

Time-Resolved Anisotropic Multiple Light Scattering in Nematic Liquid Crystals

Diederik S. Wiersma,* Alessandro Muzzi, Marcello Colocci, and Roberto Righini

*European Laboratory for non-Linear Spectroscopy and Istituto Nazionale per la Fisica della Materia, Largo E. Fermi 2 (Arcetri),
50125 Florence, Italy*

(Received 15 April 1999)

Anisotropic multiple scattering of light is studied in monodomain nematic liquid crystals. In particular, the anisotropy of the diffusion constant is observed in time-resolved experiments. It is discussed how dynamic vs static experiments probe different properties: static experiments reveal the average step length of the random walk (transport mean free path), while dynamic experiments give the time evolution of the diffusion process (diffusion constant). For the time-resolved data, good agreement is found with (anisotropic) diffusion theory.

PACS numbers: 61.30.Gd, 42.25.Bs, 42.70.Df, 78.30.Ly

In recent years rapid progress was made in understanding the behavior of light waves in disordered media such as colloidal suspensions, semiconductor powders, or even common white paint [1]. Interesting new phenomena were discovered, for instance, coherent backscattering or weak localization [2] and short and long range intensity correlations [3], which are interference effects that survive the random multiple scattering. Inspired by solid state physics, many parallels were found between the multiple scattering of electrons and multiple scattering of light waves, for instance, the photonic Hall effect and optical magnetoresistance [4], Anderson localization of electromagnetic waves [5], and universal conductance fluctuations [6]. Important applications of multiple light scattering include medical imaging [7] and diffusing-wave spectroscopy [8]. All these studies were concerned with isotropic random media.

Liquid crystals in the nematic phase are strongly scattering materials that also give rise to coherent backscattering effects [9], but they differ fundamentally from common random media. The partial ordering in these systems leads to an anisotropic scattering function and thereby to anisotropic multiple scattering. Anisotropic multiple scattering of light was just recently observed by Kao *et al.* in an elegant experimental study on multiple light scattering in nematic liquid crystals [10]. A lot of inspiring theoretical work on light transport in these systems has been done as well [11].

The observation of anisotropic multiple light scattering by Kao *et al.* was achieved in a static experiment. The difference between static and dynamic (time-resolved) experiments on multiple light scattering is fundamental as different properties of the system are probed in the two cases. In a static experiment one principally measures the average step length of the random walk that the light waves perform, called the transport mean free path ℓ . In a time-resolved experiment one can measure the time evolution of the diffusion process as described by the diffusion constant D . The transport mean free path can be related to the diffusion constant via a velocity, called the transport velocity. This transport velocity for light

waves in disordered systems behaves in a complicated but interesting way, and only recently was well understood [12]. In liquid crystals the difference between time-resolved and static experiments is even more important, as, apart from the diffusion constant and the mean free path, also the transport velocity is anisotropic. In this paper we describe the, to our knowledge, first time-resolved experiments on anisotropic multiple scattering of light, that allowed us to observe the anisotropy in the diffusion constant for light waves.

The nematic phase of a liquid crystal is characterized by a global alignment of the molecules in a direction called the nematic director $\mathbf{n}(\mathbf{r})$, and an otherwise translational disorder. The strong opacity of the nematic phase comes about from local fluctuations in the nematic director [13] that elastically scatter light. Because of the partial order of the nematic phase, the scattering cross section σ of these director fluctuations will be anisotropic and will depend on the propagation direction of the light relative to the nematic director [14]. A light wave propagating through a large and monodomain nematic phase will therefore perform an anisotropic random walk, of which both average step length (the transport mean free path ℓ) and velocity of propagation will be anisotropic. The transport mean path ℓ will have the values ℓ_{\perp} and ℓ_{\parallel} , respectively, perpendicular and parallel to the nematic director [15]. Likewise the transport velocity v will have the perpendicular and parallel components v_{\perp} and v_{\parallel} .

For isotropic media one can make the diffusion approximation, which means that one describes the transport of the energy density of the light by a common diffusion equation with diffusion coefficient D . The diffusion constant can be related to the transport mean free path and transport velocity via $D = 1/3v\ell$. For an anisotropic medium the diffusion equation reads

$$\frac{\partial W(\mathbf{r}, t)}{\partial t} = \nabla \cdot \mathbf{D} \nabla W(\mathbf{r}, t) + S(\mathbf{r}, t), \quad (1)$$

with $W(\mathbf{r}, t)$ the energy density and $S(\mathbf{r}, t)$ a source function. Choosing the nematic director along one of the coordinate axes, the distinct elements of the diffusion tensor

will be D_{\perp} and D_{\parallel} , which can be related to the transport mean free path and transport velocity as

$$D_{\parallel} = \frac{1}{3} v_{\parallel} \ell_{\parallel}, \quad D_{\perp} = \frac{1}{3} v_{\perp} \ell_{\perp}. \quad (2)$$

We have measured the diffusion constant by recording the time evolution of the diffuse transmission of short laser pulses through a sample with a slab geometry. The slab was oriented in the x - y plane and the laser pulse incident along z . The laser beam was narrow (1 mm) and the transmitted diffuse light through the slab was recorded around $x = y = 0$. The incident laser beam could be translated in x and y . We followed two strategies to observe the anisotropy. For zero translation of the incident beam, the time evolution of the transmitted light depends only on the zz component of D . One can therefore measure D_{\perp} and D_{\parallel} by orienting the nematic director either parallel (planar alignment) or perpendicular (homeotropic alignment) to the plane of the slab. If the incident beam is translated over Δx or Δy , the transmitted intensity will also depend (weakly) on the xx or yy components of D , which allows one to measure D_{\perp} and D_{\parallel} in principle in one measurement.

The time evolution of the diffusely scattered light in transmission was recorded with an optical gating technique as often used in time-resolved fluorescence spectroscopy (see Fig. 1). Technical details of the setup will be published elsewhere. The sample was contained in a glass cell of 25 mm diameter. In this Letter we describe the results on two sample cells, with thicknesses 6.3 and

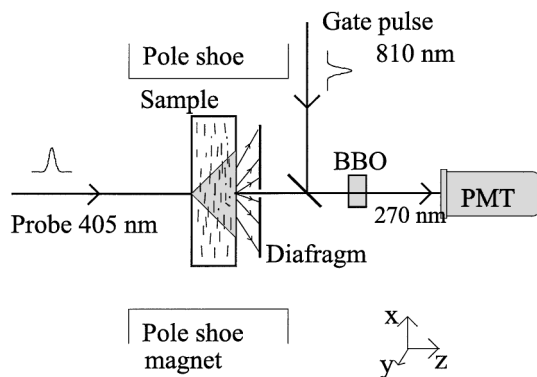


FIG. 1. Principle of the setup used to perform time-resolved measurements. A short probe pulse is incident from the left. Part of the diffuse transmission is selected by a diaphragm (diameter 1 mm), and mixed with a short gate pulse in a nonlinear crystal (BBO), to generate a sum frequency signal that is then monitored by a photomultiplier tube (PMT). By changing the time delay between probe and gate, the temporal profile of the diffuse transmission is recorded. Laser source: amplified Ti:sapphire laser, wavelength 810 nm and repetition rate 1 KHz. Probe pulse: wavelength 405 nm (obtained from frequency doubling in BBO), average power 0.1 mW, beam diameter 1 mm. Gate beam: wavelength 810 nm, average power 400 mW, diameter 1 mm. Final time resolution of the setup ≈ 1 ps.

7.9 mm. The glass cell was temperature controlled with an accuracy of more than 1 K, and placed in a magnetic field of 0.5 T, generated by an electromagnet with 10 cm diameter pole shoes to assure homogeneity of the field. We used the liquid crystal p -pentyl- p' -cyanobiphenyl (5CB), which is nematic at room temperature and which has its nematic-isotropic phase transition at 308 K. For every experiment, the sample was heated to 318 K and let cool down overnight in the magnetic field to obtain monodomain samples. We found that for achieving a homogeneous homeotropic alignment cooling slowly was important, while the monodomain planar alignment could be achieved also within tens of minutes.

The results of the time-resolved measurements for planar and homeotropic alignment of the director, keeping the incoming beam fixed at $x = y = 0$, are shown in Fig. 2. The scattering is stronger for the planar alignment

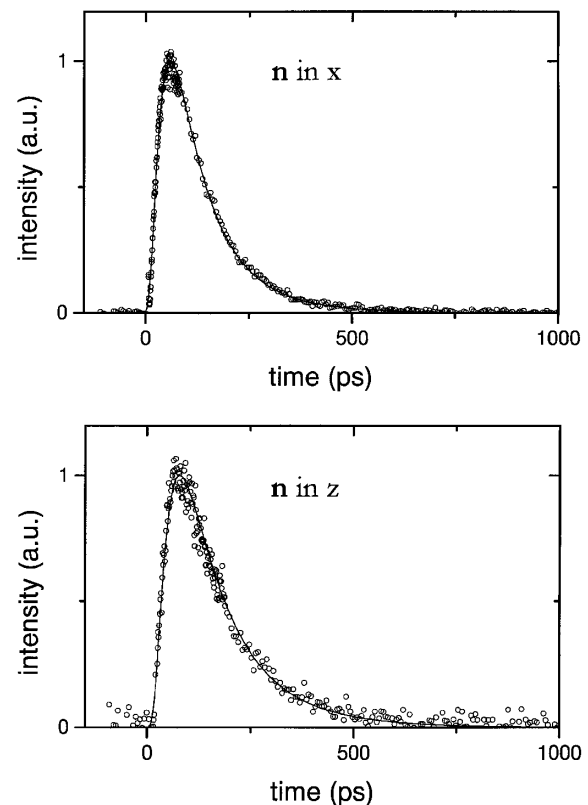


FIG. 2. Time evolution of the transmission of a short probe pulse through liquid crystal 5CB in the nematic phase, in a planar alignment (upper) and a homeotropic alignment (lower). Incident polarization vertical; observed polarization horizontal. ($T = 300$ K, $B = 0.5$ T.) The background signal (few percent of maximum) was detected at negative delay time (before presence of probe) and subtracted. The solid lines are the theoretical curves as calculated from Eq. (4), taking into account internal reflection via Eq. (3) (refractive index contrast 1.15, $R = 0.211$ [16]). From the planar alignment we find $D_{zz} = D_{\perp} = 3.62 \times 10^4$ m²/s and from the homeotropic alignment $D_{zz} = D_{\parallel} = 4.56 \times 10^4$ m²/s, which leads to an anisotropy in the diffusion constant of $D_{\parallel}/D_{\perp} = 1.26$.

(upper data set) than for the homeotropic alignment (lower data set). Therefore, in order to have about the same optical thickness in both cases, we chose the physical thickness of the planar aligned sample $L = 6.3$ mm and of the homeotropic aligned sample $L = 7.9$ mm. We have performed all experiments with both vertical and horizontal incoming polarization and found no polarization dependence in the diffuse transmission.

The solid line is the theoretical curve as obtained by solving Eq. (1), using the boundary conditions of a slab geometry: $W(\mathbf{r}, t) = 0$ at $z = -z_0$ and $z = L + z_0$, with L the physical thickness of the slab, and using the source function $S(\mathbf{r}, t) = \delta(x)\delta(y)\delta(z - \ell_z)\delta(t)$. The distance z_0 is called the extrapolation length and depends on the refractive index mismatch between sample and surrounding medium [16]:

$$z_0 = 2/3 \ell_z (1 + R)/(1 - R), \quad (3)$$

with R the average reflectivity at the sample interface and ℓ_z the transport mean free path in z . We assume that the incident pulse is fully scattered at a depth ℓ_z and, for symmetry reasons, that the last scattering event takes place at $z = L - \ell_z$. The time evolution of the transmitted intensity is given by Fick's law [$I_{tr} = -D_{zz} \nabla W(\mathbf{r}, t)|_{z=L-\ell_z}$] and reads after solving Eq. (1)

$$I_{tr} = \frac{I_0 \exp(-\Delta x^2/4D_{xx}t) \exp(-\Delta y^2/4D_{yy}t)}{\pi^{3/2}(4t)^{5/2} \sqrt{D_{xx}D_{yy}D_{zz}}} \times \sum_{n=-\infty}^{+\infty} A \exp(-A^2/4D_{zz}t) - B \exp(-B^2/4D_{zz}t), \quad (4)$$

with $A = (1 - 2n)(L + 2z_0) - 2(z_0 + \ell_z)$ and $B = (2n + 1)(L + 2z_0)$, and where Δx and Δy denote the shift of the incoming beam in x and y , respectively. Note that in the limit of long t the transmitted intensity falls off as an exponential with time constant $\tau = (L + 2z_0)^2/D_{zz}\pi^2$.

In Fig. 2 we see that there is good agreement between data and theory. From a fit of Eq. (4) to the data we find for the planar alignment $D_{zz} = D_{\perp} = 3.62(\pm 0.15) \times 10^4$ m²/s, and for the homeotropic alignment $D_{zz} = D_{\parallel} = 4.56(\pm 0.18) \times 10^4$ m²/s. The anisotropy in the diffusion constant is therefore $D_{\parallel}/D_{\perp} = 1.26 \pm 0.07$. These results are in agreement with the theoretical predictions in Ref. [11].

We cannot compare this measured anisotropy directly to the experimental results of Ref. [10], because those experiments were performed at a different wavelength (514 nm compared to our 405 nm). We therefore have measured the static anisotropy of our samples as well, in a way similar to Ref. [10]. The transmitted intensity was recorded at $x = y = 0$, while the input beam was translated either along x or along y . The results of this measurement are shown in Fig. 3. Here the sample thickness was 6.3 mm, while the director was aligned

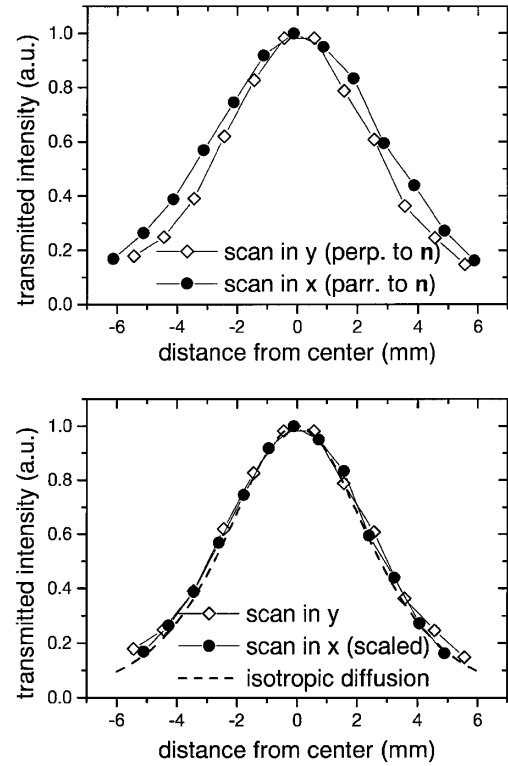


FIG. 3. Transmission through a slab of planar aligned 5CB in the nematic phase versus position of incident beam. The slab is oriented in the x - y plane (\mathbf{n} is in the x direction); input beam is translated in x or in y . ($T = 300$ K, $B = 0.5$ T). The transmitted light is detected at $x = y = 0$. The experimental error is given by the size of the symbols. Upper plot: unscaled data. Lower plot: x axis of data of x scan scaled by a factor of 1.2. The dashed line is the theoretical curve for isotropic multiple scattering.

along x . The static anisotropy was determined in the way described in Ref. [10], by rescaling the x axis of the scan parallel to \mathbf{n} , which yields the value 1.44 ± 0.06 . This is significantly larger than the anisotropy that we find for the diffusion constant in the time-resolved experiments. The theoretical curve for isotropic multiple scattering through a sample of thickness 6.3 mm is shown in Fig. 3 as a dashed line. We can see that after scaling the data almost coincide with a regular isotropic multiple scattering curve.

To check the consistency of our results, we have performed time-resolved transmission measurements with a translated input beam ($x, y \neq 0$), in which case the transmitted intensity depends on both D_{zz} and either D_{xx} or D_{yy} . By choosing a suitable orientation of the director with respect to the direction of the translation, one, in principle, could measure this way both D_{\perp} and D_{\parallel} at the same time. The dependence on D_{xx} and D_{yy} is weak, however. D_{xx} and D_{yy} influence mainly the rising slope of the signal, while the decay at long times is almost completely determined by D_{zz} . In Fig. 4 we have plotted the results for the director oriented along x and

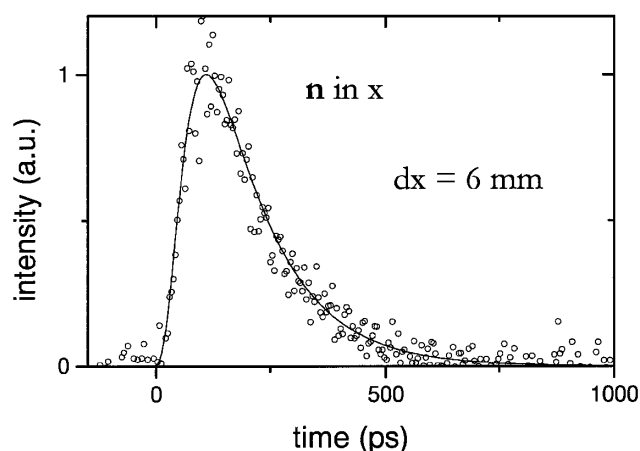


FIG. 4. Time evolution of the transmission of a short probe pulse through nematic 5CB in a planar alignment (with \mathbf{n} in x); input beam translated 6 mm in x . ($T = 300$ K, $B = 5$ T, $L = 6.3$ mm.) Translating the input beam allows one to observe contributions to the signal from both D_{zz} and D_{xx} . Solid line: theoretical curve from Eq. (4). The best fit to the data yields $D_{zz} = D_{\parallel} = 4.40(\pm 0.50) \times 10^4$ m²/s, which is consistent with the measurements presented in Fig. 2.

the input beam translated to $x = 6$ mm. The solid line is again the theoretical curve from Eq. (4). To check the consistency of our data we used the previously determined value of $D_{\perp} = 3.62 \times 10^4$ m²/s. In that case we find, for the parallel component of \mathbf{D} , $D_{\parallel} = 4.40(\pm 0.50) \times 10^4$ m²/s, which is consistent with the data measured in the homeotropic geometry.

We thank Holgar Stark and Bart van Tiggelen for stimulating discussions that inspired this work, and Cecilia Gambi and Donatella Senatra for the use of the electromagnet. This work was financially supported by the E.C. under Contract No. ERBFMGECT950017. D.S.W. was supported by Marie Curie research Grant No. ERBFMBICT972107.

*Email address: wiersma@lens.unifi.it

- [1] See for instance, P. Sheng, *Introduction to Wave Scattering, Localization, and Mesoscopic Phenomena* (Academic Press, San Diego, 1995).
- [2] Y. Kuga and A. Ishimaru, J. Opt. Soc. Am. A **8**, 831 (1984); M.P. van Albada and A. Lagendijk, Phys. Rev. Lett. **55**, 2692 (1985); P.E. Wolf and G. Maret, Phys. Rev. Lett. **55**, 2696 (1985).

- [3] 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).
- [4] G.L.J.A. Rikken and B.A. van Tiggelen, Nature (London) **381**, 54 (1996); A. Sparenberg, G.L.J.A. Rikken, and B.A. van Tiggelen, Phys. Rev. Lett. **79**, 757 (1997).
- [5] R. Dalichaouch, J.P. Armstrong, S. Schultz, P.M. Platzman, and S.L. McCall, Nature (London) **354**, 53 (1991); A.Z. Genack and N. Garcia, Phys. Rev. Lett. **66**, 2064 (1991); D.S. Wiersma, P. Bartolini, A. Lagendijk, and R. Righini, Nature (London) **390**, 671 (1997).
- [6] F. Scheffold and G. Maret, Phys. Rev. Lett. **81**, 5800 (1998).
- [7] A. Yodh and B. Chance, Phys. Today **48**, No. 3, 34 (1995).
- [8] G. Maret and P.E. Wolf, Z. Phys. B **65**, 409 (1987); D.J. Pine, D.A. Weitz, P.M. Chaikin, and E. Herbolzheimer, Phys. Rev. Lett. **60**, 1134 (1988).
- [9] D.V. Vlasov, L.A. Zubkov, N.V. Orekhova, and V.P. Romanov, Pis'ma Zh. Eksp. Teor. Fiz. **48**, 86 (1988) [JETP Lett. **48**, 91 (1988)]; H.K.M. Vithana, L. Asfaw, and D.L. Johnson, Phys. Rev. Lett. **70**, 3561 (1993).
- [10] M.H. Kao, K.A. Jester, A. Yodh, and P.J. Collins, Phys. Rev. Lett. **77**, 2233 (1996).
- [11] V.P. Romanov and A.N. Shalaginov, Opt. Spectrosc. (USSR) **64**, 774 (1988); B.A. van Tiggelen, R. Maynard, and A. Heiderich, Phys. Rev. Lett. **77**, 639 (1996); H. Stark and T.C. Lubensky, Phys. Rev. Lett. **77**, 2229 (1996); H. Stark and T.C. Lubensky, Phys. Rev. E **55**, 514 (1997); B.A. van Tiggelen, A. Heiderich, and R. Maynard, Mol. Cryst. Liq. Cryst. **293**, 205 (1997).
- [12] M.P. van Albada, B.A. van Tiggelen, A. Lagendijk, and A. Tip, Phys. Rev. Lett. **66**, 3132 (1991).
- [13] P.G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford, New York, 1993), 2nd ed.; S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, 1977); A.Y. Val'kov and V.P. Romanov, Zh. Eksp. Teor. Viz. **82**, 1777 (1982) [Sov. Phys. JETP **56**, 1028 (1983)].
- [14] D. Langevin, Solid State Commun. **14**, 435 (1974); D. Langevin and M.-A. Bouchiat, J. Phys. (Paris) C **1**, 197 (1975).
- [15] Because of the strong forward scattering, the scattering mean free path is much smaller than the transport mean free path [11], and the relationship between them in a nematic system is more complicated than it is in an isotropic medium. We consider only the transport mean free path here, as that is the relevant length for our experiments.
- [16] A. Lagendijk, R. Vreeker, and P. de Vries, Phys. Lett. A **136**, 81 (1989); J.X. Zhu, D.J. Pine, and D.A. Weitz, Phys. Rev. A **44**, 3948 (1991).