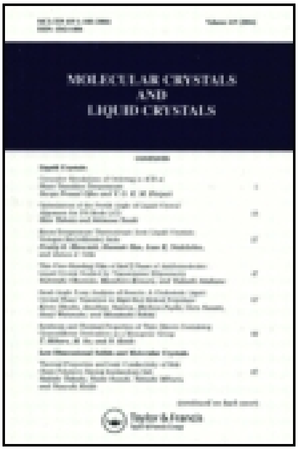

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Radiative Transfer Theory and Diffusion of Light in Nematic Liquid Crystals

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Radiative Transfer Theory and Diffusion of Light in Nematic Liquid Crystals

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In nematic liquid crystals light is strongly scattered from director fluctuations. We are interested in the limit where the incoming light wave is scattered many times. Then, the light transport can be described by a diffusion equation for the energy density of light with diffusion constants $D_{||}$ and $D_{\perp}$, respectively, parallel and perpendicular to the director. We start from a radiative transfer theory, connect the diffusion constants to the dynamic structure factor of director fluctuations, and shortly discuss our results. Temporal correlations of the diffusing light probe the dynamics of director modes on much shorter time scales than single light scattering experiments. To account for the decaying temporal correlations, one has to add an absorption term to the diffusion equation, which we also link to the dynamic structure factor.

Keywords: Nematic liquid crystals; light scattering; radiative transfer theory; diffusion

1. INTRODUCTION

More then one decade ago the discovery of coherent backscattering or weak localization of light in colloidal suspensions [1] initiated a tremendous research activity in multiple light scattering [2]. Researchers were attracted by the possibility to achieve the equivalent to the Anderson localization of electrons in disordered solids [3]. So far strong localization of light waves has not been observed.

In the theoretical description of coherent backscattering the diffusion limit for multiply scattered light is employed [4]. Photons are considered as random walkers with a scattering mean free path l, measuring the length they travel between two scattering events, and a diffusion constant $D = cl^*/3$, which involves the transport mean free path $l^* = l/\langle 1 - \cos\vartheta_s\rangle$. It stands for the path length beyond which the direction of propagation of a photon is randomized. The angular brackets denote an average over all possible scattering events and ϑ_s is the scattering angle. In 1987 Wolf and Maret discovered that diffusing light could be used for spectroscopy [5], which was later called Diffusing Wave Spectroscopy (DWS) by Pine *et al.* [6]. This was an important step forward, since so far turbid systems could not be investigated with conventional dynamic light scattering. In DWS temporal correlations of the detected intensities decay much faster than in single scattering since phase shifts of electric field waves from many scattering events are added up. DWS, therefore, detects dynamic phenomena at much shorter time scales then normal dynamic light scattering [7].

Research on diffusing light and DWS has focused on isotropic media, like colloidal suspensions [7, 8], emulsions [9], and foams [10]. Recently, diffusing photons were used for the imaging of objects [11, 12] which found its application in medicine [13]. In magnetic fields a photonic Hall effect was discovered [14]. Interest in diffusing light in nematic liquid crystals was again initiated by the observation of coherent backscattering first in multidomain samples [15] and then in a perfectly aligned nematic state [16]. In treating multiply scattered light in the nematic phase, one has to deal with the anisotropy in light propagation and a different scattering mechanism. Light is not scattered from local objects like particles in colloidal suspensions but rather from long-range correlated director fluctuations [17, 18]. The theory for diffusing light in nematic liquid crystals was developed independently by Stark and Lubensky [19, 20, 21] and Tiggelen, Maynard, and Heiderich [22, 23]. For a review see ref. [24]. Its final content can be summarized in an anisotropic diffusion equation with absorption for the electric field autocorrelation function $W(\boldsymbol{R}, T, t) = \langle \boldsymbol{E}(\boldsymbol{R}, T + t/2) \cdot \varepsilon_0 \boldsymbol{E}(\boldsymbol{R}, T - t/2)\rangle$:

$$\left[\frac{\partial}{\partial T} - D_{\|}\nabla_{\|}^{2} - D_{\perp}\nabla_{\perp}^{2} + \mu(t)\right] W(\boldsymbol{R}, T, t) = 0 \ , \qquad (1)$$

where $D_{\|}$ and $D_{\perp}$ denote, respectively, the diffusion constants parallel and perpendicular to the nematic director. The dynamic absorption coefficient $\mu(t)$, measured in DWS experiments, governs the temporal decay of the autocorrelation function $[\mu(t = 0) = 0]$. The mentioned theories link the parameters $D_{\|}$, $D_{\perp}$, and $\mu(t)$ to the structure factor of the director fluctuations. The absorption coefficient $\mu(t)$ appears as an angular average over all director modes. Careful experiments by Kao *et al.* demonstrated the anisotropic diffusion and the application of DWS [21, 25]. Their results were in excellent agreement with theory.

The developed theories used a Green function approach to arrive at the diffusion equation. In the present article we present a derivation without the extended formalism of Green functions but which nevertheless contains the main ideas. To do so we start from a radiative transfer theory which was first introduced as early as 1905 by Schuster to describe the transport of light through the atmosphere [26]. The radiative transfer theory is basically equivalent to a Boltzmann equation for the energy density of light [27, 28]. Any coherent superposition of electric field waves are omitted. For anisotropic media it needs some refinements which we present in section 3. The advantage of the radiative transfer theory is that it only requires some intuitive understanding. It can, however, be derived directly from Maxwell's theory. For nematic liquid crystals this was done first by Romanov and Shalaginov [29].

The article intends to stimulate further research on diffusing light in liquid crystals. There exists a wealth of material which scatters light very strongly, namely porous media filled with nematics [30], polymer dispersed liquid crystals [31], focal conic textures in cholesterics [32], and the Blue Phase III. Also applications to lyotropic and polymeric liquid crystals and to liquid crystalline colloids could be of interest.

Section 2 first summarizes light propagation in a homogeneous nematic phase emphasizing the differences to isotropic systems. Then we review single light scattering from director fluctuations and introduce the dynamic structure factor. Section 3 presents the transport equation for radiative transfer. An approximation for the diffusion constants is derived and the formula for the dynamic absorption coefficient is developed. The main features of both quantities are discussed.

2. LIGHT PROPAGATION AND SINGLE SCATTERING IN NEMATIC LIQUID CRYSTALS

There are two necessary ingredients to treat multiple light scattering in a turbid medium: the propagation of a plane wave between scattering events in an effectively homogeneous system and the single scattering itself. We start with the first point.

A. Light Propagation

A homogeneous nematic with the equilibrium Frank director $\boldsymbol{n}_0$ represents a uniaxial and therefore birefringent material. It posseses the dielectric tensor [17, 18]

$$\boldsymbol{\varepsilon}_0 = \varepsilon_\perp \mathbf{1} + \Delta\varepsilon \boldsymbol{n}_0 \otimes \boldsymbol{n}_0 \ , \tag{2}$$

where $\varepsilon_{||}$ and $\varepsilon_\perp$ denote the dielectric constants for electric fields, respectively, parallel and perpendicular to the director, and where $\Delta\varepsilon = \varepsilon_{||} - \varepsilon_\perp$ stands for the dielectric anisotropy. There exist two characteristic light modes which we describe by plane waves for the electric field: $\boldsymbol{E}(\boldsymbol{r}, t) = E^\alpha \boldsymbol{e}_\alpha(\hat{\boldsymbol{k}}) \exp[i(-\omega t + \boldsymbol{k} \cdot \boldsymbol{r})]$. They are characterized by the polarization vector $\boldsymbol{e}_\alpha(\hat{\boldsymbol{k}})$ and the refractive index $n_\alpha(\hat{\boldsymbol{k}}) = ck/\omega$ [33]. The ordinary light wave ($\alpha = 2$) behaves as in an isotropic medium. It has a constant index of refraction $n_2 = \sqrt{\varepsilon_\perp}$ and the polarization vector $\boldsymbol{e}_2(\hat{\boldsymbol{k}})$ is perpendicular to both $\boldsymbol{n}_0$ and $\boldsymbol{k}$. For the extraordinary mode ($\alpha = 1$), however, $n_1(\hat{\boldsymbol{k}})$ depends on the angle ϑ between $\boldsymbol{k}$ and $\boldsymbol{n}_0$:

$$\frac{1}{n_1^2(\hat{\boldsymbol{k}})} = \frac{\sin^2\vartheta}{\varepsilon_{||}} + \frac{\cos^2\vartheta}{\varepsilon_\perp} \ . \tag{3}$$

The vector $\boldsymbol{e}_1(\hat{\boldsymbol{k}})$ lies in the plane defined by $\boldsymbol{n}_0$ and $\boldsymbol{k}$ but is not perpendicular to the wave vector $\boldsymbol{k}$. It makes sense to introduce the polarization vector $\boldsymbol{d}^\alpha(\hat{\boldsymbol{k}}) = \varepsilon_0 \boldsymbol{e}_\alpha(\hat{\boldsymbol{k}})$ for the electric displacement field. Then, the biorthogonality relation $\boldsymbol{d}^\alpha \cdot \boldsymbol{e}_\beta = \delta^\alpha_\beta$ holds [20, 34]. The normalization of the polarization vectors is chosen such that the energy density $\boldsymbol{E} \cdot \boldsymbol{\varepsilon}_0 \boldsymbol{E}/4\pi$ of a light mode, averaged over on time period, becomes $W^\alpha = |E^\alpha|^2/8\pi$.

Besides the phase velocity $\boldsymbol{v}_{p\alpha} = c\hat{\boldsymbol{k}}/n_\alpha$ there exists the group velocity $\boldsymbol{v}_{g\alpha} = \boldsymbol{\nabla}_{\boldsymbol{k}}\omega_\alpha(\boldsymbol{k})$, where $\omega_\alpha(\boldsymbol{k}) = ck/n_\alpha(\hat{\boldsymbol{k}})$ stands for the dispersion relation. Electromagnetic energy is transported along the direction of $\boldsymbol{v}_{g\alpha}$. For ordinary light $\boldsymbol{v}_{g2} = \boldsymbol{v}_{p2}$. For extraordinary light the group velocity

$$\boldsymbol{v}_{g1} = cn_1(\hat{\boldsymbol{k}}) \left(\frac{\cos\vartheta}{\varepsilon_\perp}\boldsymbol{n}_0 + \frac{\sin\vartheta}{\varepsilon_\parallel}\hat{\boldsymbol{u}}_1 \right) \tag{4}$$

differs in direction and magnitude from the phase velocity. We introduced the unit vector $\hat{\boldsymbol{u}}_1$ perpendicular to both $\boldsymbol{n}_0$ and $\boldsymbol{e}_2(\hat{\boldsymbol{k}})$. In a medium without absorption the energy transport is described by the Poynting vector $c(\boldsymbol{E} \times \boldsymbol{H})/4\pi$. It can be rewritten so that for each light mode it equals the energy density times the group velocity: $\boldsymbol{S}^\alpha = W^\alpha \boldsymbol{v}_{g\alpha}$ [33].

B. Single Scattering

Single light scattering from thermally activated director modes has been well understood for a long time [17, 18]. The fluctuating part of the director, $\delta\boldsymbol{n}(\boldsymbol{r}, t)$, induces fluctuations in the dielectric tensor, $\delta\boldsymbol{\varepsilon} = \Delta\varepsilon[\delta\boldsymbol{n} \otimes \boldsymbol{n}_0 + \boldsymbol{n}_0 \otimes \delta\boldsymbol{n}]$, which scatter light. The typical scattering experiment involves incoming light with wave vector $\boldsymbol{k}^\alpha = \omega n_\alpha \hat{\boldsymbol{k}}/c$ and with polarization $\boldsymbol{e}_\alpha(\hat{\boldsymbol{k}})$ which is partially scattered into light with wave vector $\boldsymbol{q}^\beta = \omega n_\beta \hat{\boldsymbol{q}}/c$ and polarization $\boldsymbol{e}_\beta(\hat{\boldsymbol{q}})$. In the weak-scattering approximation, the temporal autocorrelation function of the scattered electric field is proportional to the dynamic structure factor

$$B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, t) = \frac{\omega^4}{c^4} \langle\, \delta\varepsilon_{\alpha\beta}(\boldsymbol{q}_s, t)\, \delta\varepsilon^*_{\alpha\beta}(\boldsymbol{q}_s, 0)\, \rangle \ , \tag{5}$$

where $\boldsymbol{q}_s = \boldsymbol{q}^\beta - \boldsymbol{k}^\alpha$ denotes the scattering vector and $\delta\varepsilon_{\alpha\beta}(\boldsymbol{q}_s, t) = \boldsymbol{e}_\beta(\hat{\boldsymbol{q}}) \cdot \delta\boldsymbol{\varepsilon}(\boldsymbol{q}_s, t)\boldsymbol{e}_\alpha(\hat{\boldsymbol{k}})$ stands for the projection of $\delta\boldsymbol{\varepsilon}$ on the polarization vectors. In its final form we obtain for the structure factor:

$$B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, t) = (\Delta\varepsilon)^2 \frac{\omega^4}{c^4} \sum_{\delta=1}^{2} N(\alpha, \beta, \delta) \frac{k_{\mathrm{B}}T}{K_\delta(\boldsymbol{q}_s)} \exp\left[-\frac{K_\delta(\boldsymbol{q}_s)}{\eta_\delta(\boldsymbol{q}_s)} t \right] \ . \tag{6}$$

The term $k_{\mathrm{B}}T/K_\delta(\boldsymbol{q}_s)$ represents the thermally activated director modes. It involves the elastic coefficient $K_\delta(\boldsymbol{q}_s) = K_\delta q_\perp^2 + K_3 q_\parallel^2 + \Delta\chi H^2$ with

Frank constants K_i, magnetic field H, magnetic anisotropy $\Delta\chi$, and the components of $\boldsymbol{q}_s = (q_\perp, q_\parallel)$. The exponential factor reflects the diffusive nature of the director modes. The relaxation frequency depends on the viscosity $\eta_\delta(\boldsymbol{q}_s) = \gamma - \mu(\boldsymbol{q}_s)$, where the rotational viscosity γ plays the important role. Finally, $N(\alpha, \beta, \delta)$ stands for a geometry factor which forbids ordinary-to-ordinary scattering and forward scattering along the director. From the structure factor we derive the scattering mean free path $l_\alpha(\hat{\boldsymbol{k}})$ [20, 22, 35]:

$$\frac{1}{l_\alpha(\hat{\boldsymbol{k}})} = n_\alpha(\hat{\boldsymbol{k}}) \sum_\beta \int \frac{d\Omega_q}{(4\pi)^2} B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, 0) n_\beta^3(\hat{\boldsymbol{q}}) \ , \tag{7}$$

which depends on the polarization α and the direction $\hat{\boldsymbol{k}}$ of light. In the photon picture it gives the average path length a photon travels between two scattering events. For light intensity it gives the distance after which the initial intensity I_0 has decayed to I_0/e. However, multiple scattering events are totally neglected in the last interpretation. For a careful interpretation of the scattering mean free path in connection with $\hat{\boldsymbol{k}}$ and $\boldsymbol{v}_{g\alpha}$ see ref. [21]. The mean free path is discussed in refs. [24, 35]. We only note, that $l_1(\hat{\boldsymbol{k}})$ goes to zero when $H \to 0$ since the structure factor for extraordinary-to-extraordinary scattering diverges for $\boldsymbol{q}_s \to \boldsymbol{0}$.

Finally, we make some comments about the symmetry of the structure factor. In isotropic systems $B(\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{q}})$ only depends on the scattering angle ϑ_s via $\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{q}} = \cos\vartheta_s$. Therefore, if expanded into spherical harmonics $Y_{l'm'}(\hat{\boldsymbol{k}})$ and $Y_{lm}(\hat{\boldsymbol{q}})$, it is fully diagonal: $\langle l'm'|B(\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{q}})|lm\rangle \propto \delta_{ll'}\delta_{mm'}$. The structure factor for the director modes just posseses the rotational symmetry around the equilibrium director $\boldsymbol{n}_0$. It can be written as a function of the relative azimuthal angle $\varphi = \varphi_q - \varphi_k$ between $\hat{\boldsymbol{q}}$ and $\hat{\boldsymbol{k}}$. Using the additional symmetry $B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, 0) = B_{\alpha\beta}(-\hat{\boldsymbol{k}}, -\hat{\boldsymbol{q}}, 0)$ the following expansion holds:

$$B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, 0) = \sum_{m \geq 0} B_{\alpha\beta}^m(\vartheta_k, \vartheta_q) \cos[m(\varphi_q - \varphi_k)] \ , \tag{8}$$

where ϑ_k and ϑ_q are polar angles of $\hat{\boldsymbol{k}}$ and $\hat{\boldsymbol{q}}$ with respect to $\boldsymbol{n}_0$. It expresses the fact that $\langle l'm'|B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, 0)|lm\rangle \propto \delta_{mm'}$ is diagonal in the index m but not in l.

3. RADIATIVE TRANSFER THEORY AND DIFFUSION APPROXIMATION

In the following we deal with the temporal auto correlation function of the electric field

$$n_\alpha^3(\hat{\boldsymbol{k}}) W_{\hat{\boldsymbol{k}}}^\alpha(\boldsymbol{R}, T, t) = \langle E_{\hat{\boldsymbol{k}}}^\alpha(\boldsymbol{R}, T - t/2)\, E_{\hat{\boldsymbol{k}}}^{\alpha*}(\boldsymbol{R}, T + t/2) \rangle \ . \tag{9}$$

For $t = 0$, it stands for the energy density of a light wave at time T and space point $\boldsymbol{R}$ travelling into direction $\hat{\boldsymbol{k}}$ with polarization α. The light frequency ω is omitted. We pulled out a factor $n_\alpha^3(\hat{\boldsymbol{k}})$. It is proportional to the number $N_\alpha(\omega, \hat{\boldsymbol{k}}) d\omega d\Omega_{\boldsymbol{k}}$ of photon states for a given polarization α, frequency ω, and direction $\hat{\boldsymbol{k}}$, since $N_\alpha(\omega, \hat{\boldsymbol{k}}) d\omega d\Omega_{\boldsymbol{k}} \propto k^2 dk d\Omega_{\boldsymbol{k}} = n_\alpha^3(\hat{\boldsymbol{k}}) \omega^2 d\omega d\Omega_{\boldsymbol{k}} / c^3$.

The equation of radiative transfer theory formally corresponds to a Boltzmann equation balancing all the changes in $W_{\hat{\boldsymbol{k}}}^\alpha(\boldsymbol{R}, T, t)$:

$$\begin{aligned} &\left(\frac{\partial}{\partial T} + \boldsymbol{v}_{g\alpha} \cdot \boldsymbol{\nabla} + \frac{1}{l_\alpha} \frac{c}{n_\alpha} \right) W_{\hat{\boldsymbol{k}}}^\alpha(\boldsymbol{R}, T, t) \\ &\quad = c \sum_\beta \int \frac{d\Omega_q}{(4\pi)^2} B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, t) n_\beta^3(\hat{\boldsymbol{q}}) W_{\hat{\boldsymbol{q}}}^\beta(\boldsymbol{R}, T, t) + S_{\hat{\boldsymbol{k}}}^\alpha(\boldsymbol{R}, T) \ . \end{aligned} \tag{10}$$

The first term gives temporal variations of $W_{\hat{\boldsymbol{k}}}^\alpha(\boldsymbol{R}, T, t)$ due to e.g. time dependent light sources. The second term involves the divergence of the Poynting vector $\boldsymbol{v}_{g\alpha} W_{\hat{\boldsymbol{k}}}^\alpha(\boldsymbol{R}, T, t)$. The correlation function $W_{\hat{\boldsymbol{k}}}^\alpha(\boldsymbol{R}, T, t)$ changes when there is a net flow of energy ($t = 0$) or correlation ($t \neq 0$) out of the volume element around $\boldsymbol{R}$. The third and fourth terms describe losses and gains due to scattering. The scattering mean free path $l_\alpha(\hat{\boldsymbol{k}})$ has been already introduced in Eq. (7). Finally, $S_{\hat{\boldsymbol{k}}}^\alpha(\boldsymbol{R}, T)$ indicates a source term. The transport equation (10) is intuitively understandable. Compared to standard textbooks on multiple light scattering [27, 28] it contains two generalizations. First, it is valid for general anisotropic random media. Secondly, for $t \neq 0$, it describes the transport of electric field correlations [11, 36]. The transport equation can be derived from first principles, i. e. starting from Maxwell's theory. It follows in a straightforward way from the Bethe-Salpeter equation for the averaged "two-particle" Green function [19, 20, 22, 29]. Its validity is restricted to length and time scales much longer than the wavelength and the time period of light.

A. Diffusion Approximation

To derive the diffusion approximation from Eq. (10) we set $t = 0$ and neglect any source terms. We first study the equilibrium solution of Eq. (10), where $W^\alpha_{\hat{k}}(\boldsymbol{R}, T)$ equals a constant W_0. As a result formula (7) for the scattering mean free path $l_\alpha(\hat{\boldsymbol{k}})$ is reproduced. The energy density $n^3_\alpha(\hat{\boldsymbol{k}})W_0$ still depends on the direction $\hat{\boldsymbol{k}}$ and polarization α of light, due to the equipartition of the light energy on all available photon states. So far, this still needs an experimental confirmation. The diffusion approximation follows when the $\hat{\boldsymbol{k}}$ dependence of $W^\alpha_{\hat{k}}(\boldsymbol{R}, T)$ deviates only slightly from the equilibrium angular distribution [27, 28]. Let us therefore look at an angular expansion of $W^\alpha_{\hat{k}}(\boldsymbol{R}, T)$:

$$\begin{aligned} W^\alpha_{\hat{k}}(\boldsymbol{R}, T) &= \frac{1}{8\pi} W_0(\boldsymbol{R}, T) + \frac{3}{4\pi}\frac{1}{c\overline{n^3_\alpha}} n_\alpha \hat{\boldsymbol{k}} \cdot \boldsymbol{J}^\alpha(\boldsymbol{R}, T) \\ &\quad + \sum_{l>1,m} W^\alpha_{lm}(\boldsymbol{R}, T)\tilde{Y}^\alpha_{lm}(\hat{\boldsymbol{k}}) \ , \end{aligned} \tag{11}$$

where we introduced the total energy density

$$\overline{n^3} W_0(\boldsymbol{R}, T) = \sum_\alpha \int d\Omega_{\boldsymbol{k}} n^3_\alpha(\hat{\boldsymbol{k}}) W^\alpha_{\hat{k}}(\boldsymbol{R}, T) \tag{12}$$

as W_0 times an angular average over the cubes of both refractive indices:

$$\overline{n^3} = (\overline{n^3_1} + \overline{n^3_2})/2 = \int d\Omega_{\boldsymbol{k}} [n^3_1(\hat{\boldsymbol{k}}) + n^3_2(\hat{\boldsymbol{k}})]/8\pi = (\varepsilon_\perp^{1/2}\varepsilon_\| + \varepsilon_\perp^{3/2})/2 \ . \tag{13}$$

Our goal is to establish a diffusion equation for $W_0(\boldsymbol{R}, T)$. We also defined the total energy density current $\boldsymbol{J}^\alpha(\boldsymbol{R}, T)$ of light with polarization α,

$$\boldsymbol{J}^\alpha(\boldsymbol{R}, T) = \int d\Omega_{\boldsymbol{k}} n^3_\alpha \boldsymbol{v}_{g\alpha} W^\alpha_{\hat{k}}(\boldsymbol{R}, T) \ . \tag{14}$$

A few comments are necessary to understand Eq. (11). In isotropic systems, the second term on the right-hand side just corresponds to an expansion into the components of $\hat{\boldsymbol{k}} = (\sin\vartheta\cos\varphi, \sin\vartheta\sin\varphi, \cos\vartheta)$, which basically stand for $l = 1$ spherical harmonics. Here, for uniaxial systems, it is useful to choose basis functions with $n_\alpha^3(\hat{\boldsymbol{k}})$ as a weight function:

$$\int d\cos\vartheta\, d\varphi\, n_\alpha^3(\hat{\boldsymbol{k}}) \tilde{Y}^\alpha_{lm}(\hat{\boldsymbol{k}}) \tilde{Y}^\alpha_{l'm'}(\hat{\boldsymbol{k}}) = \overline{n_\alpha^3}\,\delta_{ll'}\delta_{mm'} \ . \tag{15}$$

We will see below that this choice establishes an approximation scheme for the diffusion constants of light. For ordinary waves we still obtain the conventional spherical harmonics. For extraordinary waves we introduce a new coordinate $C = n_1(\hat{\boldsymbol{k}})\cos\vartheta/n_2$, which is equivalent to $\boldsymbol{n}_0 \cdot \hat{\boldsymbol{k}} = \cos\vartheta$ since it also ranges from -1 to 1. With this choice the weight function becomes a constant:

$$\int d\cos\vartheta\, n_1^3(\hat{\boldsymbol{k}}) \ldots = \overline{n_1^3} \int dC \ldots \tag{16}$$

Hence, the basis functions $\tilde{Y}^1_{lm}(\hat{\boldsymbol{k}})$ for $\alpha = 1$ simply follow from spherical harmonics when $\cos\vartheta$ is replaced by C. With the abbreviation $C = \cos\vartheta$ for ordinary light, the generalized spherical harmonics are the same for $\alpha = 1$ and 2. For $l = 1$ in real representation, they read:

$$\tilde{Y}^\alpha_{10}(\hat{\boldsymbol{k}}) = \sqrt{\frac{3}{4\pi}}\,C \quad , \quad \frac{\tilde{Y}^\alpha_{11}(\hat{\boldsymbol{k}}) \pm \tilde{Y}^\alpha_{1-1}(\hat{\boldsymbol{k}})}{2} = \sqrt{\frac{3}{4\pi}}\sqrt{1-C^2}\left\{\begin{array}{c}\cos\varphi \\ \sin\varphi\end{array}\right. \tag{17}$$

In expansion (11) we have already used them explicitly in the second term. We also note that $n_1(\hat{\boldsymbol{k}})\sin\vartheta/n_2 = \sqrt{\varepsilon_\parallel/\varepsilon_\perp}\sqrt{1-C^2}$.

We are ready to extract the diffusion approximation from the transport equation (10). Multiplying Eq. (10) by n_α^3 and summing over all directions of $\hat{\boldsymbol{k}}$ and the two polarizations leads to the continuity equation for the energy density

$$\frac{\partial}{\partial T}\overline{n^3}W_0 + \boldsymbol{\nabla} \cdot \boldsymbol{J} = 0 \ . \tag{18}$$

The vector $\boldsymbol{J} = \boldsymbol{J}^1 + \boldsymbol{J}^2$ denotes the total energy density current. A second equation, Fick's law, relates $\boldsymbol{J}$ to the gradient of the energy density:

$$\boldsymbol{J} = -\boldsymbol{D}\boldsymbol{\nabla}\overline{n^3}W_0 \ . \tag{19}$$

It will be derived below. We introduced the diffusion tensor

$$\boldsymbol{D} = D_{\perp}\mathbf{1} + (D_{\parallel} - D_{\perp})\boldsymbol{n}_0 \otimes \boldsymbol{n}_0 \tag{20}$$

with its two independent light diffusion constants $D_{\parallel}$ and $D_{\perp}$, respectively, parallel and perpendicular to the director $\boldsymbol{n}_0$. Eliminating the current $\boldsymbol{J}$ finally gives the diffusion equation for $W_0(\boldsymbol{R}, T)$,

$$\left(\frac{\partial}{\partial T} - D_{\parallel}\nabla_{\parallel}^2 - D_{\perp}\boldsymbol{\nabla}_{\perp}^2\right) W_0(\boldsymbol{R}, T) = 0 \ , \tag{21}$$

where $\boldsymbol{\nabla} = (\boldsymbol{\nabla}_{\perp}, \nabla_{\parallel})$.

To obtain Fick's law (19), we first look at components parallel to the director $\boldsymbol{n}_0$. We project the transport equation (10) on $\tilde{Y}_{10}^{\alpha}(\hat{\boldsymbol{k}}) \propto C_{\boldsymbol{k}}$ and arrive at a set of equations which couple the energy density W_0 and the components $J_{\parallel}^1$ and $J_{\parallel}^2$:

$$\frac{(4\pi)^3}{18}\frac{c}{n_2^2}\nabla_{\parallel}W_0\begin{pmatrix}1\\1\end{pmatrix} + \begin{pmatrix}\mathcal{B}_{11}^{\parallel} & \mathcal{B}_{12}^{\parallel}\\ \mathcal{B}_{12}^{\parallel} & \mathcal{B}_{22}^{\parallel}\end{pmatrix}\begin{pmatrix}J_{\parallel}^1\\ J_{\parallel}^2\end{pmatrix} + \ldots = \mathbf{0} \ . \tag{22}$$

The quantitites $\mathcal{B}_{\alpha\beta}^{\parallel}$ are extended matrix elements of $B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}})$:

$$\begin{aligned}
\mathcal{B}_{11}^{\parallel} &= \int_{\hat{\boldsymbol{k}}}\int_{\hat{\boldsymbol{q}}}[(C_{\boldsymbol{k}}^2 - C_{\boldsymbol{k}}C_{\boldsymbol{q}})B_{11}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}) + C_{\boldsymbol{k}}^2\frac{\varepsilon_{\perp}}{\varepsilon_{\parallel}}B_{12}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}})]\\
\mathcal{B}_{22}^{\parallel} &= \int_{\hat{\boldsymbol{k}}}\int_{\hat{\boldsymbol{q}}}[(C_{\boldsymbol{k}}^2 - C_{\boldsymbol{k}}C_{\boldsymbol{q}})B_{22}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}) + C_{\boldsymbol{k}}^2\frac{\varepsilon_{\perp}}{\varepsilon_{\parallel}}B_{21}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}})]\\
\mathcal{B}_{12}^{\parallel} &= -\int_{\hat{\boldsymbol{k}}}\int_{\hat{\boldsymbol{q}}}C_{\boldsymbol{k}}C_{\boldsymbol{q}}B_{12}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}})
\end{aligned} \tag{23}$$

where we used the abbreviation $\int_{\hat{\boldsymbol{k}}} = \int dC_{\boldsymbol{k}}d\varphi_{\boldsymbol{k}}$. In Eq. (22) we neglected terms proportional to $\partial J_{\parallel}^{\alpha}/\partial T$. We also assumed that further contributions containing W_{l0}^{α} with $l > 1$ are small and discuss this approximation below. Solving for the two currents $J_{\parallel}^1$ and $J_{\parallel}^2$ leads to the parallel component of Eq. (19):

$$J_{\|} = J^1_{\|} + J^2_{\|} = -D_{\|}\nabla_{\|}\overline{n^3}W_0 \tag{24}$$

with the diffusion constant

$$D_{\|} = \frac{(4\pi)^3}{18}\frac{c}{n_2^2\overline{n^3}}\frac{\mathcal{B}^{\|}_{11} + \mathcal{B}^{\|}_{22} - 2\mathcal{B}^{\|}_{12}}{\mathcal{B}^{\|}_{11}\mathcal{B}^{\|}_{22} - (\mathcal{B}^{\|}_{12})^2} \ . \tag{25}$$

The perpendicular component of Eq. (19) follows in an analogous way after projecting the transport equation (10) on $[\tilde{Y}^{\alpha}_{11}(\hat{\boldsymbol{k}}) + \tilde{Y}^{\alpha}_{1-1}(\hat{\boldsymbol{k}})] \propto \sqrt{1 - C^2_{\boldsymbol{k}}}\cos\varphi_{\boldsymbol{k}}$:

$$J_{\perp} = J^1_{\perp} + J^2_{\perp} = -D_{\perp}\nabla_{\perp}\overline{n^3}W_0 \tag{26}$$

with

$$D_{\perp} = \frac{(4\pi)^3}{18}\frac{c}{n_2^2\overline{n^3}}\frac{\mathcal{B}^{\perp}_{11} + \mathcal{B}^{\perp}_{22}\varepsilon_{\perp}/\varepsilon_{\|} - 2\mathcal{B}^{\perp}_{12}\sqrt{\varepsilon_{\perp}/\varepsilon_{\|}}}{\mathcal{B}^{\perp}_{11}\mathcal{B}^{\perp}_{22} - (\mathcal{B}^{\perp}_{12})^2} \ . \tag{27}$$

The matrix elements $\mathcal{B}^{\perp}_{\alpha\beta}$ are defined as in Eqs. (23) but with C replaced by $\sqrt{1 - C^2}\cos\varphi$.

The expressions (25) and (27) for the diffusion constants are approximate formulas since in Eq. (22) we have neglected terms containing W^{α}_{l0} with $l > 1$. In ref. [20] we showed that corrections of $D_{\|}$ and $D_{\perp}$ resulting from l=3 spherical harmonics are essentially 1% or smaller. One could ask for the reason. The additional coefficients W^{α}_{l0} in Eq. (22) with the non-diagonal matrix elements $\langle 10|B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, 0)|l0\rangle$ as prefactors have to be determined by projecting the transport equation on higher generalized spherical harmonics ($l > 1$). Because of the choice of our basis functions the resulting equations only couple W^{α}_{l0} to $J^{\beta}_{\|}$. The coefficient W_0 does not appear. That means W^{α}_{l0} ($l > 1$) depends in a complicated way but directly on $J^{\beta}_{\|}$. As a result the matrix elements $\mathcal{B}^{\|}_{\alpha\beta}$ are renormalized. However, the renormalization is small if the non-diagonal elements $\langle 10|B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, 0)|l0\rangle$ are small. For symmetry reasons it is clear that $D_{\|}$ and $D_{\perp}$ involve, respectively, $m = 0$ or $|m| = 1$ spherical harmonics only. In isotropic systems higher spherical harmonics do not contribute at all, since $\langle 10|B(\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{q}}, 0)|l0\rangle \propto \delta_{l1}$, and $D \propto \langle 1 - \cos\vartheta_s\rangle^{-1}$ follows.

An extensive discussion of the diffusion constants and their dependence on Frank constants K_i, dielectric anisotropy $\Delta\varepsilon$, and applied magnetic field H is given in refs. [20, 21] and by Tiggelen *et al.* [22]. We just summarize the important results. For a typical material, 5CB, we find $D_{\parallel} = 1.43 \times 10^9 \mathrm{cm}^2/\mathrm{s}$ and $D_{\perp} = 0.98 \times 10^9 \mathrm{cm}^2/\mathrm{s}$ with a ratio of $D_{\parallel}/D_{\perp} = 1.45$ in excellent agreement with experiment and numerical simulations [21, 25]. The values were calculated in the limit of $H \rightarrow 0$, which demonstrates that the divergence of the structure factor for $\boldsymbol{q}_s \rightarrow \mathbf{0}$ does not affect the diffusion constants. If one introduces transport mean free paths via $l^*_{\parallel/\perp} = 3n_2 D_{\parallel/\perp}/c$, one arrives at $l_{\parallel} = 2.2\mathrm{mm}$ and $l_{\perp} = 1.5\mathrm{mm}$ for 5CB. We stress that it is not obvious how to define transport mean free paths in anisotropic turbid media. The calculated values give an orientation only. In the case of $\Delta\varepsilon = 0$ and the one-constant approximation $K_i = K$ there is still a remaining anisotropy of $D_{\parallel}/D_{\perp} = 1.06$ due to the inherent anisotropy in the nematic structure factor. For $\Delta\varepsilon < 0$ there exists a point with $D_{\parallel} = D_{\perp}$ beyond which the ratio $D_{\parallel}/D_{\perp}$ is smaller than 1. This behavior should be observable in discotic nematics.

B. Dynamic Absorption

Now, we set $t \neq 0$ and look at the transport of electric field correlations. In doing so, we restrict ourselves to times t much smaller than typical director relaxation times $\tau = \gamma/(Kq_s^2)$. For wave numbers q_s of light they cover the range $\tau = 10 - 100\,\mu\mathrm{s}$. We rewrite the dynamical structure factor,

$$B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, t) = B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, 0) + [B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, t) - B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, 0)] \ , \tag{28}$$

where the second part on the right-hand side assumes the form

$$B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, t) - B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, 0) = -(\Delta\varepsilon)^2 k_{\mathrm{B}} T \frac{\omega^4}{c^4} \sum_{\delta=1}^{2} \frac{N(\alpha, \beta, \delta)}{\eta_\delta(\boldsymbol{q}_s)}\, t \tag{29}$$

after an expansion of the exponential factor in $B_{\alpha\beta}(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}, t)$. All the coefficients in an angular expansion of $W^{\alpha}_{\hat{\boldsymbol{k}}}(\boldsymbol{R}, T, t)$ now carry the relative time t

as a further argument. The important quantity is the total autocorrelation function

$$\overline{n^3}W_0(\boldsymbol{R},T,t) = \sum_\alpha \int d\Omega_{\boldsymbol{k}} n_\alpha^3(\hat{\boldsymbol{k}}) W_{\boldsymbol{k}}^\alpha(\boldsymbol{R},T,t) \ . \tag{30}$$

In repeating the derivation of the continuity equation (18) we have to add a dynamic absorption term $\mu(t)\overline{n^3}W_0(\boldsymbol{R},T,t)$:

$$\left[\frac{\partial}{\partial T} + \mu(t)\right] \overline{n^3}W_0(\boldsymbol{R},T,t) + \boldsymbol{\nabla}\cdot\boldsymbol{J}(\boldsymbol{R},T,t) = 0 \ , \tag{31}$$

which means that temporal correlations are not conserved quantities because they decay to zero. The dynamic absorption coefficient $\mu(t)$ follows generally from an angular average over all dynamic modes of a system:

$$\mu(t) = \frac{c}{8\pi\overline{n^3}} \sum_{\alpha\beta} \int\!\!\int \frac{d\Omega_{\boldsymbol{k}} d\Omega_{\boldsymbol{q}}}{(4\pi)^2} n_\alpha^3(\hat{\boldsymbol{k}})[B_{\alpha\beta}(\hat{\boldsymbol{k}},\hat{\boldsymbol{q}},0) - B_{\alpha\beta}(\hat{\boldsymbol{k}},\hat{\boldsymbol{q}},t)] n_\beta^3(\hat{\boldsymbol{q}}) \ . \tag{32}$$

Further terms in Eq. (31) containing coefficients W_{lm}^α are small, due to the assumption that $B_{\alpha\beta}(\hat{\boldsymbol{k}},\hat{\boldsymbol{q}},0) \gg B_{\alpha\beta}(\hat{\boldsymbol{k}},\hat{\boldsymbol{q}},0) - B_{\alpha\beta}(\hat{\boldsymbol{k}},\hat{\boldsymbol{q}},t)$, and can be neglected. The same applies to Fick's law in Eq. (19), so that we arrive at the diffusion equation with absorption which we already formulated in the introduction.

Using Eq. (29) for director modes we calculate

$$\mu(t) = \mu_0 t \quad \text{with} \quad \mu_0 = \frac{2k_BT}{9\pi}\frac{\omega^4}{c^3}\frac{(\Delta\varepsilon)^2}{\sqrt{\varepsilon_\perp}}\frac{\tilde{\mu}}{\gamma} \ , \tag{33}$$

where the numerical factor $\tilde{\mu}$ stands for a dimensionless angular average over the geometrical factor $N(\alpha,\beta,\delta)$ and the viscosities $\eta_\delta(\boldsymbol{q}_s)/\gamma$. The factor $\tilde{\mu}$ is of the order of 1 in thermotropic nematics but always larger than 1 [20]. Note that $\mu(t)$ only depends on viscosities and not at all on elastic properties. They cancel because they determine both static light scattering and hydrodynamics of the director modes. For 5CB, $\gamma = 0.81$ P which agrees very well with the experimentally determined value of $\gamma/\tilde{\mu} = 0.60 \pm 0.20$ P [21, 25]. In experiments one fits the autocorrelation function with the help of a numerical or exact solution of the diffusion equation under the appropriate boundary conditions [7].

Down to the experimental resolution of 4×10^{-8} s no deviation of the director dynamics from the Leslie-Erickson theory was observed. It should show up in a different temporal power law of $\mu(t)$. It would be interesting to study systems with higher viscosities like polymer liquid crystals and to look for such a deviation. The Brownian motion of colloidal particles in a fluid e.g. clearly does not show a simple diffusive behavior on very short time scales [7, 37].

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