(\Omega)/|\mathcal{E}_o|^2_\Omega$$

$$Q(\Omega) = [\beta < S(0)S(0) > + i\Omega\beta\int_o^\infty <S(0)S(t) > e^{-i\Omega t}dt](2\Delta\alpha/3N)|\mathcal{E}_{\ell oc}|^2_\Omega$$

$$= \gamma(\Omega)|\mathcal{E}_{\ell oc}|^2_\Omega \qquad (2)$$

where $\Delta\alpha = \alpha_\parallel - \alpha_\perp$ is the anisotropy of the molecular polarizability, $S = \sum_{i=1}^{N} s_i$, $s_i = (3\cos^2\theta_i - 1)/2$ such that $Q = \langle S \rangle /N$ is the usual order parameter, N is the number of molecules per unit volume, θ_i is the angle between $\vec{E}_o$ and the long axis of the ith molecule, and $|\mathcal{E}_{\ell oc}|^2$ is the local field which is related to $|\mathcal{E}_o|^2$ by

$$(2\Delta\alpha/3)|\mathcal{E}_{\ell oc}|^2_\Omega = V_o Q(\Omega) + (2\Delta\alpha/3)|\mathcal{E}_o|^2_\Omega \qquad (3)$$

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

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

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

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

where α is the average polarizability.

Now that the spectrum of scattered radiation is given by

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

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 only need to find $\gamma(\Omega)$.

We have calculated $\gamma(\Omega)$ following Zwanzig's approach.[7] In fact, the present case resembles very closely Zwanzig's case except that here, induced dipoles are involved and hence the mathematical manipulation is more complicated. Because of limitation in space, we shall only sketch in the following the important steps of the calculations. The details will be published elsewhere.

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

$$(1/N)\int_0^\infty dt\ e^{-i\Omega t}\langle S(0)S(t)\rangle = (1/N)\int_0^\infty dt\ e^{-i\Omega t}\times$$

$$\times\int d\hat{u}_o d\hat{u}\rho(\hat{u}_o)g(\hat{u}_o,\hat{u},t)\sum_{i,j} s_i(0)s_j(t) \tag{8}$$

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

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

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

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

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

$$\partial g/\partial t = \mathcal{L}g$$

$$= (kT/\zeta\sum_n \vec{\Omega}_n \cdot [\vec{\Omega}_n g + \beta g\vec{\Omega}_n V]$$

$$\vec{\Omega}_n = \vec{r}_n \times \nabla_n \tag{11}$$

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

$$g(t) = [\exp(t\mathcal{D})]\ \delta(\hat{u} - \hat{u}_o)$$

or

$$\int_o^\infty dt\ g(t)\ e^{i\Omega t} = -\delta(\hat{u} - \hat{u}_o)/(i\Omega + \mathcal{D}). \tag{12}$$

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

$$\gamma(\Omega) = \gamma(0) + i\Omega\beta\ \frac{2\Delta\alpha}{3N} \int d\hat{u}(\sum_j s_j)\ \frac{-1}{i\Omega+\mathcal{D}}\ \rho(\hat{u}) \sum_i s_i$$

$$\gamma(0) = \beta(2\Delta\alpha/3N) \int d\hat{u}\ \rho(\hat{u}) \sum_{i,j} s_i s_j. \tag{13}$$

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. The detailed calculations and the results are very similar to those in Zwanzig's case.[7] We find to the second order[9]

$$\gamma(\Omega) \cong \gamma(0) + a_o + a_1 + a_2$$

$$a_o = i\Omega\tau\gamma(0)/(1 - i\Omega\tau)$$

$$\gamma(0) = \frac{2}{3}\beta(\Delta\alpha)\ [\frac{1}{5} + \frac{23}{4} R(\beta^2 C^2)]$$

$$\tau = \zeta/6kT$$

$$a_1 = \frac{2}{3}\beta(\Delta\alpha)\ \frac{i\Omega\tau}{1-i\Omega\tau}\ [\frac{2}{1-i\Omega\tau/2} + \frac{-36/65}{1-i3\Omega\tau/13}]R(\beta^2 C^2)$$

$$a_2 = \frac{2}{3}\beta(\Delta\alpha)\ \frac{i\Omega\tau}{(1-i\Omega\tau)^2}\ [\frac{3}{1-i\Omega\tau/2} + \frac{-256/65}{1-i3\Omega\tau/13}]R(\beta^2 C^2)$$

$$R(\beta^2 C^2) = (2/35)^2\beta^2 \sum_{\ell,k} C_{\ell k} C_{k\ell}. \tag{14}$$

With some manipulation, we can reduce $\gamma(\Omega)$ to the form

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

Then, from Eqs. (4) and (5), we obtain the expression

$$F(\Omega) = B \sum_k [C_k/(1-i\Omega\tau_k)] \tag{16}$$

where

$$B = \frac{N}{1-4\pi N\alpha/3}\ \frac{2}{75}\ (\Delta\alpha)^2.$$

$$\tau_1 = \tau/[1-(3V_o/2\Delta\alpha)\gamma(0) + \theta(\beta^3C^3)]$$

$$\tau_2 = \tau/2[1+\theta(\beta^3C^3)]$$

$$\tau_3 = 3\tau/13[1+\theta(\beta^3C^3)]$$

$$C_1 = [1-(3V_o/2\Delta\alpha)\gamma(0)]^{-1}[1+\theta(\beta^2C^2)]$$

$$C_2 = \theta(\beta^2C^2)$$

$$C_3 = \theta(\beta^2C^2) \tag{17}$$

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

The spectrum of light scattering by orientational fluctuations can now be obtained by inserting Eq. (16) 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 halfwidth $1/\tau_1$. We notice in Eq. (17) that if we neglect terms of $\theta(\beta^nC^n)$ with $n \geqslant 2$, then we can write

$$C_1 = T/(T - T_c)$$

$$\tau_1 = \zeta/6k(T - T_c) \tag{18}$$

where $T_c = V_o/5k$. We recognize that C_1 and τ_1 in Eq. (18) have the same forms as those derived for order-parameter fluctuations from the Landau-de Gennes theory,[10] and 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 dampled harmonic oscillators. In both cases, new modes are created through coupling. We notice that C_2 and C_3 are of the order of $(\beta C)^2$ smaller than C_1. The corresponding halfwidths $1/\tau_2$ and $1/\tau_3$ are the damping characteristics of the orientational fluctuations of a few molecules. Both components do not show the critical behavior as T approaches T_c. The experimental results of Rayleigh-wing scattering in liquid crystals indeed show two broad Lorentzian components.[3] They agree qualitatively with the above description. In particular, the results confirm the temperature dependence of τ_2 and τ_3 described by Eq. (17).

From Eqs. (1) and (16), we can also find the time variation of the field-induced refractive index induced by a time-dependent field $|\mathcal{E}_o|^2(t)$[6]

$$\delta n(t) = (2\pi/n)B \sum_k (C_k/\tau_k)\int_{-\infty}^{t}|\mathcal{E}_o|^2(t') \exp[-(t-t')/\tau_k]dt'. \qquad (19)$$

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.[11]

Finally, we can obtain the equation of motion for $\delta n(t)$ or $\delta\chi(t) = n\delta n(t)/2\pi$ from Eq. (19)

$$\frac{\partial}{\partial t}\,\delta\chi(t) + A\sum_k \frac{C_k}{\tau_k^2}\int_{-\infty}^{t}|\mathcal{E}_o|^2(t')\,\exp[-(t-t')/\tau_k]dt' = A\sum_k (C_k/\tau_k)|\mathcal{E}_o|^2(t). \tag{20}$$

If we retain only the C_1 terms in Eq. (20), we then find

$$\left(\frac{\partial}{\partial t} + \frac{1}{\tau_1}\right)\delta\chi(t) = A\,\frac{C_1}{\tau_1}\,|\mathcal{E}_o|^2. \tag{21}$$

de Gennes[10] has pointed out that $\delta\chi$ can be taken as the macroscopic order parameter. We recognize Eq. (21) 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 critical behavior of the central component results from the mean local-field correction on the orientational motion of the molecules. The broad wing is due to coupling between fluctuating

molecules through intermolecular interaction. From the results for light scattering, we can derive 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 be reported.[12,13]

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