9-9-1996

Observation Of Light Diffusion And Correlation Transport In Nematic Liquid Crystals

M. H. Kao

Kristen Anne Jester , '94

A. G. Yodh

Peter J. Collings
Swarthmore College, pcollin1@swarthmore.edu

Observation of Light Diffusion and Correlation Transport in Nematic Liquid Crystals

M. H. Kao, K. A. Jester, and and A. G. Yodh
Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6396

P. J. Collings
Department of Physics and Astronomy, Swarthmore College, Swarthmore, Pennsylvania 19081-1397
(Received 11 December 1995)

Light diffusion and temporal correlation transport are studied in an orientationally ordered multiply scattering medium. In particular, we experimentally demonstrate the anisotropic diffusion of light through a turbid nematic liquid crystal, and we measure the temporal correlations of these diffused speckle fields for the first time. The measurements are shown to provide useful information about this material, specifically the average rotational viscosity of the director. Computer simulations corroborate both the experimental observations and a more rigorous analytic theoretical formulation of this problem. [S0031-9007(96)01117-9]

PACS numbers: 61.30.Gd, 42.70.Df, 78.20.Ci, 78.30.L y

The careful consideration of light transport through turbid media has revealed a variety of exciting phenomena and applications. Recent fundamental advances include, for example, the discoveries of coherent backscattering [1] and hidden correlations [2] from disordered media, studies of light diffusion in highly scattering media with photon gain [3], and the development and application of diffusing wave spectroscopy (DWS) [4], whereby temporal correlations of highly scattered light elucidate dynamical motions in complex fluids, particularly colloids [5]. In addition, diffusing photons are now used to generate low resolution images of absorption and scattering variations in tissues [6]. Virtually all of the media studied with diffusing light have been isotropic. In this paper we investigate the nature of light diffusion and correlation transport through an *orientationally ordered* turbid material.

Nematic liquid crystals are composed of translationally disordered rod shaped molecules that tend to align along the same direction. The preferred direction is described by a unit vector called the director. As a result of these directional correlations, nematics present interesting complications for light diffusion that extend beyond isotropic, random media. The optical properties of nematic liquid crystals are highly anisotropic [7]. For example, the light scattering cross sections originate from local director fluctuations and depend on the direction of the electric field and propagation vectors with respect to the average molecular orientation. Furthermore, nematic liquid crystals strongly scatter visible light; samples with thicknesses greater than a few millimeters appear milky white, and by analogy with milky white colloids one might expect that photons diffuse through these media. Indeed in two elegant recent papers [8], coherent backscattering from turbid nematics has been reported.

In this Letter we describe experiments that demonstrate the anisotropic diffusion of light through a nematic liquid crystal. We also study for the first time temporal fluctuations of the diffused speckle fields, obtaining temporal autocorrelation functions of the emerging speckle in several geometries, and showing that these measurements provide useful information about material properties. Finally, computer simulations of light transport through nematic liquid crystals corroborate experimental observations as well as a more rigorous theoretical formulation [9] of this problem. In total, the work elucidates the importance of anisotropy for imaging and spectroscopic studies that employ diffusing light probes. The dynamical results, for example, differ in an interesting way from previous DWS work in colloids, foams, and emulsions, because the same motional processes that give rise to material dynamics in nematic liquid crystal are also responsible for light scattering. Finally, these measurements may be useful for the investigation of hydrodynamics [10] on short time scales where single light scattering studies are ineffectual.

The scattering and dynamics in nematic liquid crystals are caused by orientational fluctuations of the director $\mathbf{n}$. The differential cross section for single light scattering depends on the amplitude of the director fluctuations $\delta\mathbf{n}(\mathbf{r}, t)$, which are perpendicular to their average value $\mathbf{n}_0$. The differential cross section for a nematic liquid crystal with volume V is [7]

$$\frac{d\sigma}{d\Omega} = V\left(\frac{\Delta\epsilon\omega^2}{4\pi c^2}\right)^2 \frac{n_f k_B T}{n_i \cos\delta_i} \sum_{\alpha=1}^{2} \frac{(i_\alpha f_z + i_z f_\alpha)^2}{K_\alpha(q)}. \quad (1)$$

Here $K_\alpha(q) = K_3 q_\parallel^2 + K_\alpha q_\perp^2 + \chi_a H^2$, the K_i are the Frank elastic constants, $\Delta\epsilon = \epsilon_\parallel - \epsilon_\perp$ is the difference in dielectric constant parallel and perpendicular to the director, respectively, χ_a is the anisotropy of the magnetic susceptibility, $\mathbf{H}$ is an applied magnetic field that aligns the director, $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ is the scattering wave vector which depends on the incoming ($\mathbf{k}_i$) and outgoing ($\mathbf{k}_f$) light wave vectors and has components parallel ($q_\parallel$) and perpendicular ($q_\perp$) to $\mathbf{n}_0$, $\mathbf{f}$ is the output light polarization direction, in components f_z along $\mathbf{n}_0$ and f_α along the unit vectors $\mathbf{e}_\alpha$ of the director fluctuation eigenmodes [11], and $\mathbf{i}$ is the input light polarization direction, which can also be

broken into components parallel and perpendicular to $\mathbf{n}_0$. ω is the light frequency, c is the speed of light in vacuum, n_i is the index of refraction associated with incident wave direction $\mathbf{k}_i$ and polarization direction $\mathbf{i}$, n_f is the index of refraction associated with scattered wave direction $\mathbf{k}_f$ and polarization direction $\mathbf{f}$, δ_i is the angle between $\mathbf{k}_i$ and its associated Poynting vector, k_B is Boltzmann's constant, and T is the sample temperature. Examination of Eq. (1) reveals that the scattering is strongly peaked in the forward direction, depends on $\mathbf{k}_i$ and $\mathbf{k}_f$ rather than $\mathbf{q}$ alone, and will typically cross couple ordinary and extraordinary light beams.

The director fluctuations are viscously damped. The damping time $\tau_\alpha(\mathbf{q})$, for the q-space mode $\delta\mathbf{n}_\alpha(\mathbf{q}, t)$ is given by $\tau_\alpha(\mathbf{q}) = \eta_\alpha(\mathbf{q})/K_\alpha(\mathbf{q})$, where the mode viscosity $\eta_\alpha(\mathbf{q})$ is a combination of viscosities that appear in the Leslie-Erickson equations [10] governing the director hydrodynamics. Thus the normalized single scattering electric field temporal autocorrelation function is

$$G_1(\mathbf{k}_i, \mathbf{i}, \mathbf{k}_f, \mathbf{f}; \tau) = \frac{\sum_{\alpha=1}^{2} F_\alpha(\mathbf{q}; \mathbf{k}_i, \mathbf{i}, \mathbf{k}_f, \mathbf{f}) \exp(\frac{-\tau}{\tau_\alpha})}{\sum_{\alpha=1}^{2} F_\alpha(\mathbf{q}; \mathbf{k}_i, \mathbf{i}, \mathbf{k}_f, \mathbf{f})},$$

where $F_\alpha(\mathbf{q}; \mathbf{k}_i, \mathbf{i}, \mathbf{k}_f, \mathbf{f}) = (i_\alpha f_z + i_z f_\alpha)^2/K_\alpha(q)$. Following the spirit of DWS, we envision the transport of photons through an optically thick nematic liquid crystal as a sequence of independent single scattering events from local volumes within the sample. After N scattering events, the autocorrelation function of the emerging speckle field, $g_1^N(\tau)$, equals the average value of $G_1(\mathbf{q}; \mathbf{k}_i, \mathbf{i}, \mathbf{k}_f, \mathbf{f}; \tau)$ among the scattering events in the sequence, raised to the power N [12]. When $\tau/\tau_\alpha(\mathbf{q}) \ll 1$, the phase-dependent piece of this result takes a simple form,

$$g_1^N(\tau) = \{\exp[-(K'/\eta')\tau]\}^N, \tag{2}$$

where

$$\frac{1}{K'} = \left\langle \sum_{\alpha=1}^{2} \frac{p_\alpha}{K_\alpha(\mathbf{q})} \right\rangle_{\mathbf{k}_i, \mathbf{i}, \mathbf{k}_f, \mathbf{f}}$$
$$\frac{1}{\eta'} = \left\langle \sum_{\alpha=1}^{2} \frac{p_\alpha}{\eta_\alpha(\mathbf{q})} \right\rangle_{\mathbf{k}_i, \mathbf{i}, \mathbf{k}_f, \mathbf{f}}, \tag{3}$$

where $p_\alpha = (i_\alpha f_z + f_\alpha i_z)^2$. The averages $\langle \cdots \rangle_{\mathbf{k}_i, \mathbf{i}, \mathbf{k}_f, \mathbf{f}}$ in Eq. (3) are calculable, but are considerably more complex than in conventional DWS in that they necessarily involve an integration over all possible $\mathbf{k}_i$ and $\mathbf{k}_f$. Furthermore, for cw temporal autocorrelation measurements, we must add up the contributions of all possible photon paths between our source and detector. In a nematic liquid crystal this problem is complicated by the fact that diffusion is anisotropic so that the average time interval between photon entry and exit does not depend purely on source-detector separation.

The light energy density $U(\mathbf{r}, t)$ obeys an anisotropic diffusion equation [9] in these media which, in the absence of sources, is simply

$$\frac{\partial U(\mathbf{r}, t)}{\partial t} = (D_\parallel \nabla_\parallel^2 + D_\perp \nabla_\perp^2) U(\mathbf{r}, t). \tag{4}$$

The nematic liquid crystal has light diffusion constant $D_\parallel(D_\perp)$ in the direction parallel (perpendicular) to $\mathbf{n}_0$. The anisotropic diffusion equation may be solved to yield $P(t)$, the probability per unit time that a photon launched on the input side of the sample arrives at the detector. $P(t)$ depends on geometry $D_\parallel$, $D_\perp$, and, in contrast to the isotropic case, it also depends on the orientation of the source-detector displacement vector relative to $\mathbf{n}_0$. On the other hand, the average value of $G_1(\mathbf{k}_i, \mathbf{i}, \mathbf{k}_f, \mathbf{f}; \tau)$ among the scattering events in the sequence does not depend on path since, in the limit of many scattering events, the net photon momentum transfer for the entire process does not introduce a significant constraint on $\mathbf{k}_i, \mathbf{k}_f$, and $\mathbf{q}$ for a typical event in the sequence. Setting $N = t/\langle t \rangle$, where $\langle t \rangle = \langle l(\mathbf{k}_i, \mathbf{i})/v \rangle_{\mathbf{k}_i, \mathbf{i}}$ is the average time between scattering events in the sample, and $l(\mathbf{k}_i, \mathbf{i})$ is the mean free path for a photon traveling with wave vector $\mathbf{k}_i$, polarization $\mathbf{i}$, and velocity $\mathbf{v}$, we may obtain [9] the measured DWS electric field autocorrelation function, $g_1(\tau)$, i.e.,

$$g_1(\tau) = \int_0^\infty dt\, P(t) \exp[-(A\tau/\gamma_{\text{eff}})t], \tag{5}$$

where $A = 2k_B T \Delta\epsilon^2 \omega^4/9\pi c^3 \sqrt{\epsilon_\perp}$ is a constant related to the optical anisotropy, and γ_{eff} is an effective viscosity which comes from an arithmetic and angular average of the mode viscosities $\eta_\alpha(\mathbf{q})$ mentioned above. In Eq. (5) we see that the light diffusion affects only $P(t)$. This is quite different from the isotropic problem in colloidal suspensions where the photon random walk step appears in the *dynamical decay rate as well as in* $P(t)$. Physically this arises because the light scattering process in liquid crystals is the same process that gives rise to dynamics in the sample, whereas in colloids particle scattering affects light diffusion while particle motion affects the dynamical decay rates. We see from Eq. (5) that the measured temporal decay will provide direct information about the γ_{eff}.

We have performed experiments with p-pentyl-p'-cyanobiphenyl (5CB), a nematic liquid crystal with $T_c = 35$ °C, in order to test these ideas. Our experimental setup is shown in Fig. 1. The liquid crystal was housed in a temperature controlled glass cylindrical cell that was 1 cm thick and 2 cm in diameter. The entire sample was placed in a 2 kG magnetic field that oriented the director along the z direction shown in Fig. 1(a). The sample was slowly cooled from the isotropic phase in this field in order to improve sample homogeneity. The magnetic coherence length at these fields was about 12 μm. Light at $\lambda = 514.5$ nm from an Ar-ion laser was incident on the center of the sample face for all measurements. Generally, the polarization of input and output beams could be independently oriented parallel and perpendicular to the director. The illuminating area was about 1 mm^2 in all experiments except the backscattering temporal correlation measurements. For detection in

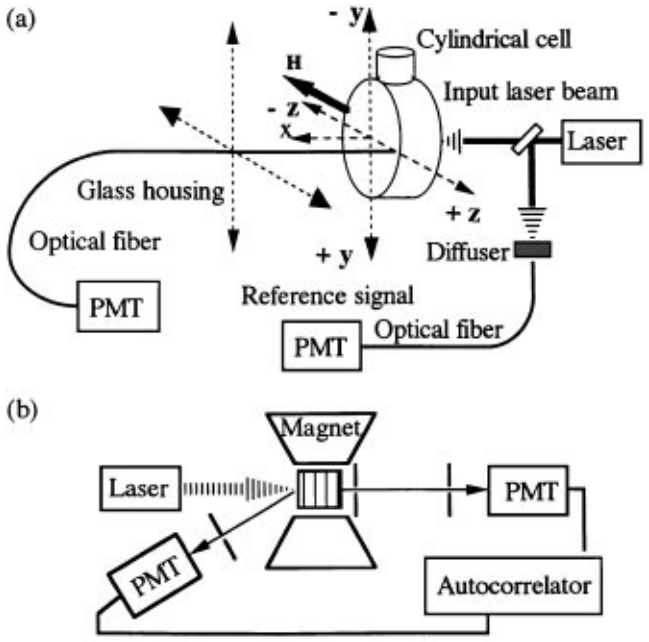

FIG. 1. (a) Diffuse transmission measurement. (b) Temporal correlation measurement. The coordinate system chosen uses the x axis along the incident light direction, the z axis along the director, and the y axis along the direction perpendicular to both the director and light incident direction.

transmission we used a multimode fiber that we translated to different locations on the back face of the cylindrical cell. The fiber was coupled directly to a photomultiplier tube (PMT), from which the detected photons were passed to a digital temporal autocorrelator with 25 nsec minimum bin width. Consistency checks were performed using colloidal suspensions with comparable optical properties in the same apparatus (see discussion below).

The results of our first set of measurements are shown in Fig. 2. Here we measured the diffuse transmission through the cell in directions parallel and perpendicular to the director, i.e., along the z and y axes of Fig. 1(a), respectively. The accuracy of the measurements was determined by finding, for each point, the standard deviation of the mean of each of the 16 runs performed, which gives an accuracy of about 0.5%. Variation of input and output relative polarizations were not observed to affect either these profiles or their ratio. Clearly, anisotropy exists, and, as seen in the relative widths of the transmission intensity profiles, $D_{\parallel}$ is larger than $D_{\perp}$. In Fig. 2(a) we exhibit the transmitted intensity profile parallel to the director in both the positive and negative z directions. For the transmitted intensity profile perpendicular to the director, we only consider the positive y direction because, referring back to Fig. 1, measurements along the negative y direction have a different boundary condition than the other three portions of the scan due to the opening in the sample cell; therefore we neglect this data. Also, a slight asymmetry about the center of the sample cell exists in the scan parallel to the director. This asymmetry is due, in part, to the difficulty in locating the precise center of the sample cell, and therefore the center of the intensity distribution. In Fig. 2(b) we plot the ratio of parallel to perpendicular transmissions as a function of radial position from the sample center. The graph is an average of the positive z data and the negative z data, each divided by the data in the positive y direction. The error bars are determined by the difference in each of these ratios. This average takes into account the asymmetry in Fig. 2(a). As expected, the anisotropy increases rapidly over the length scales probed. Using the anisotropic diffusion equation [Eq. (4)] for light transport in the cylindrical cell, it is possible to estimate the ratio of $D_{\parallel}$ to $D_{\perp}$ by finding the best numerical fit to the data. We have performed these studies and conclude that $D_{\parallel}/D_{\perp}$ is 1.60 ± 0.25.

In a set of control measurements we filled the same cell with a colloidal suspension of comparable optical density created from polystyrene spheres. No anisotropy in diffuse transmission was observed within the experimental error of 0.5%, and by adjusting the particle concentration we were able to determine the value of the isotropic photon random walk step that gave a transmission profile midway between the profiles shown in Fig. 2(a). The colloid random walk step l^* was 0.75 ± 0.10 mm. This gives us a rough estimate for the light diffusion constant of the turbid nematic 5CB at 514.5 nm, and indicates that the sample thickness was well over 10 random walk steps.

The dynamics of the system were probed in two different geometries. The measured temporal autocorrelation functions for backscattering and transmission are shown in Fig. 3. In the case of backscattering, an approximate

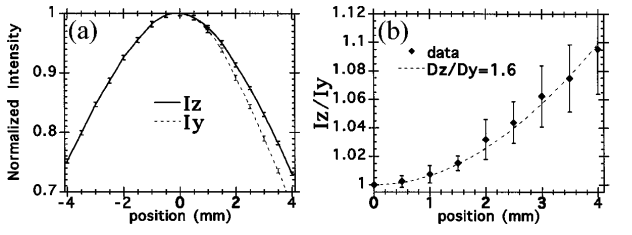

FIG. 2. Anisotropic diffusive transmission in 5CB. The coordinate system follows Fig. 1. (a) Normalized diffuse transmission intensity parallel and perpendicular to the director. (b) The ratio of the diffusive transmission intensity parallel to the director to that perpendicular to the director as a function of distance from the center of the cylindrical cell. The dashed line is the calculated result obtained by solving Eq. (4).

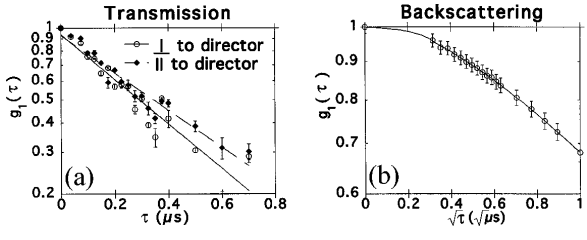

FIG. 3. Dynamical temporal measurements in 5CB. (a) Forward scattering. (b) Backscattering.

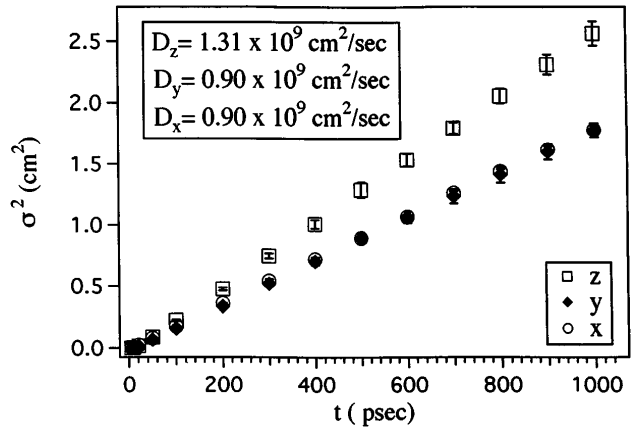

FIG. 4. Results of computer simulations. The square of the width of photon distribution as function of time is plotted. The linear relationship indicates the photon propagation is diffusive. The coordinate system follows Fig. 1.

plane-wave-in/point-out geometry was employed where the input spot size was ~4 mm in diameter.

For the transmission experiments, we measured the correlation function at two detector locations radially symmetric about the input beam (4 mm from the central axis), but with one detector displaced along the director and the other displaced perpendicular to the director. Again, no polarization effects were found. We were able to obtain correlation functions in both cases, and while some differences were observed, we found that within our signal-to-noise it was difficult to distinguish these two curves. To extract the temporal decay rates, and hence the director's effective rotational viscosity, we used both the forward scattering and backscattering temporal correlation functions, and we demanded that the light diffusion constants, and the rotational viscosity agree in all cases. We obtained good agreement between the three values. The γ_{eff} was found to be 60 $\pm$ 10 cps, in reasonable agreement with the value of 70 cps that may be obtained by other techniques [7]. In addition, the average l^* was found to be about 0.75 $\pm$ 0.2 mm. Because of the rather similar observed decays from the different source-detector configurations, a single l^* was sufficient for these fits.

As a final check we performed numerical simulations of diffusion in the 5CB system using experimental values for the elastic constants [13]. In the simulations, we launched photons into the medium and allowed these photons to propagate and scatter according to probabilities that can be determined using the measured constants and Eq. (1). Some key results of these simulations are shown in Fig. 4. Here we plot the square of the half-width, σ^2, of the photon distribution in space as a function of time for motion parallel and perpendicular to the director. We see that the motion is diffusive and that the diffusion constants and their ratio are easily determined from these curves. We obtain $D_{\parallel} = 1.3 \times 10^9$ cm^2/sec and $D_{\perp} = 0.9 \times 10^9$ cm^2/sec. This is in reasonable agreement with experiment and a more rigorous analytical theory that uses these same input parameters for 5CB [9].

We acknowledge useful discussions with Holger Stark, Tom Lubensky, and David Pine. This work has been supported by the NSF through Grant No. DMR93-06814, through the MRL program Grant No. DMR91-20668, both to the University of Pennsylvania, and through Grant No. DMR92-24617 to Swarthmore College.

Note added.—While this paper was being processed for publication, a related theoretical paper [B. A. van Tiggelen, R. Maynard, and A.Heiderich, Phys. Rev. Lett. **77**, 639 (1996)] was published. Its results are in good agreement with ours.

[1] Y. Kuga and A. Ishimaru, J. Opt. Soc. Am. A **1**, 831 (1984); P. E. Wolf and G. Maret, Phys. Rev. Lett. **55**, 2696 (1985); M. P. van Albada and A. Lagendijk, Phys. Rev. Lett. **55**, 2692 (1985).

[2] S. Feng and P. A. Lee, Science **251**, 633 (1991); N. Garcia and A. Z. Genack, Phys. Rev. Lett. **63**, 1678 (1989); M. P. van Albada, J. F. de Boer, and A. Lagendijk, Phys. Rev. Lett. **64**, 2787 (1990).

[3] N. M. Lawandy, R. Balachandran, A. Gomes, and E. Sauvin, Nature (London) **368**, 436–438 (1994); D. S. Wierswa, M. P. Vanalbada, and A. Lagendijk, Phys. Rev. Lett. **75**, 1739–1742 (1995).

[4] G. Maret and P. E. Wolf, Z. Phys. B **65**, 409 (1987); M. J. Stephen, Phys. Rev. B **37**, 1 (1988); D. J. Pine, D. A. Weitz, P. M. Chaikin, and E. Herbolzheimer, Phys. Rev. Lett. **60**, 1134 (1988).

[5] X. Qiu *et al.*, Phys. Rev. Lett. **65**, 516 (1990); P. D. Kaplan, A. G. Yodh, and D. J. Pine, Phys. Rev. Lett. **68**, 393 (1992); J. X. Zhu *et al.*, Phys. Rev. Lett. **68**, 2559 (1992); M. H. Kao, A. G. Yodh, and D. J. Pine, Phys. Rev. Lett. **70**, 242 (1993); S. J. Nilsen and A. P. Gast, J. Chem. Phys. **101**, 4975 (1994); A. J. C. Ladd, H. Gang, J. X. Zhu, and D. A. Weitz, Phys. Rev. Lett. **74**, 318 (1995).

[6] A. Yodh and B. Chance, Phys. Today **48**, 34–40 (1995), and references therein.

[7] P. G. deGennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1994), 2nd ed.; V. L. Kuz'min, V. P. Romanov, and L. A. Zubkov, Phys. Rep. **248**, 368 (1994); D. Langevin and M.-A. Boudiat, J. Phys. Colloq. **36**, 197 (1975).

[8] H. Vithana, L. Asfaw, and D. L. Johnson, Phys. Rev. Lett. **70**, 3561 (1993); D. V. Vlasov, L. Zubkov, N. Orekhova, and V. Romanov, JETP Lett. **48**, 91 (1988).

[9] H. Stark and T. C. Lubensky, preceding Letter, Phys. Rev. Lett **77**, 2229 (1996).

[10] A. Smondyrev, G. Loriot, and R. Pelcovits, Phys. Rev. Lett. **75**, 2340 (1995), and references therein.

[11] $\mathbf{e}_1$ represents the direction of the component of $\delta n(\mathbf{r}, t)$ [i.e., $\delta n_1(\mathbf{r}, t)$] that lies in the plane of $\mathbf{q}$ and $\mathbf{n}_0$, while $\mathbf{e}_2$ lies perpendicular to the plane of $\mathbf{q}$ and $\mathbf{n}_0$. See [7].

[12] Please note that in using F_α as defined in the text, we have implicitly assumed the media that bound the scattering volume are isotropic.

[13] N. V. Madhusudana and R. Pratibha, Mol. Cryst. Liq. Cryst. **89**, 249 (1982).