Notes

Transmission of Polarized Light through a Randomly Birefringent Medium

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Recent experiments[1-3] have demonstrated the usefulness of birefringence as a sensitive probe of the order–disorder transition (ODT) in lamellar block copolymers. The experiments, simple in practice, consist essentially of analyzing the change in the polarization state of a laser beam after it passes through a sample of block copolymer. One advantage of the experiment is that it is quite sensitive to the ODT even if the layers in the sample are heterogeneously aligned.

In one such study,[3] the transmission of a beam of polarized light through a sample assumed to consist of randomly oriented birefringent domains was analyzed quantitatively, in order to determine the characteristic size of the domains in the sample. The analysis reported in ref 3, restricted to sufficiently thin samples, described the effect on the light passing through a succession of randomly oriented birefringent domains as a succession of small random changes of the polarization vector. This physical picture was also described at some length in ref 1.

In the experiment, the beam diameter d is certainly large compared to the domain size l (several microns), and so the light passing through the sample may be regarded as broken up into a large number $n \approx (d/l)^2$ of parallel "channels". Each channel comprises a different random succession of orientations for the birefringent grains. For $kl \gg 1$, the light propagation is well described by the eikonal or semiclassical optics approximation. In such a description, different light paths illuminate different portions of the detector; thus, the measured intensity is a sum of the intensities of each independent path. The experimentally important quantity is the distribution function for polarization states of the light passing through the sample, with each channel representing a different trajectory in phase space.

In this paper, I shall derive a Fokker–Planck (FP) equation for the distribution function of polarization states of the light passing through the sample. The distance traveled through the sample corresponds to "time" in the FP equation. This analysis generalizes the results of ref 3 to samples of arbitrary thickness and arbitrary input polarization. The results of this paper also apply to beams of arbitrary diameter. When the beam diameter becomes comparable to the grain size, the experiment corresponds to taking a small number n of "samples" from the distribution function, with corresponding fluctuations of order $1/\sqrt{n}$ in the experimental result as the beam is moved from place to place on the sample.

A lamellar material is optically uniaxial, with different indices of refraction for polarization parallel and perpendicular to the layer normal $\hat{n}$. To understand the effect of the randomly oriented medium on the polarization state of the light passing through it, consider light propagating along $\hat{z}$ through a succession of slabs of birefringent material of thickness l. The polarization vector v characterizing the light is a complex vector in the x–y plane. It may be decomposed in the orthonormal basis $\{\hat{n}_\parallel, \hat{n}_\perp\}$, where $\hat{n}_\parallel$ is the projection of the optic axis $\hat{n}$ into the x–y plane and $\hat{n}_\perp$ is orthogonal to $\hat{n}$.

The two components of $\mathbf{v}$ along $\hat{n}_\parallel$ and $\hat{n}_\perp$ acquire different phase factors as they pass through the slab; the polarization vector evolves according to[4]

$$\mathbf{v} \to \mathbf{M}\cdot\mathbf{v},\ \mathbf{M} = \phi_\parallel \hat{n}_\parallel \hat{n}_\parallel^{\mathrm{T}} + \phi_\perp \hat{n}_\perp \hat{n}_\perp^{\mathrm{T}} \tag{1}$$

The phase factors are $\phi_\parallel = \exp(i\Gamma_\parallel)$ and similarly for $\phi_\perp$, with

$$\Gamma_\parallel = (2\pi l/\lambda) n_\parallel(\alpha)$$
$$\Gamma_\perp = (2\pi l/\lambda) n_{\mathrm{o}} \tag{2}$$
$$\frac{1}{n_\parallel(\alpha)^2} = \frac{\cos^2(\alpha)}{n_0^{\,2}} + \frac{\sin^2(\alpha)}{n_{\mathrm{e}}^{\,2}}$$

Here α is the angle between the layer normal $\hat{n}$ and the z-axis, and n_{e} and n_{o} are respectively the refractive indices with polarization parallel to and perpendicular to $\hat{n}$. (See Figure 1.)

Now suppose that the thickness l is small enough that each slab makes a small perturbation on the polarization vector, i.e., that $\Gamma \equiv \Gamma_\parallel - \Gamma_\perp \ll 2\pi$. Then, with $\hat{n}_\parallel = \hat{x}\cos\psi + \hat{y}\sin\psi$, one obtains

$$\begin{pmatrix} v_x \\ v_y \end{pmatrix} \to \begin{pmatrix} v_x \\ v_y \end{pmatrix} + \frac{i\Gamma}{2}\begin{pmatrix} \cos 2\psi & \sin 2\psi \\ \sin 2\psi & -\cos 2\psi \end{pmatrix}\begin{pmatrix} v_x \\ v_y \end{pmatrix} \tag{3}$$

(Here an overall phase factor has been ignored; when the different light paths do not interfere, the overall phase of the polarization vector is irrelevant.)

The polarization vector may be represented as a general combination of left circularly polarized (LCP) and right circularly polarized (RCP) light, as

$$\begin{pmatrix} v_x \\ v_y \end{pmatrix} = \frac{1}{\sqrt{2}}\cos(\theta/2)e^{-i\Delta}\begin{pmatrix} 1 \\ i \end{pmatrix} + \frac{1}{\sqrt{2}}\sin(\theta/2)e^{i\Delta}\begin{pmatrix} 1 \\ -i \end{pmatrix} \tag{4}$$

Using eq 3, the effect of a single birefringent slab on the values of θ, ϕ_{L}, and ϕ_{R} to $O(\Gamma)$ is

$$\theta \to \theta + \frac{1}{4}\Gamma \sin 2(\psi + \Delta)$$

$$\Delta \to \Delta + \frac{1}{4}\Gamma \cot\theta \cos 2(\psi + \Delta) \tag{5}$$

The quantity of interest is the polarization distribution function $P(\theta,\Delta)$, where $\theta \in (0, \pi)$ and $\phi \in (0, 2\pi)$; these variables may be represented geometrically as the inclination and asimuthal angles on the "Poincare sphere".

The FP equation is derived in the standard way,[5] by expanding the master equation in moments of the transition rates, i.e., in powers of the small changes in the

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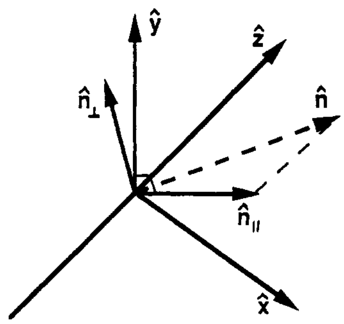

Figure 1. Kinematics of a light beam propagating along $\hat{z}$ through a uniaxial medium, with exceptional axis $\hat{n}$. The projection of $\hat{n}$ into the polarization (x–y) plane is $\hat{n}_{\|}$; $\hat{n}_{\perp}$ is orthogonal to $\hat{n}$ and $\hat{z}$.

polarization vector upon passing through a single domain. Now I assume that the layer normals of the domains are uniformly distributed; with this assumption, one obtains

$$\langle \delta\theta^2 \rangle = \langle \Gamma^2 \rangle / 32$$

$$\langle \delta\Delta^2 \rangle = \cot^2\theta \langle \Gamma^2 \rangle / 32 \tag{6}$$

(If the layer normals were not isotropically distributed, the above averages would be changed, and in addition the averages $\langle \delta\theta \rangle$ and $\langle \delta\Delta \rangle$ would no longer vanish.)

The resulting FP equation is

$$\partial_z P = D(\partial_\theta^{\ 2} P + \cot^2\theta \partial_\Delta^{\ 2} P) \tag{7}$$

Here z measures the distance along the propagation direction, and $D \equiv \langle \Gamma^2 \rangle / (64l)$.

If the ordinary and exceptional refractive indices n_o and n_e are nearly equal, such that $|n_o - n_e| \ll (n_o + n_e)$, then

$$\Gamma \approx (2\pi l(n_e - n_o)/\lambda) \sin^2(\alpha)$$

$$\langle \Gamma^2 \rangle \approx (3/8)(2\pi l(n_e - n_o)/\lambda)^2 \tag{8}$$

Equation 7 may now be applied to two typical cases of experimental interest; namely, illumination of the sample with a beam of either (1) circularly polarized[1] (CP) or (2) linearly polarized[3] (LP) coherent laser light. In each case, the initial state is a narrow distribution function consisting of a single state.

For incident CP, the initial state may be taken as $\theta = 0$; the initial value of Δ is arbitrary and may be taken to be uniformly distributed. As a result, we may integrate eq 7 over Δ to obtain simply

$$\partial_z P = D\partial_\theta^{\ 2} P \tag{9}$$

After the beam propagates through n parallel and independent sequences of domains, each of total length L, the light impinges on a detector, after passing through a polarization analyzer of some sort. (See Figure 2.) The intensity at the detector is then reduced by a factor

$$I/I_0 = \int d\hat{v} P(\hat{v}) \langle |\hat{e}_f \cdot \hat{v}|^2 \rangle \equiv \langle |\hat{e}_f \cdot \hat{v}|^2 \rangle \tag{10}$$

If the incident beam is $\hat{v}_i = (1,i)/\sqrt{2}$, natural choices for the analyzer polarization vector are $\hat{e}_f = \hat{v}_i$ (aligned) and $\hat{e}_f = \hat{v}_k^*$ (crossed). The exiting polarization vector is of the form eq 4, so

$$I/I_0 = \begin{cases} \langle \cos^2(\theta/2) \rangle = {}^1/_2(1 + \exp[-DL]), & \text{aligned} \\ \langle \sin^2(\theta/2) \rangle = {}^1/_2(1 - \exp[-DL]), & \text{crossed} \end{cases} \tag{11}$$

(The time dependence is obtained simply by applying $\int d\theta \cos\theta$ to eq 9 and using the half-angle formula.) For sufficiently thick samples, such that $DL \gg 1$, the distribution of θ will become uniform, and the entire signal will become of order $1/\sqrt{n}$. Equation 9 describes the evolution of the distribution function for all sample thicknesses, connecting the thin-sample and thick-sample results.

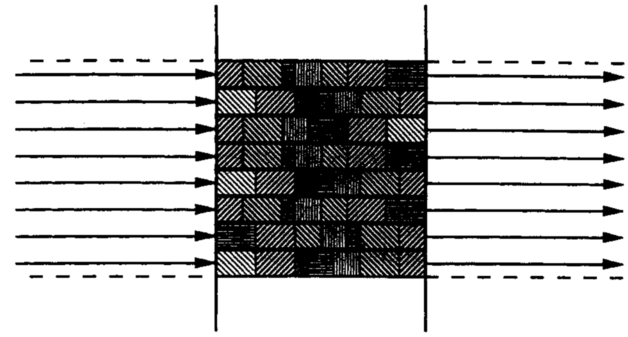

Figure 2. Coherent beam of diameter d passing through a randomly birefringent medium with a small characteristic grain size l regarded as propagating along $n \approx (d/l)^2$ independent paths, each of which presents a sequence of randomly oriented domains. Each path impinges on a different part of the detector.

If the values of n_e and n_o for the oriented lamellar phase are known, or calculated theoretically in terms of form and molecular birefringence of the lamellar phase,[6] then the reduction of the amplitude for a sample of known thickness determines the characteristic domain size l.

A second typical initial condition is a state of linear polarization (LP); the initial state if $\theta = \pi/2$, and $\Delta = \Delta_0$ is the linear polarization angle, resulting in $\hat{v} = (\cos \Delta_0, \sin \Delta_0)$. The intensity at the detector is again given by eq 10, but now with a polarization analyzer $\hat{e}_f = (\cos \alpha, \sin \alpha)$, leading to

$$I/I_0 = \frac{1}{2}(1 + \langle \sin\theta \cos^2(\Delta - \alpha) \rangle) \tag{12}$$

Since $\cot \pi/2 = 0$, Δ does not diffuse until θ has spread appreciably away from the initial value of $\pi/2$; if $\langle(\theta - \pi/2)^2\rangle \sim 2DL$ for $DL \ll 1$, then $\langle(\Delta - \Delta_0)^2\rangle \sim (DL)^2$. Hence, for thin samples such that $DL \ll 1$, one obtains

$$I/I_0 \approx \frac{1}{2}(1 + (1 - DL)\cos 2(\Delta_0 - \alpha)) \tag{13}$$

The magnitude of the intensity variation as the polarizer is rotated decreases linearly with sample thickness.

For thicker samples, the distribution $P(\theta,\Delta)$ becomes uniform, at which point I/I_0 is independent of α; the characteristic thickness scale at which this begins to occur is clearly $DL \sim 1$. Equation 7 may be solved numerically to obtain detailed thickness dependence of $I(L)/I_0$.

Besides the changes in the polarization vector, the propagation direction also changes as light passes through a randomly birefringent medium. For the simpler problem of a medium with a slowly varying index of refraction $n(r)$, the propagation direction p obeys

$$n\frac{dp}{ds} = \nabla n - p(p \cdot \nabla n) \tag{14}$$

where s denotes the arc length along the path of propagation. This is essentially a differential form of Snell's law; the propagation direction unit vector is continually bent in the direction of the gradient in the refractive index.

If $n(r)$ fluctuates with a small amplitude δn and a correlation length l, a FP equation may be derived for the distribution function $Q(p)$ of propagation directions:

$$\frac{\partial Q}{\partial s} = D_p \frac{\partial}{\partial p}\cdot(\delta - pp)\cdot\frac{\partial}{\partial p}Q \qquad (15)$$

where $D_p \sim (\delta n/n)^2/l$. The FP operator is simply the diffusion operator restricted to the unit sphere.

For sufficiently thick samples, the propagation direction is thus randomized, even if $kl \gg 1$ and $\delta n/n \ll 1$; the mean free path for p is of order $1/D_p$. For samples thinner than $1/D_p$, the variance in p is of order $\langle(\delta p)^2\rangle \sim D_p L$.

An analogous FP equation for the propagation directions of light passing through a randomly birefringent medium may also be derived in various limits, by the methods of semiclassical optics, in which the Maxwell equations are expanded in powers of $1/k$.[4] The first limit is $kl \gg 1$ and $kl(n_\parallel - n_\perp) \gg 1$, so that the medium properties are slowly varying in space and the phase shifts of the two eigenmodes within a correlation length l are large compared to unity. In this case, a semiclassical expansion results in two independent modes: one undeflected beam with polarization adiabatically maintained in the local ordinary direction $\hat{n}_\perp(r)$, and one deflected beam with polarization adiabatically maintained in the direction $\hat{n}_\perp(r)$.

The second limit, of more interest experimentally, is $kl \gg 1$, but $kl(n_\parallel - n_\perp) \ll 1$. In this case of sufficiently weak anisotropy, it is appropriate to assume $n_\parallel - n_\perp$ to be itself of order $1/k$ in performing the semiclassical expansion. The result is then an undeflected beam, with a polarization vector evolving according to a differential version of eq 1, namely

$$\partial_s \mathbf{v} = i(\Gamma_\parallel \hat{n}_\parallel \hat{n}_\parallel^{T} + \Gamma_\perp \hat{n}_\perp \hat{n}_\perp^{T})\cdot\mathbf{v} \qquad (16)$$

In the experimental system, the value of the orientational average $n \equiv (2n_\perp + n_\parallel)/3$ is not truly constant but varies over the sample, e.g., as the concentration of solvent fluctuates. As a result, even with $kl(n_\parallel - n_\perp) \ll 1$, an expansion in $1/k$ gives a propagation direction that evolves according to eq 14 (and spreads according to eq 15).

When the condition of large domains $kl \gg 1$ is not satisfied but the birefringence fluctuations are sufficiently weak, a more conventional description of the interaction of the incident light and the medium is given by the Born approximation. The differential cross section is

$$A^{-1}\frac{d\sigma}{d\Omega} = \frac{k^4}{(4\pi)^2} L S_{\epsilon\epsilon}(q)$$

$$S_{\epsilon\epsilon}(r-r') = \langle \delta\epsilon_{fi}(r)\, \delta\epsilon_{fi}(r')\rangle, \quad \delta\epsilon_{fi} \equiv \hat{e}_f\cdot\delta\epsilon\cdot\hat{e}_i \qquad (17)$$

Here $\hat{e}_i$ and $\hat{e}_f$ are the incident and final polarization vectors, and A and L are the area and thickness of the sample.

If the dielectric fluctuations are purely birefringence fluctuations and the correlation length is the same parallel and perpendicular to the optic axis, then

$$\langle \delta\epsilon_{ij}(r)\, \delta\epsilon_{kl}(r')\rangle = (\delta\epsilon)^2 f(|r - r'|)\left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \frac{2}{3}\delta_{ij}\delta_{kl}\right) \qquad (18)$$

with $f(r)$ decaying on a scale l. This leads to a total cross section

$$\frac{\sigma}{A} = \frac{k^4 L}{8\pi}\left(\frac{\delta\epsilon}{\epsilon}\right)^2\left(1 + \frac{1}{3}|\hat{e}_f\cdot\hat{e}_i|^2\right)\int f(2k\sin(\theta/2))\sin\theta\, d\theta$$
$$\sim k^2 l L\left(\frac{\delta\epsilon}{\epsilon}\right)^2\left(1 + \frac{1}{3}|\hat{e}_f\cdot\hat{e}_i|^2\right)\log(1 + (2kl)^2) \qquad (19)$$

where the last line obtains for a Lorentzian $f(q)$. If kl is reasonably large, most of the scattering is near the forward direction, and so the detector integrates the scattered intensity.

The Born approximation holds as long as most of the light is not scattered, i.e., for $\sigma/A < 1$ or for

$$L < l^* \sim [k^2 l(\delta\epsilon/\epsilon)^2]^{-1} \qquad (20)$$

where $kl \gg 1$ has been assumed and the log factor omitted.

The optical theorem guarantees that the intensity in the unscattered beam is reduced by the total scattered intensity. As a result, the total intensity incident on the detector is

$$I/I_0 = \frac{L}{l^*}\left(1 + \frac{1}{3}|\hat{e}_f\cdot\hat{e}_i|^2\right) + \left(1 - \frac{7}{3}\frac{L}{l^*}\right)|\hat{e}_f\cdot\hat{e}_i|^2 \qquad (21)$$

where the first term is the scattered light and the second term is the unscattered beam (still in polarization state $\hat{e}_i$). Identifying $D \sim 1/l^*$ (compare eq 8 and eq 20) and using the half-angle formula, this is the same result as the semiclassical optics result (eq 13).

The Born approximation would appear to give a distribution of propagation directions that is in conflict with semiclassical optics. While semiclassical optics predicts a distribution of propagation directions that is broadened on the unit sphere, the Born approximation says that most of the light is not scattered at all. However, when $L < l^*$ and $kl \gg 1$ so that both the Born and semiclassical optics approximations are valid, the spread in propagation directions estimated below eq 15 is bounded by $\langle(\delta d)^2\rangle < 1/(kl)^2 \ll 1$. Thus when both approximations are valid, both predict essentially no spreading of the propagation directions.

If a sample is partially aligned, i.e., the layer normals have a nontrivial distribution function $p(\hat{n})$, a FP equation still may be derived, once a model for $p(\hat{n})$ is specified. Partial alignment leads to a bias in the random motions of the polarization vectors and an average anisotropy of the sample. The progressive alignment of samples under shear may be studied experimentally by such a measurement and analysis.

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References and Notes

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