Pure Appl. Opt. **5** (1996) 417–443. Printed in the UK

Optical properties of isotropic chiral media

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Received 24 November 1994, in final form 8 January 1996

Abstract. A review is given of the optical properties of isotropic chiral media, based on the symmetrized constitutive relations of Condon. The review includes discussion of wave propagation in chiral media, and derivation of the reflection and transmission amplitudes of an isotropic optically active medium, and of a layer resting on a substrate. Boundary conditions and energy conservation relations are derived. For the chiral layer, simple formulae are given for the reflection and transmission coefficients at normal incidence, in the weak chirality limit, near the critical angles, and for a thin layer. Analytic expressions are given for all the reflection and transmission amplitudes in the general case. An ellipsometric method of measuring the chirality of very small sample volumes is suggested.

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0963-9659/96/040417+27$19.50

1. Introduction

1.1. Historical sketch

Optical activity is the ability of some crystals, liquids and gases to rotate the plane of polarization of light. Optical activity, or rotatory power, is caused by chirality, either of the molecules making up the substance, or in the helical arrangement of the atomic or molecular constituents in a crystal. (A chiral object is one which cannot be superimposed on its mirror image.) In 1811 Arago found that a plate of quartz produced effects on light polarized by reflection from a pile of glass plates which are now understood to arise from the rotation plane of polarization of the light. In five memoirs presented to the Académie des Sciences from 1812 to 1837, Biot showed that the rotatory power is proportional to the thickness of the quartz plates (propagation is along the optic axis of the crystals), that the rotation depends on the wavelength, approximately as λ^{-2}, and that optical activity appears in liquids and gases, as well as in crystals. Fresnel conjectured in 1822 that on entering an optically active medium light is split into two beams of opposite circular polarization which travel with different phase velocities. In 1848 Pasteur demonstrated that the optical activity of a tartrate solution is related to the form that the crystals of the tartrate take: crystals of opposite handedness dissolve to give solutions with opposite rotatory power. References to these early works and further details may be found in the thorough historical account given by Lowry in his book on *Optical Rotatory Power* [1]. Other historical outlines may be found in [2–4], and a selection of papers on natural optical activity is given in [5].

1.2. Constitutive relations

Modern electromagnetism begins with Maxwell and the electromagnetic theory of light, but although he considered the propagation of light in crystals [6], Maxwell did not treat chiral media. In current notation, the propagation of light in isotropic non-chiral media is describable in terms of a dielectric function ϵ and a magnetic permeability μ which relate the fields $\boldsymbol{D}$ to $\boldsymbol{E}$ and $\boldsymbol{B}$ to $\boldsymbol{H}$ via $\boldsymbol{D} = \epsilon\boldsymbol{E}$ and $\boldsymbol{B} = \mu\boldsymbol{H}$. The curl equations of Maxwell in non-chiral media are

$$c\nabla\times\boldsymbol{E} = -\partial\boldsymbol{B}/\partial t \qquad c\nabla\times\boldsymbol{H} = \partial\boldsymbol{D}/\partial t \tag{1}$$

and all researchers seem to agree that these are retained in chiral media. All researchers do not agree on the constitutive relations in chiral media, namely on what to replace $\boldsymbol{D} = \epsilon\boldsymbol{E}$ and $\boldsymbol{B} = \mu\boldsymbol{H}$ by. The results given in this paper are based on the symmetrized Condon set [7]

$$\boldsymbol{D} = \epsilon\boldsymbol{E} - g\partial\boldsymbol{H}/\partial t \qquad \boldsymbol{B} = \mu\boldsymbol{H} + g\partial\boldsymbol{E}/\partial t \tag{2}$$

as advocated by Silverman [8]. (Condon omitted the μ; hence the adjective *symmetrized*.) Silverman [8] has shown that the constitutive relations due to Born [9], namely

$$\boldsymbol{D} = \epsilon_{\mathrm{B}}\boldsymbol{E} + g_{\mathrm{B}}\nabla\times\boldsymbol{E} \qquad \boldsymbol{B} = \mu_{\mathrm{B}}\boldsymbol{H} \tag{3}$$

lead to reflectances in excess of unity in the vicinity of critical angles. Another choice, known as the Drude–Born–Fedorov relations, is discussed in section 1.2.1 of [4]:

$$\boldsymbol{D} = \epsilon_{\mathrm{DBF}}(\boldsymbol{E} + b\nabla\times\boldsymbol{E}) \qquad \boldsymbol{B} = \mu_{\mathrm{DBF}}(\boldsymbol{H} + b\nabla\times\boldsymbol{H}). \tag{4}$$

From the curl equations (1) it is clear that (2) and (4) are equivalent to first order in g and b.

For monochromatic waves in which the fields have a time dependence given by the factor $\exp(-\mathrm{i}\omega t)$, the relations (2) become, with $\gamma = \omega g$,

$$\boldsymbol{D} = \epsilon\boldsymbol{E} + \mathrm{i}\gamma\boldsymbol{H} \qquad \boldsymbol{B} = \mu\boldsymbol{H} - \mathrm{i}\gamma\boldsymbol{E}. \tag{5}$$

The Drude–Born–Fedorov relations become, with the use of (1) and on setting $\chi = \omega b/c$,

$$\boldsymbol{D} = \epsilon_{\mathrm{DBF}}(\boldsymbol{E} + \mathrm{i}\chi\boldsymbol{B}) \qquad \boldsymbol{B} = \mu_{\mathrm{DBF}}(\boldsymbol{H} - \mathrm{i}\chi\boldsymbol{D})\,. \tag{6}$$

These relations are equivalent to (5) if the dielectric constants and permeabilities differ by a term second order in the chiral index γ:

$$\epsilon_{\mathrm{DBF}} = \epsilon - \gamma^2/\mu \qquad \mu_{\mathrm{DBF}} = \mu - \gamma^2/\epsilon \qquad \chi = \frac{\gamma}{\epsilon\mu - \gamma^2}\,. \tag{7}$$

The inverse relations are [10, 4]

$$\epsilon = \frac{\epsilon_{\mathrm{DBF}}}{1 - \epsilon_{\mathrm{DBF}}\mu_{\mathrm{DBF}}\chi^2} \qquad \mu = \frac{\mu_{\mathrm{DBF}}}{1 - \epsilon_{\mathrm{DBF}}\mu_{\mathrm{DBF}}\chi^2} \qquad \gamma = \frac{\epsilon_{\mathrm{DBF}}\mu_{\mathrm{DBF}}\chi}{1 - \epsilon_{\mathrm{DBF}}\mu_{\mathrm{DBF}}\chi^2}\,. \tag{8}$$

Bassiri *et al* [2] use the relations

$$\boldsymbol{D} = \epsilon_{\mathrm{BPE}}\boldsymbol{E} + \mathrm{i}\xi\boldsymbol{B} \qquad \boldsymbol{H} = \mathrm{i}\xi\boldsymbol{E} + \boldsymbol{B}/\mu_{\mathrm{BPE}}\,. \tag{9}$$

This form was deduced by them from the work of Jaggard *et al* [11], who calculated the properties of a medium composed of short wire helices. (The effect of the scattered fields of the helices on each other was neglected.)

The Born relations (3) can be eliminated on physical grounds: they predict reflectances in excess of unity in the vicinity of critical angles, and also a difference in the normal incidence reflectance of the two circular polarizations which is first order in the chirality parameter g_{B}, and in disagreement with experiment [12, 13].

As we shall see in section 3.3, the relations (5) lead to normal incidence reflectances from an achiral–chiral interface which are independent of the chiral index γ, while the relations (9) give reflectances which contain terms of second order in the chiral parameter ξ. In section 4.3 it is shown that the chiral index γ is related to the rotation δ of the plane of polarization on passing normally through a chiral plate of thickness d by

$$\gamma = \frac{\lambda\delta}{2\pi d}\,. \tag{10}$$

The specific rotation δ/d for $AgGaS_2$ is large, for example, 0.95° per μm at $\lambda = 0.485$ μm, yet even this relatively large value gives $\gamma \approx 1.28 \times 10^{-3}$. The differential reflectance measurement reported in [13] was on α-$LiIO_3$ crystals cut normal to the optic axis, with $\delta/d = 86.8^\circ$/mm at $\lambda = 0.63$ μm and $\gamma \approx 1.52 \times 10^{-4}$. No difference in the normal incidence reflectance of the two circular polarizations was detected to within 10^{-7}, but an effect of order γ^2 is smaller than this. Thus experiment does not yet rule out or confirm normal incidence differential reflectances which are of second order in the chirality index.

The specific rotation δ/d which follows from (9) is related to ξ via

$$\xi\mu_{\mathrm{BPE}} = \frac{\lambda\delta}{2\pi d} \tag{11}$$

([2], equation (72)). Comparison of (5) and (9) identifies $\xi\mu_{\mathrm{BPE}}$ with γ, and substitution of $\xi = \gamma/\mu_{\mathrm{BPE}}$ into (9) gives

$$\boldsymbol{D} = (\epsilon_{\mathrm{BPE}} + \gamma^2/\mu_{\mathrm{BPE}})\boldsymbol{E} + \mathrm{i}\gamma\boldsymbol{H} \qquad \boldsymbol{B} = \mu_{\mathrm{BPE}}\boldsymbol{H} - \mathrm{i}\gamma\boldsymbol{E}\,. \tag{12}$$

Thus equations (5) and (9) are in agreement if

$$\mu_{\mathrm{BPE}} = \mu \qquad \epsilon_{\mathrm{BPE}} = \epsilon - \gamma^2/\mu \qquad \xi = \gamma/\mu \tag{13}$$

that is if the Bassiri, Papas and Engheta dielectric function is made to depend on the square of the chirality index γ. If indeed we set $\epsilon_{\mathrm{BPE}} = \epsilon - \gamma^2/\mu$ in the formulae of [2], we find that for the achiral–chiral interface the normal incidence reflection and transmission amplitudes become independent of γ.

In this paper we henceforth adopt the constitutive relations (2) and (5) advocated by Silverman [8], with ϵ and μ independent of the chiral index γ. This is also the choice made in the monograph [4], and is consistent with experiment: Silverman *et al* [12] have used optical phase modulation to measure chiral asymmetries in specular reflection from a gyrotropic medium, and have found agreement with the reflection amplitudes calculated by Silverman [8] using equation (2).

1.3. Reflection and transmission amplitudes, conservation laws

The optics of stratified chiral and/or anisotropic media can be quantified in terms of four reflection and four transmission amplitudes. These can be of two kinds, depending on whether the wave description is in terms of planar or circular polarization.

In the case of plane polarized states, the electric field components of the incident, reflected and transmitted waves are resolved along the $\boldsymbol{p}$ and $\boldsymbol{p}'$ directions which lie in the plane of incidence, and the $\boldsymbol{s}(=\boldsymbol{s}')$ direction perpendicular to the plane of incidence. If propagation is in the zx plane (the plane of incidence) and in the direction of positive x, with wavevector components in the (homogeneous) medium of incidence $\boldsymbol{k}_1 = (K, 0, q_1)$, an s-polarized wave of unit electric field magnitude will be

$$\boldsymbol{E}_{\rm s} = (0, 1, 0)\exp \mathrm{i}(Kx + q_1 z)\,. \tag{14}$$

If θ_1 is the angle of incidence, the reflected wave electric field will be (by definition of the reflection amplitudes $r_{\rm ss}$ and $r_{\rm sp}$)

$$\boldsymbol{E}' = (r_{\rm sp}\cos\theta_1, r_{\rm ss}, r_{\rm sp}\sin\theta_1)\exp \mathrm{i}(Kx - q_1 z)\,. \tag{15}$$

For an incident p-polarized wave the incoming and reflected waves are

$$\boldsymbol{E}_{\rm p} = (\cos\theta_1, 0, -\sin\theta_1)\exp \mathrm{i}(Kx + q_1 z) \tag{16}$$

$$\boldsymbol{E}' = (r_{\rm pp}\cos\theta_1, r_{\rm ps}, r_{\rm pp}\sin\theta_1)\exp \mathrm{i}(Kx - q_1 z)\,. \tag{17}$$

(The reflection amplitude for the x component is $r_{\rm pp}$, while for the z component it is $-r_{\rm pp}$: see equations (26) and (27) of section 1–2 of [14].)

The cause of the reflection is assumed to be a general planar-stratified layer (which may be chiral and anisotropic) resting on a homogeneous achiral isotropic substrate, in which the wavevector of the transmitted wave is $\boldsymbol{k}_2 = (K, 0, q_2)$. Note that the component of the wavevector along the stratification (the x component K) is a constant of the motion, because of translational invariance in the x direction. The transmitted wave when the incident wave is s-polarized is

$$\boldsymbol{E}'' = (t_{\rm sp}\cos\theta_2, t_{\rm ss}, -t_{\rm sp}\sin\theta_2)\exp \mathrm{i}[Kx + q_2(z - d)] \tag{18}$$

where θ_2 is the angle of refraction in the substrate and d is the total thickness of the chiral (and possibly anisotropic) layer. The corresponding transmitted electric field when a p-polarized wave is incident is

$$\boldsymbol{E}'' = (t_{\rm pp}\cos\theta_2, t_{\rm ps}, -t_{\rm pp}\sin\theta_2)\exp \mathrm{i}[Kx + q_2(z - d)]\,. \tag{19}$$

These relations define the transmission amplitudes $t_{\rm ss}$, $t_{\rm sp}$, $t_{\rm pp}$ and $t_{\rm ps}$.

If the chiral layer is non-absorbing, the reflected plus transmitted fluxes of energy must add up to the incident flux. The energy density of a plane electromagnetic wave in a medium with dielectric constant ϵ and permeability μ is proportional to $\epsilon|\boldsymbol{E}|^2$ and the speed is $c/\sqrt{\epsilon\mu}$; thus the energy flux is proportional to $\sqrt{\epsilon/\mu}|\boldsymbol{E}|^2$. The amount of energy in the primary wave which is incident on a unit area of the interface in unit time is proportional to $\sqrt{\epsilon_1/\mu_1}\cos\theta_1$, the amount reflected to $\sqrt{\epsilon_1/\mu_1}\cos\theta_1$ times the absolute square of the reflected field, and the amount carried away by the transmitted wave similarly to $\sqrt{\epsilon_2/\mu_2}\cos\theta_2$ times the absolute square of the transmitted electric field. (See figure 2.1 of [14] for the geometry leading to the factors $\cos\theta_1$ and $\cos\theta_2$.) Thus energy conservation reads, for incident s and p polarizations,

$$\begin{aligned}\sqrt{\frac{\epsilon_1}{\mu_1}}\cos\theta_1(1-|r_{\rm ss}|^2-|r_{\rm sp}|^2) &= \sqrt{\frac{\epsilon_2}{\mu_2}}\cos\theta_2(|t_{\rm ss}|^2+|t_{\rm sp}|^2)\\ \sqrt{\frac{\epsilon_1}{\mu_1}}\cos\theta_1(1-|r_{\rm pp}|^2-|r_{\rm ps}|^2) &= \sqrt{\frac{\epsilon_2}{\mu_2}}\cos\theta_2(|t_{\rm pp}|^2+|t_{\rm ps}|^2)\,.\end{aligned}\tag{20}$$

These relations hold for arbitrary non-absorbing stratifications. When there is absorption, the difference between the left- and right-hand sides gives the absorption in the stratification.

An alternative characterization of polarization states is in terms of positive and negative helicities (opposite circular polarizations). For circularly polarized incident light we need the reflection and transmission amplitudes $r_{++}, r_{+-}, r_{-+}, r_{--}$ and $t_{++}, t_{+-}, t_{-+}, t_{--}$, where, for example, r_{+-} gives the complex amplitude of the light reflected with negative helicity when positive helicity light is incident. (We avoid the left and right circular polarization terminology, because two opposite conventions are in use.) Let $(\boldsymbol{p}, \boldsymbol{s}, \boldsymbol{k}_1)$ denote a right-handed triplet of vectors for the incident light, with $\boldsymbol{p}$ and $\boldsymbol{s}$ being unit vectors perpendicular to the direction of propagation, and, respectively, parallel and perpendicular to the plane of incidence. Similarly, let $(\boldsymbol{p}', \boldsymbol{s}', \boldsymbol{k}_1')$ be a similar triplet for the reflected light (the choice $\boldsymbol{s}' = \boldsymbol{s}$ then implies that $\boldsymbol{p}' \to -\boldsymbol{p}$ at normal incidence, and $\boldsymbol{p}' \to \boldsymbol{p}$ at glancing incidence). Then $(\boldsymbol{p}+{\rm i}\boldsymbol{s})/\sqrt{2}$ represents an incident wave of positive helicity and unit magnitude. We have chosen the zx plane as the plane of incidence, with $\boldsymbol{s} = (0, 1, 0) = \boldsymbol{s}'$, $\boldsymbol{p} = (\cos\theta_1, 0, -\sin\theta_1)$ and $\boldsymbol{p}' = (-\cos\theta_1, 0, -\sin\theta_1)$. From equations (15) and (17), an electric field of unit magnitude along $\boldsymbol{s}$ reflects to $r_{\rm ss}\boldsymbol{s}' - r_{\rm sp}\boldsymbol{p}'$, and an electric field of unit magnitude along $\boldsymbol{p}$ reflects to $-r_{\rm pp}\boldsymbol{p}' + r_{\rm ps}\boldsymbol{s}'$. The reflected field is therefore

$$[(-r_{\rm pp}-{\rm i}r_{\rm sp})\boldsymbol{p}' + (r_{\rm ps}+{\rm i}r_{\rm ss})\boldsymbol{s}']/\sqrt{2}\tag{21}$$

from which we extract the coefficients of positive and negative helicity, namely of $(\boldsymbol{p}'\pm{\rm i}\boldsymbol{s}')/\sqrt{2}$, to find

$$\begin{aligned}r_{++} &= \tfrac{1}{2}(r_{\rm ss}-r_{\rm pp}) - \tfrac{1}{2}{\rm i}(r_{\rm sp}+r_{\rm ps})\\ r_{+-} &= -\tfrac{1}{2}(r_{\rm ss}+r_{\rm pp}) - \tfrac{1}{2}{\rm i}(r_{\rm sp}-r_{\rm ps})\,.\end{aligned}\tag{22}$$

Similarly, when the incident wave is $(\boldsymbol{p}-{\rm i}\boldsymbol{s})/\sqrt{2}$ (negative helicity), the reflected field is

$$\frac{1}{\sqrt{2}}[(-r_{\rm pp}+{\rm i}r_{\rm sp})\boldsymbol{p}' + (r_{\rm ps}-{\rm i}r_{\rm ss})\boldsymbol{s}']\tag{23}$$

and the corresponding reflection amplitudes are

$$\begin{aligned}r_{-+} &= -\tfrac{1}{2}(r_{\rm ss}+r_{\rm pp}) + \tfrac{1}{2}{\rm i}(r_{\rm sp}-r_{\rm ps})\\ r_{--} &= \tfrac{1}{2}(r_{\rm ss}-r_{\rm pp}) + \tfrac{1}{2}{\rm i}(r_{\rm sp}+r_{\rm ps})\,.\end{aligned}\tag{24}$$

For all the cases considered in this review, $r_{\rm sp} = r_{\rm ps}$ and so $r_{+-} = r_{-+}$.

The transmission amplitudes as characterized by helicity are found as follows. Let $(\boldsymbol{p}\pm{\rm i}\boldsymbol{s})/\sqrt{2}$ represent the electric fields of incident waves of positive and negative helicity, and likewise $(\boldsymbol{p}''\pm{\rm i}\boldsymbol{s}'')/\sqrt{2}$ for the transmitted helicities. When $(\boldsymbol{p}+{\rm i}\boldsymbol{s})/\sqrt{2}$ is incident, the transmitted field is

$$[(t_{\rm pp}+{\rm i}t_{\rm sp})\boldsymbol{p}'' + (t_{\rm ps}+{\rm i}t_{\rm ss})\boldsymbol{s}'']/\sqrt{2}\,.\tag{25}$$

The coefficients of positive and negative helicity in (25) give

$$
\begin{aligned}
t_{++} &= \tfrac{1}{2}(t_{\rm pp} + t_{\rm ss}) + \tfrac{1}{2}{\rm i}(t_{\rm sp} - t_{\rm ps}) \\
t_{+-} &= \tfrac{1}{2}(t_{\rm pp} - t_{\rm ss}) + \tfrac{1}{2}{\rm i}(t_{\rm sp} + t_{\rm ps})\,.
\end{aligned}
\tag{26}
$$

Similarly, for negative helicity incident we find

$$
\begin{aligned}
t_{-+} &= \tfrac{1}{2}(t_{\rm pp} - t_{\rm ss}) - \tfrac{1}{2}{\rm i}(t_{\rm sp} + t_{\rm ps}) \\
t_{--} &= \tfrac{1}{2}(t_{\rm pp} + t_{\rm ss}) - \tfrac{1}{2}{\rm i}(t_{\rm sp} - t_{\rm ps})\,.
\end{aligned}
\tag{27}
$$

The inverse relations are as follows:

$$
\begin{aligned}
r_{\rm ss} &= \tfrac{1}{2}(r_{++} + r_{--}) - \tfrac{1}{2}(r_{+-} + r_{-+}) \\
r_{\rm pp} &= -\tfrac{1}{2}(r_{++} + r_{--}) - \tfrac{1}{2}(r_{+-} + r_{-+}) \\
r_{\rm sp} &= \tfrac{1}{2}{\rm i}(r_{++} - r_{--}) + \tfrac{1}{2}{\rm i}(r_{+-} - r_{-+}) \\
r_{\rm ps} &= \tfrac{1}{2}{\rm i}(r_{++} - r_{--}) - \tfrac{1}{2}{\rm i}(r_{+-} - r_{-+})
\end{aligned}
\tag{28}
$$

$$
\begin{aligned}
t_{\rm ss} &= \tfrac{1}{2}(t_{++} + t_{--}) - \tfrac{1}{2}(t_{+-} + t_{-+}) \\
t_{\rm pp} &= \tfrac{1}{2}(t_{++} + t_{--}) + \tfrac{1}{2}(t_{+-} + t_{-+}) \\
t_{\rm sp} &= -\tfrac{1}{2}{\rm i}(t_{++} - t_{--}) - \tfrac{1}{2}{\rm i}(t_{+-} - t_{-+}) \\
t_{\rm ps} &= \tfrac{1}{2}{\rm i}(t_{++} - t_{--}) - \tfrac{1}{2}{\rm i}(t_{+-} - t_{-+})\,.
\end{aligned}
\tag{29}
$$

Energy conservation relations may also be written down in terms of the helicity reflection and transmission amplitudes. For incident waves of respectively positive and negative helicity, energy conservation implies

$$
\begin{aligned}
\sqrt{\frac{\epsilon_1}{\mu_1}}\cos\theta_1(1 - |r_{++}|^2 - |r_{+-}|^2) &= \sqrt{\frac{\epsilon_2}{\mu_2}}\cos\theta_2(|t_{++}|^2 + |t_{+-}|^2) \\
\sqrt{\frac{\epsilon_1}{\mu_1}}\cos\theta_1(1 - |r_{--}|^2 - |r_{-+}|^2) &= \sqrt{\frac{\epsilon_2}{\mu_2}}\cos\theta_2(|t_{--}|^2 + |t_{-+}|^2)\,.
\end{aligned}
\tag{30}
$$

1.4. Differential reflectance, ellipsometry

Chiral media in general reflect opposite circular polarizations differently. When a wave of unit amplitude and positive helicity is incident, the amplitudes of the reflected waves of positive and negative helicities are r_{++} and r_{+-}, respectively. If the detector is polarization-insensitive, the reflected intensity is proportional to $R_+ = |r_{++}|^2 + |r_{+-}|^2$. (This result may be verified by expressing the reflected wave as $r_{++}(\boldsymbol{p}' + {\rm i}\boldsymbol{s}')/\sqrt{2} + r_{+-}(\boldsymbol{p}' - {\rm i}\boldsymbol{s}')/\sqrt{2} = (r_{++}+r_{+-})\boldsymbol{p}'/\sqrt{2}+{\rm i}(r_{++}-r_{+-})\boldsymbol{s}'/\sqrt{2}$, with $|\boldsymbol{E}'|^2$ given by $(|r_{++}+r_{+-}|^2+|r_{++}-r_{+-}|^2)/2$.) Similarly, a wave of unit amplitude and negative helicity produces a reflected intensity proportional to $R_- = |r_{--}|^2 + |r_{-+}|^2$. The differential circular reflectance (DCR) is defined as [8]

$$
{\rm DCR} = \frac{R_+ - R_-}{R_+ + R_-}\,. \tag{31}
$$

If linearly polarized waves of s or p polarization are incident, and the detector is polarization-insensitive, the reflected intensities will be proportional to $R_{\rm s} = |r_{\rm ss}|^2 + |r_{\rm sp}|^2$ or $R_{\rm p} = |r_{\rm pp}|^2 + |r_{\rm ps}|^2$, respectively. Differential linear reflectance (DLR) is defined as [12]

$$
{\rm DLR} = \frac{R_{\rm s} - R_{\rm p}}{R_{\rm s} + R_{\rm p}}\,. \tag{32}
$$

Measurements on chiral media of DLR [12] and DCR [15–18] have been made by Silverman and collaborators.

The reflection amplitudes $r_{\mathrm{pp}}, r_{\mathrm{ss}}, r_{\mathrm{ps}}$ and r_{sp} can be used to calculate the reflection ellipsometric signal, which in the common experimental configurations is one of the ratios ρ_P or ρ_A, where [19]

$$\rho_P = \frac{r_{\mathrm{pp}} + r_{\mathrm{sp}} \tan P}{r_{\mathrm{ps}} + r_{\mathrm{ss}} \tan P} \qquad \rho_A = \frac{r_{\mathrm{pp}} + r_{\mathrm{ps}} \tan A}{r_{\mathrm{sp}} + r_{\mathrm{ss}} \tan A} \tag{33}$$

where P is the angle between the polarizer easy axis and the incident p direction, while A is the angle between the analyser easy axis and the reflected p direction. (The p or TM directions lie in the plane of incidence and are perpendicular to the incoming or reflected beams, the s or TE direction is perpendicular to the plane of incidence.)

We note in passing that at the polarizing Brewster angle defined by $r_{\mathrm{pp}} r_{\mathrm{ss}} = r_{\mathrm{sp}} r_{\mathrm{ps}}$ (see section 3.3), ρ_P and ρ_A become independent of the orientations of the polarizer and analyser, and take the respective values $r_{\mathrm{pp}}/r_{\mathrm{ps}}$ and $r_{\mathrm{pp}}/r_{\mathrm{sp}}$. For the cases considered in this paper, $r_{\mathrm{sp}} = r_{\mathrm{ps}}$, so ρ_P and ρ_A are equal at the polarizing angle.

Ellipsometry of chiral media will be discussed in more detail in section 5.

2. Wave propagation in chiral media

2.1. Inhomogeneous media

We will henceforth assume the validity of the two curl equations (1) and of the constitutive relations (2). At first we will consider a general inhomogeneous medium, where ϵ, μ and γ are all functions of position. Since the equations are linear in the fields, we can deal with one Fourier component at a time; we assume a time dependence $\mathrm{e}^{-\mathrm{i}\omega t}$, so that we can use (5) and

$$c\nabla \times \boldsymbol{E} = \mathrm{i}\omega \boldsymbol{B} \qquad c\nabla \times \boldsymbol{H} = -\mathrm{i}\omega \boldsymbol{D}\,. \tag{34}$$

The fields $\boldsymbol{B}, \boldsymbol{H}$ and $\boldsymbol{D}$ can be eliminated from (5) and (34) by substitution of $\boldsymbol{B} = (c/\mathrm{i}\omega)\nabla \times \boldsymbol{E}$ into $\boldsymbol{H} = (\boldsymbol{B} + \mathrm{i}\gamma\boldsymbol{E})/\mu$, and then of the latter expression into $\boldsymbol{D} = (\mathrm{i}c/\omega)\nabla \times \boldsymbol{H} = \epsilon\boldsymbol{E} + \mathrm{i}\gamma\boldsymbol{H}$. The result is a second-order equation for $\boldsymbol{E}$, namely

$$\mu\nabla \times \left(\frac{1}{\mu}\nabla \times \boldsymbol{E}\right) = \left(\epsilon\mu - \gamma^2\right)\frac{\omega^2}{c^2}\boldsymbol{E} + \frac{\omega}{c}\left[\gamma\nabla \times \boldsymbol{E} + \mu\nabla \times \left(\frac{\gamma}{\mu}\boldsymbol{E}\right)\right]. \tag{35}$$

The equation for $\boldsymbol{H}$ has the same form, with the roles of ϵ and μ interchanged.

When the medium is z-stratified, ϵ, μ and γ are functions of z only. Let us assume also that there is a plane wave incident on the stratification, propagating in the zx plane. Because of the assumed translational invariance in the x and y directions, there will be no y dependence in any field component, and the x dependence of all field components is contained in the factor $\exp(\mathrm{i}Kx)$. K is the x-component of the wavevector, and is a constant of the motion because of the translational invariance in the x direction. For a z-stratified chiral medium, the three components E_x, E_y and E_z satisfy the coupled ordinary differential equations

$$
\begin{aligned}
&E_x'' - \frac{\mu'}{\mu}E_x' + (\epsilon\mu - \gamma^2)\frac{\omega^2}{c^2}E_x - \frac{\omega}{c}\left\{2\gamma E_y' + \left(\gamma' - \gamma\frac{\mu'}{\mu}\right)E_y\right\} - \mathrm{i}K\left(E_z' - \frac{\mu'}{\mu}E_z\right) = 0 \\
&E_y'' - \frac{\mu'}{\mu}E_y' + \left[\left(\epsilon\mu - \gamma^2\right)\frac{\omega^2}{c^2} - K^2\right]E_y \\
&\qquad\qquad + \frac{\omega}{c}\left\{2\gamma E_x' + \left(\gamma' - \gamma\frac{\mu'}{\mu}\right)E_x\right\} - 2\mathrm{i}\frac{\omega}{c}\gamma K E_z = 0 \\
&\left[(\epsilon\mu - \gamma^2)\frac{\omega^2}{c^2} - K^2\right]E_z - \mathrm{i}KE_x' + 2\mathrm{i}\frac{\omega}{c}\gamma K E_y = 0\,.
\end{aligned}
\tag{36}
$$

(The primes denote differentiation with respect to z.)

2.2. *Homogeneous chiral media*

Finally, we specialize to a homogeneous chiral medium. In this case ϵ, μ and γ are constant within the medium. We look for plane wave eigenstates, in which all field components have the variation $\exp(\mathrm{i}qz)$, where q is the z-component of the wavevector. The differential equations (36) then reduce to the three homogeneous linear algebraic equations

$$
\begin{aligned}
&\left[(\epsilon\mu - \gamma^2)\frac{\omega^2}{c^2} - q^2\right]E_x - 2\mathrm{i}\frac{\omega}{c}\gamma q E_y + qKE_z = 0 \\
&2\mathrm{i}\frac{\omega}{c}\gamma q E_x + \left[(\epsilon\mu - \gamma^2)\frac{\omega^2}{c^2} - K^2 - q^2\right]E_y - 2\mathrm{i}\frac{\omega}{c}\gamma K E_z = 0 \\
&qKE_x + 2\mathrm{i}\frac{\omega}{c}\gamma K E_y + \left[(\epsilon\mu - \gamma^2)\frac{\omega^2}{c^2} - K^2\right]E_z = 0\,.
\end{aligned}
\tag{37}
$$

A solution with non-zero $\boldsymbol{E}$ is possible only if the determinant of the coefficients of E_x, E_y and E_z in this set of equations is zero. This gives the condition

$$
\begin{vmatrix}
k_\gamma^2 - q^2 & -2\mathrm{i}\frac{\omega}{c}\gamma q & qK \\
2\mathrm{i}\frac{\omega}{c}\gamma q & k_\gamma^2 - q^2 - K^2 & -2\mathrm{i}\frac{\omega}{c}\gamma K \\
qK & 2\mathrm{i}\frac{\omega}{c}\gamma K & k_\gamma^2 - K^2
\end{vmatrix} = 0
\tag{38}
$$

where

$$
k_\gamma^2 = (\epsilon\mu - \gamma^2)\frac{\omega^2}{c^2}\,.
\tag{39}
$$

(A similar eigenvalue equation for q is obtained for anisotropic media: compare (38) with equation (20) of [29], for example.) Equation (38) is a quartic in q, with solutions $\pm q_+$ and $\pm q_-$, where

$$
q_\pm^2 = \left(\sqrt{\epsilon\mu} \pm \gamma\right)^2\frac{\omega^2}{c^2} - K^2\,.
\tag{40}
$$

The four possible plane waves in the chiral medium have wavevectors

$$
(K, 0, \pm q_+) \qquad \text{and} \qquad (K, 0, \pm q_-)\,.
\tag{41}
$$

(Two are for waves propagating in the $+z$ direction, two for waves propagating in the $-z$ direction.) The square of the wavevector is thus

$$
K^2 + q_\pm^2 = \left(\sqrt{\epsilon\mu} \pm \gamma\right)^2\frac{\omega^2}{c^2} \equiv k_\pm^2 \equiv n_\pm^2\frac{\omega^2}{c^2}\,.
\tag{42}
$$

Thus there are two effective indices for the chiral medium,

$$n_\pm = \sqrt{\epsilon\mu} \pm \gamma \equiv n \pm \gamma \tag{43}$$

which correspond to waves of positive and negative helicity, as we shall see shortly. The average of the two indices is $n = \sqrt{\epsilon\mu}$, and their product is $\epsilon\mu - \gamma^2 = (ck_\gamma/\omega)^2$. (The refractive indices are those of Silverman [8] but differ from the Condon [7] expressions by terms proportional to second and higher powers of γ.)

The electric field eigenstates which correspond to the eigenvalues $q_\pm$ given in (42) are obtained from equations (37) by substituting $q_\pm$ for q. We find, for the waves propagating in the $+z$ direction

$$\boldsymbol{E}_+ \sim (q_+, \mathrm{i}k_+, -K) \qquad \boldsymbol{E}_- \sim (q_-, -\mathrm{i}k_-, -K) \tag{44}$$

where $k_\pm = n_\pm\omega/c$. The corresponding wavevectors are $\boldsymbol{k}_\pm = (K, 0, q_\pm)$, and we see that, for each mode, the electric field eigenstate is perpendicular to the wavevector. The fields given in (44) have a phase difference of 90° between their y and zx components. Also $k_\pm^2 = K^2 + q_\pm^2$, so the two eigenstates correspond to circularly polarized light of positive and negative helicity.

The other fields can be found from $\boldsymbol{E}$ by means of $\boldsymbol{B} = (c/\omega)\boldsymbol{k}\times\boldsymbol{E}$, $\boldsymbol{H} = (\boldsymbol{B}+\mathrm{i}\gamma\boldsymbol{E})/\mu$ and $\boldsymbol{D} = \epsilon\boldsymbol{E} + \mathrm{i}\gamma\boldsymbol{H}$. They are

$$\begin{aligned} &\boldsymbol{B}_+ = -\mathrm{i}n_+\boldsymbol{E}_+ && \boldsymbol{B}_- = \mathrm{i}n_-\boldsymbol{E}_- \\ &\boldsymbol{H}_+ = -\mathrm{i}\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{E}_+ && \boldsymbol{H}_- = \mathrm{i}\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{E}_- \\ &\boldsymbol{D}_+ = n_+\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{E}_+ && \boldsymbol{D}_- = n_-\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{E}_- . \end{aligned} \tag{45}$$

The Poynting vectors have the appropriate directions: for example, $\boldsymbol{E}_+\times\boldsymbol{H}_+^*$ is proportional to $\boldsymbol{k}_+$. The corresponding fields for plane waves propagating in the $-z$ direction are obtained by replacing q_+ by $-q_+$ and q_- by $-q_-$ in $\boldsymbol{k}_\pm$ and in (44). The helicities are then negative for $\boldsymbol{E}_+ \sim (-q_+, \mathrm{i}k_+, -K)$ and positive for $\boldsymbol{E}_- \sim -(q_-, \mathrm{i}k_-, K)$.

2.3. Eigenstates of curl

An elegant alternative approach to propagation in homogeneous chiral media is in terms of two related linear combinations of the $\boldsymbol{E}$ and $\boldsymbol{H}$ fields [21] (see also [22] and [4])

$$\boldsymbol{F}_\pm = \boldsymbol{E}\pm\mathrm{i}\eta\boldsymbol{H} \qquad \eta = (\mu/\epsilon)^{1/2} . \tag{46}$$

Provided that η is constant in space, the curl equations (34) and the constitutive equations (5) together imply that $\boldsymbol{F}_+$ and $\boldsymbol{F}_-$ are eigenstates of the curl operator

$$\nabla \times \boldsymbol{F}_\pm = \pm k_\pm \boldsymbol{F}_\pm \tag{47}$$

where $k_\pm = n_\pm\omega/c = (n \pm \gamma)\omega/c$ as before. If we write (47) collectively as $\nabla\times\boldsymbol{F} = k\boldsymbol{F}$ (with $\boldsymbol{F} = \boldsymbol{F}_\pm$ and $k = \pm k_\pm$), plane wave propagation in the zx plane, with $\boldsymbol{F}$ proportional to $\exp \mathrm{i}(Kx + qz)$, is possible if

$$-\mathrm{i}qF_y = kF_x \qquad \mathrm{i}qF_x - \mathrm{i}KF_z = kF_y \qquad \mathrm{i}KF_y = kF_z . \tag{48}$$

These are three homogeneous equations in the field components (F_x, F_y, F_z) and a non-zero solution will exist only if the determinant of their coefficients is zero, namely if

$$\begin{vmatrix} k & \mathrm{i}q & 0 \\ -\mathrm{i}q & k & \mathrm{i}K \\ 0 & -\mathrm{i}K & k \end{vmatrix} = 0 . \tag{49}$$

This determinant factors to $k(k^2 - K^2 - q^2)$. The two values of k are $\pm k_\pm$, and thus we regain (42). From equation (45) we see that for the positive helicity wave $\boldsymbol{H}_+ = \boldsymbol{E}_+/(\mathrm{i}\eta)$ and so $\boldsymbol{F}_+ = 2\boldsymbol{E}_+$. For the negative helicity wave $\boldsymbol{H}_- = \boldsymbol{E}_-/(-\mathrm{i}\eta)$ and $\boldsymbol{F}_- = 2\boldsymbol{E}_-$. Thus for plane wave eigenstates in homogeneous chiral media, (47) reads

$$\nabla\times\boldsymbol{E}_+ = k_+\boldsymbol{E}_+ \qquad \nabla\times\boldsymbol{E}_- = -k_-\boldsymbol{E}_- \tag{50}$$

(or the same equations with $\boldsymbol{E}_\pm$ replaced by $\boldsymbol{H}_\pm$).

For inhomogeneous media the positive and negative helicities are coupled: equation (47) is replaced by

$$\nabla\times\boldsymbol{F}_\pm = \pm\left[k_\pm\boldsymbol{F}_\pm + (2\eta)^{-1}\nabla\eta\times(\boldsymbol{F}_+ - \boldsymbol{F}_-)\right]. \tag{51}$$

2.4. Boundary conditions

The boundary conditions at an interface between chiral media are the continuity of the tangential components of $\boldsymbol{E}$ and $\boldsymbol{H}$. For a z-stratified medium and plane waves propagating in the zx plane, the curl of $\boldsymbol{E}$ is

$$\nabla\times\boldsymbol{E} = (-E_y', E_x' - \mathrm{i}KE_z, \mathrm{i}KE_y). \tag{52}$$

Since the time derivative of $\boldsymbol{B}$, which by (1) is proportional to $\nabla\times\boldsymbol{E}$, is expected to be free of singularity at the interface, it follows that E_x' and E_y' are non-singular, and thus that E_x and E_y are continuous across the interface. Likewise, since the time derivative of $\boldsymbol{D}$, which is proportional to the curl of $\boldsymbol{H}$, is expected to be free of singularity at the interface, H_x and H_y should be continuous across the boundary.

The continuity of E_x also follows directly from the last equation in (36), while the terms containing derivatives in the first two equations of (36) can be written as $\mathrm{i}\omega/c$ times

$$\mu H_y' + \mathrm{i}\gamma E_y' \qquad \text{and} \qquad \mu H_x' + \mathrm{i}\gamma E_x'. \tag{53}$$

Thus the continuity of E_x and H_x follows from the differential equations for the components of $\boldsymbol{E}$, whereas these differential equations allow discontinuities in E_y and H_y across the interface, provided $\mu H_y' + \mathrm{i}\gamma E_y'$ remains non-singular. The possibility of discontinuities ΔH_y and ΔE_y satisfying $\mu\Delta H_y + \mathrm{i}\gamma\Delta E_y = 0$ is eliminated by the differential equations for H_x, H_y and H_z. These have the same form as those for the components of $\boldsymbol{E}$, with H_x replacing E_x, etc, and μ interchanged with ϵ. They imply that $\epsilon E_x' + \mathrm{i}\gamma H_x'$ and $\epsilon E_y' + \mathrm{i}\gamma H_y'$ are non-singular, and that H_x is continuous at the boundary. Discontinuities in E_y and H_y would then have to satisfy both $\mu\Delta H_y + \mathrm{i}\gamma\Delta E_y = 0$ and $\epsilon\Delta E_y + \mathrm{i}\gamma\Delta H_y = 0$. The determinant of the coefficients of ΔE_y and ΔH_y is $\epsilon\mu + \gamma^2$, which is normally non-zero, thus implying $\Delta E_y = 0$ and $\Delta H_y = 0$. We conclude that the continuity of the tangential components of $\boldsymbol{E}$ and $\boldsymbol{H}$ follows from the differential equations.

3. Reflection from an achiral–chiral interface

Reflection by a chiral medium was considered by Silverman [8] and Bassiri *et al* [2]; extensions to reflection at a chiral–achiral interface are given in [23, 24]. Here the reflection and transmission amplitudes are derived and their properties discussed.

3.1. Wavefunctions

Let a plane wave be incident from an optically non-active medium (dielectric and permeability constants ϵ_1 and μ_1), at an angle θ_1 to the interface normal. We wish to find the four reflection amplitudes r_{ss}, r_{sp}, r_{pp} and r_{ps} which completely characterize the reflection properties of the interface.

Inside the optically active medium the two plane wave eigenstates which propagate in the $+z$ direction have electric field vectors

$$\begin{aligned} \boldsymbol{E}_+ &= (\cos\theta_+, \mathrm{i}, -\sin\theta_+) \exp \mathrm{i}(Kx + q_+ z) \\ \boldsymbol{E}_- &= (\cos\theta_-, -\mathrm{i}, -\sin\theta_-) \exp \mathrm{i}(Kx + q_- z) \end{aligned} \tag{54}$$

where

$$\cos\theta_\pm = q_\pm / k_\pm \qquad \sin\theta_\pm = K/k_\pm \tag{55}$$

and $\theta_\pm$ are the angles of refraction for the two plane waves of opposite helicity. For incident s (TE) plane-polarized waves, the incoming and reflected waves have electric fields given by (14) and (15). Thus the electric field in medium 1 is

$$\boldsymbol{E}_1 = (r_{sp} \cos\theta_1\, \mathrm{e}^{-\mathrm{i}q_1 z},\ \mathrm{e}^{\mathrm{i}q_1 z} + r_{ss}\, \mathrm{e}^{-\mathrm{i}q_1 z}, r_{sp} \sin\theta_1\, \mathrm{e}^{-\mathrm{i}q_1 z})\, \mathrm{e}^{\mathrm{i}Kx}\,. \tag{56}$$

The magnetic field $\boldsymbol{H}_1$ in medium 1 is given by

$$\boldsymbol{H}_1 = \boldsymbol{B}_1/\mu_1 = \left(\frac{c}{\mathrm{i}\omega\mu_1}\right) \nabla \times \boldsymbol{E}_1\,. \tag{57}$$

At the boundary $z = 0$ this is

$$\boldsymbol{H}_1(z=0) = \frac{n_1}{\mu_1} \left(-(1 - r_{ss})\cos\theta_1, -r_{sp}, (1 + r_{ss})\sin\theta_1\right) \mathrm{e}^{\mathrm{i}Kx}\,. \tag{58}$$

Inside the optically active medium, the electric and magnetic fields are

$$\boldsymbol{E} = t_{s+}\boldsymbol{E}_+ + t_{s-}\boldsymbol{E}_- \qquad \boldsymbol{H} = -\mathrm{i}\sqrt{\frac{\epsilon}{\mu}}(t_{s+}\boldsymbol{E}_+ - t_{s-}\boldsymbol{E}_-) \tag{59}$$

where t_{s+} and t_{s-} are the transmission amplitudes for the two circularly polarized waves in the chiral medium.

3.2. Reflection and transmission amplitudes

The continuity of the tangential components of $\boldsymbol{E}$ and $\boldsymbol{H}$ across the interface at $z = 0$ gives four relations, which can be solved for the four unknowns r_{ss}, r_{sp}, t_{s+} and t_{s-}. We find, with

$$\begin{aligned} &c_1 = \cos\theta_1 \qquad c_\pm = \cos\theta_\pm = \sqrt{1 - (n_1 \sin\theta_1/n_\pm)^2} \qquad m = \sqrt{\frac{\epsilon\mu_1}{\mu\epsilon_1}} \\ &D = c_1^2 + c_1(c_+ + c_-)(m + m^{-1})/2 + c_+c_- \end{aligned} \tag{60}$$

that the reflection and transmission amplitudes when s-polarized light is incident are given by

$$\begin{aligned} r_{ss} &= \left[c_1^2 - c_1(c_+ + c_-)(m - m^{-1})/2 - c_+c_-\right]/D \\ r_{sp} &= -\mathrm{i}c_1(c_+ - c_-)/D \\ t_{s+} &= -\mathrm{i}c_1(c_1 + c_-/m)/D \\ t_{s-} &= \mathrm{i}c_1(c_1 + c_+/m)/D\,. \end{aligned} \tag{61}$$

For p polarization incident (a TM wave) the incoming and reflected waves have electric fields

$$\begin{aligned} &(\cos\theta_1, 0, -\sin\theta_1) \exp \mathrm{i}(Kx + q_1 z) \\ &(r_{pp}\cos\theta_1, r_{ps}, r_{pp}\sin\theta_1) \exp \mathrm{i}(Kx - q_1 z)\,. \end{aligned} \tag{62}$$

The electric field $\boldsymbol{E}_1$ is the sum of these; the magnetic field $\boldsymbol{H}_1$ given by (57) takes the value at the $z = 0$ boundary

$$\boldsymbol{H}_1(z=0) = \frac{n_1}{\mu_1}(r_{\mathrm{ps}}\cos\theta_1, 1 - r_{\mathrm{pp}}, r_{\mathrm{ps}}\sin\theta_1)\,\mathrm{e}^{\mathrm{i}Kx}\,. \tag{63}$$

The fields inside the chiral medium are now

$$\boldsymbol{E} = t_{\mathrm{p}+}\boldsymbol{E}_+ + t_{\mathrm{p}-}\boldsymbol{E}_- \qquad \boldsymbol{H} = -\mathrm{i}\sqrt{\frac{\epsilon}{\mu}}(t_{\mathrm{p}+}\boldsymbol{E}_+ - t_{\mathrm{p}-}\boldsymbol{E}_-)\,. \tag{64}$$

The reflection and transmission amplitudes when p-polarized light is incident are

$$\begin{aligned} r_{\mathrm{pp}} &= -[c_1^2 + c_1(c_+ + c_-)(m - m^{-1})/2 - c_+c_-]/D \\ r_{\mathrm{ps}} &= -\mathrm{i}c_1(c_+ - c_-)/D \\ t_{\mathrm{p}+} &= c_1(c_1/m + c_-)/D \\ t_{\mathrm{p}-} &= c_1(c_1/m + c_+)/D\,. \end{aligned} \tag{65}$$

These formulae are in accord with those of Silverman [8], but are not identical to those of Bassiri *et al* [2], unless we make the identification (13). We note that $r_{\mathrm{sp}} = r_{\mathrm{ps}}$. When the chirality is zero, r_{sp} and r_{ps} are also zero, while r_{ss} and r_{pp} reduce to the usual Fresnel amplitudes. From equations (61) and (65) we find

$$\begin{aligned} 1 - r_{\mathrm{ss}}^2 &= c_1(c_+ + c_- + 2c_1 m)[c_1(c_+ + c_-)m + 2c_+c_-]/mD \\ 1 - r_{\mathrm{pp}}^2 &= c_1((c_+ + c_-)m + 2c_1)[c_1(c_+ + c_-) + 2c_+c_-m]/mD\,. \end{aligned} \tag{66}$$

Since the right-hand sides of (66) are non-negative, the ss and pp reflectivities cannot exceed unity. Also the magnitude of $r_{\mathrm{sp}} = r_{\mathrm{ps}}$ is less than unity, by inspection.

At normal incidence $K \to 0$ and the cosines c_1 and $c_\pm$ tend to unity; the reflection and transmission amplitudes then take values independent of the chirality parameter γ:

$$\begin{aligned} &r_{\mathrm{ss}}, r_{\mathrm{pp}} \to \frac{1-m}{1+m} \qquad r_{\mathrm{sp}}, r_{\mathrm{ps}} \to 0 \\ &t_{\mathrm{p}\pm} \to \frac{1}{1+m} \qquad t_{s\pm} \to \frac{\mp\mathrm{i}}{1+m}\,. \end{aligned} \tag{67}$$

The transmission amplitudes for positive and negative helicities follow from the definitions of $t_{s\pm}$ and $t_{\mathrm{p}\pm}$ in (59) and (64). An incident wave with electric field vector $\boldsymbol{p} \pm \mathrm{i}\boldsymbol{s}$ transmits to $t_{\mathrm{p}+}\boldsymbol{E}_+ + t_{\mathrm{p}-}\boldsymbol{E}_- \pm \mathrm{i}t_{\mathrm{s}+}\boldsymbol{E}_+ \pm \mathrm{i}t_{\mathrm{s}-}\boldsymbol{E}_- = (t_{\mathrm{p}+} \pm \mathrm{i}t_{\mathrm{s}+})\boldsymbol{E}_+ + (t_{\mathrm{p}-} \pm \mathrm{i}t_{\mathrm{s}-})\boldsymbol{E}_-$. Therefore

$$\begin{aligned} t_{++} &= t_{\mathrm{p}+} + \mathrm{i}t_{\mathrm{s}+} \qquad t_{+-} = t_{\mathrm{p}-} + \mathrm{i}t_{\mathrm{s}-} \\ t_{-+} &= t_{\mathrm{p}+} - \mathrm{i}t_{\mathrm{s}+} \qquad t_{--} = t_{\mathrm{p}-} - \mathrm{i}t_{\mathrm{s}-}\,. \end{aligned} \tag{68}$$

The helicity reflection and transmission amplitudes for an achiral–chiral interface are all real when the chiral medium is non-absorbing:

$$\begin{aligned} &r_{+-} = c_1(c_+ + c_-)(m - m^{-1})/2D = r_{-+} \\ &r_{++} = (c_1 - c_+)(c_1 + c_-)/D \qquad r_{--} = (c_1 + c_+)(c_1 - c_-)/D \\ &t_{++} = c_1(c_- + c_1)(1 + m^{-1})/D \qquad t_{+-} = c_1(c_+ - c_1)(1 - m^{-1})/D \\ &t_{--} = c_1(c_+ + c_1)(1 + m^{-1})/D \qquad t_{-+} = c_1(c_- - c_1)(1 - m^{-1})/D\,. \end{aligned} \tag{69}$$

The normal-incidence limiting values are

$$\begin{aligned} &r_{++}, r_{--} \to 0 \qquad r_{+-}, r_{-+} \to \frac{m-1}{m+1} \\ &t_{++}, t_{--} \to \frac{2}{1+m} \qquad t_{+-}, t_{-+} \to 0\,. \end{aligned} \tag{70}$$

At glancing incidence ($c_1 \to 0$) all the transmission amplitudes go to zero, r_{++} and r_{--} tend to -1, r_{+-} and r_{-+} tend to zero, $r_{\rm pp} \to 1$ and $r_{\rm ss} \to -1$. The probability for photon spin-flip is zero at both normal and glancing incidence. (Helicity is reversed at normal incidence because of the reversal of the direction of travel of the light on reflection.)

Reflection near the critical angles $\theta_1^{\pm}$ given by $\sin\theta_1^{\pm} = n_{\pm}/n$ is discussed in section 4.5, together with the chiral layer case. The off-diagonal reflection amplitudes $r_{\rm sp}, r_{\rm ps}$ and r_{+-}, r_{-+} are proportional to the square root of the chiral index γ.

The energy conservation conditions to be satisfied by the reflection and transmission amplitudes follow from arguments along the lines given in section 1.3, and were first written down by Silverman and Badoz [15]. The helicity amplitudes satisfy

$$\begin{aligned}
&\sqrt{\frac{\epsilon_1}{\mu_1}}\cos\theta_1(1-|r_{++}|^2-|r_{+-}|^2) = \sqrt{\frac{\epsilon}{\mu}}(\cos\theta_+|t_{++}|^2+\cos\theta_-|t_{+-}|^2)\\
&\sqrt{\frac{\epsilon_1}{\mu_1}}\cos\theta_1(1-|r_{--}|^2-|r_{-+}|^2) = \sqrt{\frac{\epsilon}{\mu}}(\cos\theta_+|t_{-+}|^2+\cos\theta_-|t_{--}|^2)\,.
\end{aligned} \tag{71}$$

Since plane-polarized waves are not eigenstates within the chiral medium, the corresponding relations involving $r_{\rm ss}, r_{\rm sp}, r_{\rm ps}$ and $r_{\rm pp}$ are of a hybrid form:

$$\begin{aligned}
&\sqrt{\frac{\epsilon_1}{\mu_1}}\cos\theta_1(1-|r_{\rm ss}|^2-|r_{\rm sp}|^2) = 2\sqrt{\frac{\epsilon}{\mu}}(\cos\theta_+|t_{\rm s+}|^2+\cos\theta_-|t_{\rm s-}|^2)\\
&\sqrt{\frac{\epsilon_1}{\mu_1}}\cos\theta_1(1-|r_{\rm pp}|^2-|r_{\rm ps}|^2) = 2\sqrt{\frac{\epsilon}{\mu}}(\cos\theta_+|t_{\rm p+}|^2+\cos\theta_-|t_{\rm p-}|^2)\,.
\end{aligned} \tag{72}$$

The reason for the factor of 2 on the right-hand sides of (72) lies in our definition of the electric fields and of the transmission amplitudes: from equation (54) we see that $|\boldsymbol{E}_{\pm}|^2 = 2$, while the incoming s-polarized or p-polarized electric fields are normalized to unity (see equations (14) and (16)).

3.3. The Brewster angles

At the boundary between two non-chiral media, zero reflection of a p-polarized incident wave occurs at the Brewster angle $\theta_{\rm B}$, where

$$\tan^2\theta_{\rm B} = \left(\frac{\epsilon}{\epsilon_1}\right)\left(\frac{\epsilon\mu_1-\epsilon_1\mu}{\epsilon\mu-\epsilon_1\mu_1}\right) = \frac{\epsilon\mu(m^2-1)}{\epsilon\mu-\epsilon_1\mu_1}\,. \tag{73}$$

(When $\mu = \mu_1$ this simplifies to the more familiar $\tan^2\theta_{\rm B} = \epsilon/\epsilon_1$.)

For the achiral–chiral interface we can ask for the angle $\theta_{\rm pp}$ at which $r_{\rm pp}$ is zero, in analogy with the anisotropic crystal case [25]. From (65) we see that this occurs when

$$2(c_+c_- - c_1^2)m = c_1(c_+ + c_-)(m^2-1)\,. \tag{74}$$

The squares of the cosines of the angles of incidence and refraction can be expressed in terms of $s_1^2 = \sin^2\theta_1$ (by use of Pythagoras' theorem, and of Snell's law $n_1\sin\theta_1 = n_{\pm}\sin\theta_{\pm}$):

$$c_1^2 = 1 - s_1^2 \qquad c_{\pm}^2 = 1 - \left(\frac{n_1}{n_{\pm}}\right)^2 s_1^2\,. \tag{75}$$

Thus if we square both sides of (74), isolate the product c_+c_-, and then square again, we will obtain an algebraic equation for s_1^2. This turns out to a quartic in s_1^2, or equivalently a quartic in $t_1^2 = \tan^2\theta_1$, one of the solutions of which gives $\tan^2\theta_{\rm pp}$. When we substitute (43) into the quartics, we find that $\tan^2\theta_{\rm pp}$ is given by the right-hand side of (73) plus a term of order γ^2. Because γ is small for natural optically active media, the second-order correction to (73) is usually not of experimental interest.

Another possible definition of a Brewster angle is that used by Bassiri *et al* [2] and others (see section 3.5.4 of [4]): it is the angle at which a monochromatic plane wave of arbitrary polarization becomes linearly polarized on reflection. For a linearly polarized wave, the angle α between the electric field vector $\boldsymbol{E}$ and the $\boldsymbol{p}$ direction is given by $\tan\alpha = \boldsymbol{s}\cdot\boldsymbol{E}/\boldsymbol{p}\cdot\boldsymbol{E}$, where $\boldsymbol{p}$ and $\boldsymbol{s}$ are unit vectors as before. For the reflected wave the azimuthal angle is given by $\tan\alpha' = \boldsymbol{s}'\cdot\boldsymbol{E}'/\boldsymbol{p}'\cdot\boldsymbol{E}'$, where $\boldsymbol{E}' = (\boldsymbol{p}\cdot\boldsymbol{E})(r_{\rm pp}\boldsymbol{p}' + r_{\rm ps}\boldsymbol{s}') + (\boldsymbol{s}\cdot\boldsymbol{E})(r_{\rm sp}\boldsymbol{p}' + r_{\rm ss}\boldsymbol{s}')$. Thus

$$\tan\alpha' = \frac{r_{\rm ps} + r_{\rm ss}\tan\alpha}{r_{\rm pp} + r_{\rm sp}\tan\alpha}\,. \tag{76}$$

The condition for α' to be independent of α is

$$r_{\rm pp}r_{\rm ss} - r_{\rm ps}r_{\rm sp} = 0\,. \tag{77}$$

The condition (77) thus guarantees that the same polarization azimuth α' will result for all incident azimuths α, namely

$$\tan\alpha' = \frac{r_{\rm ps}}{r_{\rm pp}} = \frac{r_{\rm ss}}{r_{\rm sp}}\,. \tag{78}$$

For isotropic non-chiral media, the condition (77) reduces to $r_{\rm pp}r_{\rm ss} = 0$, which for $\mu = \mu_1$ is satisfied by $r_{\rm pp} = 0$ at $\theta_{\rm B}$ given by $\tan^2\theta_{\rm B} = \epsilon/\epsilon_1$, and gives an s-polarized reflected wave. For chiral media (77) implies

$$2(c_1^2 + c_+c_-)m = c_1(c_+ + c_-)(m^2+1)\,. \tag{79}$$

The same method that we outlined for the $r_{\rm pp} = 0$ case reduces (79) to a quadratic in $\sin^2\theta_1$, or equivalently, to a quadratic in $\tan^2\theta_1$. As we found for $\tan^2\theta_{\rm pp}$, the Brewster angle determined by (79) is given by (73) plus a term of second order in the chirality parameter γ. Thus measurement of either kind of Brewster angle is not a viable method of determining γ. The full formula for the angle of incidence at which the reflected light is linearly polarized is

$$\tan^2\theta_{\rm B} = \frac{(m^2-1)\left\{(m^2-1)[2n_+^2n_-^2 - n_1^2(n_+^2+n_-^2)] + 2(m^2+1)n_+n_-[(n_+^2-n_1^2)(n_-^2-n_1^2)]^{1/2}\right\}}{4m^2(n_+^2-n_1^2)(n_-^2-n_1^2)} \tag{80}$$

where $n_1 = (\epsilon_1\mu_1)^{1/2}$, $n_\pm = (\epsilon\mu)^{1/2} \pm \gamma$ and $m = (\epsilon\mu_1/\epsilon_1\mu)^{1/2}$.

4. Optical properties of a chiral layer

The optical properties of a chiral layer are discussed in [2, 4, 24, 26], among others. Here we give a first-principles derivation of the reflection and transmission amplitudes, with a discussion of special cases. The appendix gives (for the first time) analytic expressions for the exact reflection and transmission amplitudes.

4.1. Electric and magnetic fields

We consider reflection and transmission by an optically active layer of thickness d, between the medium of incidence with index of refraction $n_1 = (\epsilon_1\mu_1)^{1/2}$ and the substrate with index $n_2 = (\epsilon_2\mu_2)^{1/2}$. The layer lies between $z = 0$ and $z = d$, and is characterized by two indices $n_\pm = (\epsilon\mu)^{1/2} \pm \gamma$. Because of multiple reflections within the layer, the electromagnetic field inside is made up of four eigenstates or modes, two propagating in the positive z direction, and two in the negative z direction; for each direction of propagation there are two possible helicities. The electric fields have the space and time dependence

$$\boldsymbol{E}_{\pm}^{f} \exp \mathrm{i}(Kx + q_{\pm}z - \omega t) \qquad \boldsymbol{E}_{\pm}^{b} \exp \mathrm{i}(Kx - q_{\pm}z - \omega t) \tag{81}$$

where the superscripts f and b denote forward and backward propagation inside the slab, and $q_{\pm}$ are given by (40).

The reflection and transmission amplitudes are found by applying the continuity of the tangential (x and y) components of $\boldsymbol{E}$ and $\boldsymbol{H}$ at the two boundaries $z = 0$ and $z = d$ of the chiral slab. The s wave in the medium of incidence has electric and magnetic fields given by (56) and (58). The electric field inside the slab is

$$\boldsymbol{E} = f_{+}\boldsymbol{E}_{+}^{f} + f_{-}\boldsymbol{E}_{-}^{f} + b_{+}\boldsymbol{E}_{+}^{b} + b_{-}\boldsymbol{E}_{-}^{b} \tag{82}$$

where $\boldsymbol{E}_{+}^{f,b}$ and $\boldsymbol{E}_{-}^{f,b}$ are given by (with upper and lower signs corresponding to f and b)

$$\begin{aligned} \boldsymbol{E}_{+}^{f,b} &= (\pm\cos\theta_{+}, \mathrm{i}, -\sin\theta_{+}) \exp \mathrm{i}(Kx \pm q_{+}z) \\ \boldsymbol{E}_{-}^{f,b} &= (\pm\cos\theta_{-}, -\mathrm{i}, -\sin\theta_{-}) \exp \mathrm{i}(Kx \pm q_{-}z)\,. \end{aligned} \tag{83}$$

The corresponding magnetic field is

$$\boldsymbol{H} = -\mathrm{i}\sqrt{\frac{\epsilon}{\mu}}\left\{f_{+}\boldsymbol{E}_{+}^{f} - f_{-}\boldsymbol{E}_{-}^{f} + b_{+}\boldsymbol{E}_{+}^{b} - b_{-}\boldsymbol{E}_{-}^{b}\right\}. \tag{84}$$

The transmitted fields are, for s polarization incident,

$$\begin{aligned} \boldsymbol{E}_2 &= (t_{\mathrm{sp}}\cos\theta_2, t_{\mathrm{ss}}, -t_{\mathrm{sp}}\sin\theta_2) \exp \mathrm{i}[Kx + q_2(z-d)] \\ \boldsymbol{H}_2 &= \frac{n_2}{\mu_2}(-t_{\mathrm{ss}}\cos\theta_2, t_{\mathrm{sp}}, t_{\mathrm{ss}}\sin\theta_2) \exp \mathrm{i}[Kx + q_2(z-d)] \end{aligned} \tag{85}$$

where θ_2 is the angle of refraction in the substrate, given by $n_2 \sin\theta_2 = n_1 \sin\theta_1$. The continuity of E_x, E_y, H_x and H_y at $z = 0$ gives

$$\begin{aligned} & r_{\mathrm{sp}}c_1 = f_{+}c_{+} + f_{-}c_{-} - b_{+}c_{+} - b_{-}c_{-} \\ & 1 + r_{\mathrm{ss}} = \mathrm{i}(f_{+} - f_{-}) + \mathrm{i}(b_{+} - b_{-}) \\ & -\sqrt{\frac{\epsilon_1}{\mu_1}}(1 - r_{\mathrm{ss}})c_1 = -\mathrm{i}\sqrt{\frac{\epsilon}{\mu}}\{f_{+}c_{+} - f_{-}c_{-} - b_{+}c_{+} + b_{-}c_{-}\} \\ & -\sqrt{\frac{\epsilon_1}{\mu_1}}r_{\mathrm{sp}} = \sqrt{\frac{\epsilon}{\mu}}\{f_{+} + f_{-} + b_{+} + b_{-}\}\,. \end{aligned} \tag{86}$$

At $z = d$ the boundary conditions read

$$\begin{aligned} & t_{\mathrm{sp}}c_2 = f'_{+}c_{+} + f'_{-}c_{-} - b'_{+}c_{+} - b'_{-}c_{-} \\ & t_{\mathrm{ss}} = \mathrm{i}(f'_{+} - f'_{-}) + \mathrm{i}(b'_{+} - b'_{-}) \\ & -\sqrt{\frac{\epsilon_2}{\mu_2}}t_{\mathrm{ss}}c_2 = -\mathrm{i}\sqrt{\frac{\epsilon}{\mu}}\left\{f'_{+}c_{+} - f'_{-}c_{-} - b'_{+}c_{+} + b'_{-}c_{-}\right\} \\ & \sqrt{\frac{\epsilon_2}{\mu_2}}t_{\mathrm{sp}} = \sqrt{\frac{\epsilon}{\mu}}\left\{f'_{+} + f'_{-} + b'_{+} + b'_{-}\right\} \end{aligned} \tag{87}$$

where

$$f'_{\pm} = f_{\pm}\,\mathrm{e}^{\mathrm{i}q_{\pm}d} \qquad b'_{\pm} = b_{\pm}\,\mathrm{e}^{-\mathrm{i}q_{\pm}d}\,. \tag{88}$$

The eight equations (86) and (87) determine the eight unknowns $r_{\mathrm{ss}}, r_{\mathrm{sp}}, t_{\mathrm{ss}}, t_{\mathrm{sp}}, f_{+}, f_{-}, b_{+}, b_{-}$.

Before discussing the solution, we will note the case of incoming p polarization, for which the incident plus reflected fields are given by (62) and (63), and the transmitted fields are

$$\begin{aligned} \boldsymbol{E}_2 &= (t_{\rm pp}\cos\theta_2, t_{\rm ps}, -t_{\rm pp}\sin\theta_2)\exp \mathrm{i}[Kx+q_2(z-d)] \\ \boldsymbol{H}_2 &= \frac{n_2}{\mu_2}(-t_{\rm ps}\cos\theta_2, t_{\rm pp}, t_{\rm ps}\sin\theta_2)\exp \mathrm{i}[Kx+q_2(z-d)]\,. \end{aligned} \tag{89}$$

The fields inside the chiral layer have the same form as for the s polarization, namely as given in (82) and (84), but with different values of the forward and backward amplitudes $f_\pm$ and $b_\pm$.

4.2. Mode, phase and layer matrices

Thus both the incident s and p polarization cases can be solved with the same matrices, as is the case for anisotropic layers [27]. We define the mode matrix M and the phase matrix P,

$$\begin{aligned} M &= \begin{pmatrix} c_+ & c_- & -c_+ & -c_- \\ 1 & -1 & 1 & -1 \\ c_+ & -c_- & -c_+ & c_- \\ 1 & 1 & 1 & 1 \end{pmatrix} \\ P &= \begin{pmatrix} \mathrm{e}^{\mathrm{i}q_+d} & 0 & 0 & 0 \\ 0 & \mathrm{e}^{\mathrm{i}q_-d} & 0 & 0 \\ 0 & 0 & \mathrm{e}^{-\mathrm{i}q_+d} & 0 \\ 0 & 0 & 0 & \mathrm{e}^{-\mathrm{i}q_-d} \end{pmatrix} \end{aligned} \tag{90}$$

and also the vectors

$$\begin{aligned} \boldsymbol{a} &= \begin{pmatrix} f_+ \\ f_- \\ b_+ \\ b_- \end{pmatrix} \qquad \boldsymbol{r}_{\rm s} = \begin{pmatrix} c_1 r_{\rm sp} \\ -\mathrm{i}(1+r_{\rm ss}) \\ -\mathrm{i}c_1(1-r_{\rm ss})/m \\ -r_{\rm sp}/m \end{pmatrix} \qquad \boldsymbol{t}_{\rm s} = \begin{pmatrix} c_2 t_{\rm sp} \\ -\mathrm{i}t_{\rm ss} \\ -\mathrm{i}c_2 t_{\rm ss}/m' \\ t_{\rm sp}/m' \end{pmatrix} \\ \boldsymbol{r}_{\rm p} &= \begin{pmatrix} c_1(1+r_{\rm pp}) \\ -\mathrm{i}r_{\rm ps} \\ \mathrm{i}c_1 r_{\rm ps}/m \\ (1-r_{\rm pp})/m \end{pmatrix} \qquad \boldsymbol{t}_{\rm p} = \begin{pmatrix} c_2 t_{\rm pp} \\ -\mathrm{i}t_{\rm ps} \\ -\mathrm{i}c_2 t_{\rm ps}/m' \\ t_{\rm pp}/m' \end{pmatrix} \end{aligned} \tag{91}$$

where $m = (\epsilon\mu_1/\epsilon_1\mu)^{1/2}$ as before, and $m' = (\epsilon\mu_2/\epsilon_2\mu)^{1/2}$. In terms of these matrices and vectors, the s-wave equations (86) and (87) read

$$\boldsymbol{r}_{\rm s} = M\boldsymbol{a} \qquad \boldsymbol{t}_{\rm s} = MP\boldsymbol{a}\,. \tag{92}$$

The amplitude vector $\boldsymbol{a}$ can be eliminated, leaving four equations linking the reflection and transmission amplitudes:

$$\boldsymbol{t}_{\rm s} = MPM^{-1}\boldsymbol{r}_{\rm s}\,. \tag{93}$$

The reflection and transmission amplitudes for incident p polarization are similarly given by

$$\boldsymbol{t}_{\rm p} = MPM^{-1}\boldsymbol{r}_{\rm p}\,. \tag{94}$$

Thus the optical properties of the layer are determined by the 4×4 layer matrix

$$L = MPM^{-1} \tag{95}$$

and by the constants m and m'. The elements of L are independent of the polarization of the incident wave; they depend on the angle of incidence through the cosines of the angles of refraction of the two waves of positive and negative helicity, $\cos\theta_\pm = c_\pm$, where

$$c_\pm^2 = 1 - \left(\frac{n_1}{n_\pm}\right)^2 \sin^2\theta_1 = 1 - \left(\frac{n_1}{n_\pm}\right)^2 (1 - c_1^2)\,. \tag{96}$$

Note that P has unit determinant, so L is unimodular also. The determinant of M is $16c_+c_-$; thus M becomes singular at the two critical angles $\theta_1^\pm$, where $c_\pm = 0$. The elements of L also depend on the phase shifts $\mathrm{e}^{\pm \mathrm{i} q_\pm d}$ that the four modes experience on traversing the layer.

The equations (93) and (94) can be solved for the reflection and transmission amplitudes. It is always true that $r_{\mathrm{sp}} = r_{\mathrm{ps}}$. We will discuss some special cases in the following sections; the general formulae are given in the appendix.

4.3. *Normal incidence*

The simplest special case is normal incidence, for which we obtain

$$\begin{aligned} r_{\mathrm{ss}} = r_{\mathrm{pp}} &= \frac{r + r'Z_+Z_-}{1 + rr'Z_+Z_-} \\ r_{\mathrm{ps}} = r_{\mathrm{sp}} &= 0 \\ t_{\mathrm{pp}} = t_{\mathrm{ss}} &= \frac{(1+r)(1+r')(Z_+ + Z_-)/2}{1 + rr'Z_+Z_-} \\ t_{\mathrm{ps}} = -t_{\mathrm{sp}} &= \frac{\mathrm{i}(1+r)(1+r')(Z_+ - Z_-)/2}{1 + rr'Z_+Z_-} \end{aligned} \tag{97}$$

where r and r' are the normal-incidence reflection amplitudes at the first and second interfaces

$$r = \frac{1-m}{1+m} \qquad r' = \frac{m'-1}{m'+1} \tag{98}$$

and Z_+ and Z_- are the phase factors for waves of positive and negative helicity traversing the layer:

$$Z_\pm = \exp(\mathrm{i} q_\pm d)\,. \tag{99}$$

At normal incidence $q_\pm = n_\pm \omega/c$, from (40) and (42). From equations (22), (24) and (97) we find that, at normal incidence,

$$r_{++} = r_{--} = 0 \qquad r_{+-} = r_{-+} = -r_{\mathrm{ss}} = -r_{\mathrm{pp}}\,. \tag{100}$$

At normal incidence the transmission amplitudes characterized by helicity reduce to (on using (26), (27) and (97))

$$\begin{aligned} t_{++} &= \frac{(1+r)(1+r')Z_+}{1 + rr'Z_+Z_-} \\ t_{--} &= \frac{(1+r)(1+r')Z_-}{1 + rr'Z_+Z_-} \\ t_{+-} &= t_{-+} = 0\,. \end{aligned} \tag{101}$$

A chiral slab will thus transmit a normally incident pure circularly polarized wave without mixing in any of the opposite circular polarization. A linearly polarized wave can be regarded as an equal mix of the two opposite circular polarizations (for example

$\boldsymbol{p} = (\boldsymbol{p} + \mathrm{i}\boldsymbol{s})/2 + (\boldsymbol{p} - \mathrm{i}\boldsymbol{s})/2)$. After transmission through the slab, the positive and negative helicities are phase-shifted by different amounts, so that a wave of unit amplitude initially linearly polarized along $\boldsymbol{p}$ will after transmission through the slab have amplitude

$$[(\boldsymbol{p}+\mathrm{i}\boldsymbol{s})t_{++} + (\boldsymbol{p}-\mathrm{i}\boldsymbol{s})t_{--}]/2 = \frac{(1+r)(1+r')}{1+rr'Z_+Z_-}[\boldsymbol{p}(Z_+ + Z_-) + \mathrm{i}\boldsymbol{s}(Z_+ - Z_-)]/2$$
$$= \frac{(1+r)(1+r')}{1+rr'Z_+Z_-}\exp(\mathrm{i}n\omega d/c)[\boldsymbol{p}\cos\delta - \boldsymbol{s}\sin\delta] \qquad (102)$$

where $n = (n_+ + n_-)/2 = \sqrt{\epsilon\mu}$, and

$$\delta = \frac{1}{2}(n_+ - n_-)\frac{\omega d}{c} = \gamma\frac{\omega d}{c} = \gamma\frac{2\pi d}{\lambda}\,. \qquad (103)$$

The plane of polarization is thus rotated by δ. For propagation along the optic axis of crystalline quartz, for example, the rotation is 18.8° per mm at $\lambda = 633$ nm, so that $n_+ - n_- \approx 6.6\times10^{-5}$ and $\gamma \approx 3.3\times10^{-5}$.

We note that at normal incidence the multiple reflections within the slab have no effect on the rotation of the plane of polarization, although they do affect the amount of light transmitted. The situation is more complicated at oblique incidence: the ratio of t_{++} to t_{--} is no longer equal to Z_+/Z_-, and also t_{+-} and t_{-+} are not zero.

4.4. First-order chirality corrections

An optically inactive layer has the reflection and transmission amplitudes

$$\begin{aligned}
r_{ss} &= \frac{s+s'Z^2}{1+ss'Z^2} \qquad & r_{sp} &= 0\\
r_{pp} &= \frac{p+p'Z^2}{1+pp'Z^2} \qquad & r_{ps} &= 0\\
t_{ss} &= \frac{(1+s)(1+s')Z}{1+ss'Z^2} \qquad & t_{sp} &= 0\\
t_{pp} &= \frac{m'}{m}\frac{(1-p(1-p')Z}{1+pp'Z^2} \qquad & t_{ps} &= 0
\end{aligned} \qquad (104)$$

where $Z = \exp(\mathrm{i}qd)$, $q^2 = \epsilon\mu\omega^2/c^2 - K^2$, and s, s', p and p' are the Fresnel reflection amplitudes at the front and rear boundaries of the layer:

$$s = \frac{c_1 - mc_0}{c_1 + mc_0} \qquad s' = \frac{m'c_0 - c_2}{m'c_0 + c_2} \qquad p = \frac{c_0 - mc_1}{c_0 + mc_1} \qquad p' = \frac{m'c_2 - c_0}{m'c_2 + c_0}\,. \qquad (105)$$

The quantities $m = (\epsilon\mu_1/\epsilon_1\mu)^{1/2}$ and $m' = (\epsilon\mu_2/\epsilon_2\mu)^{1/2}$ become ratios of refractive indices in the non-magnetic case, when $\mu_1 = \mu = \mu_2$; c_0 is the common value of c_+ and c_- when $\gamma = 0$.

We now seek the corrections to (104) to first order in the chirality parameter γ. From $n_\pm = n \pm \gamma$ and

$$c_\pm^2 = 1 - (n_1/n_\pm)^2\sin^2\theta_1 \qquad (106)$$

we find, to first order in γ,

$$c_\pm = c_0 \pm \gamma(n_1\sin\theta_1)^2/n^3c_0 \equiv c_0 \pm \Gamma\,. \qquad (107)$$

The first-order corrections to the reflection and transmission amplitudes involve terms of the type $\Delta q/q$ and Δqd, where q is the common value of $q_\pm$ when $\gamma \to 0$, and Δq stands for $q_+ - q$ or $q_- - q$. The terms proportional to $\Delta q d$ can be large for thick films, even though the chirality is weak. From equation (40) or (107) we find

$$q_\pm = \frac{2\pi}{\lambda}(nc_0 \pm \gamma/c_0) + \mathrm{O}(\gamma^2)\,. \tag{108}$$

Thus the phase factors for waves of positive and negative helicity on traversing the layer are

$$Z_\pm = Z(1 \pm 2\pi \mathrm{i}\gamma d/\lambda c_0) + \mathrm{O}(\gamma^2)\,. \tag{109}$$

From equations (107) and (109) we see that the chirality corrections will be of two kinds, proportional to

$$\Gamma = \gamma(n_1 \sin\theta_1)^2/n^3 c_0 \qquad \text{or} \qquad \Delta = \gamma 2\pi \mathrm{i} d/\lambda c_0\,. \tag{110}$$

The second kind of term will be dominant for layers which are much thicker than a wavelength. Note that both terms are inversely proportional to the cosine of the angle of refraction, and thus diverge at the critical angle for total internal reflection. Reflection near the critical angle will be considered separately in the next section.

We will denote by the superscripts Γ and Δ the coefficients of Γ and Δ in the expansions of the reflection and transmission amplitudes in powers of γ. We find that there are no first-order terms in r_{pp} or r_{ss}, and that

$$r^\Gamma_{\mathrm{ps}} = r^\Gamma_{\mathrm{sp}} = \frac{2\mathrm{i}mc_1(1 - p's'Z^2)(Z^2-1)}{(c_1+mc_0)(mc_1+c_0)(1+pp'Z^2)(1+ss'Z^2)} \tag{111}$$

$$r^\Delta_{\mathrm{ps}} = r^\Delta_{\mathrm{sp}} = \frac{8\mathrm{i}mm'c_1c_0(c_0^2 - c_2^2)Z^2}{(c_1+mc_0)(m'c_0+c_2)(mc_1+c_0)(c_0+m'c_2)(1+pp'Z^2)(1+ss'Z^2)}\,. \tag{112}$$

There are likewise no first-order corrections to t_{pp} or t_{ss}. The first-order corrections to t_{ps} and t_{sp} are

$$t^\Gamma_{\mathrm{ps}} = \frac{4\mathrm{i}m'c_1(mc_0^2 - m'c_1c_2)(Z^2-1)Z}{(c_1+mc_0)(mc_1+c_0)(m'c_0+c_2)(c_0+m'c_2)(1+pp'Z^2)(1+ss'Z^2)} \tag{113}$$

$$t^\Gamma_{\mathrm{sp}} = \frac{4\mathrm{i}m'c_1(mc_1c_2 - m'c_0^2)(Z^2-1)Z}{(c_1+mc_0)(mc_1+c_0)(m'c_0+c_2)(c_0+m'c_2)(1+pp'Z^2)(1+ss'Z^2)} \tag{114}$$

$$t^\Delta_{\mathrm{ps}} = \frac{4\mathrm{i}m'c_1c_0(1+sp'Z^2)Z}{(mc_1+c_0)(m'c_0+c_2)(1+pp'Z^2)(1+ss'Z^2)} \tag{115}$$

$$t^\Delta_{\mathrm{sp}} = \frac{-4\mathrm{i}m'c_1c_0(1+ps'Z^2)Z}{(c_1+mc_0)(c_0+m'c_2)(1+pp'Z^2)(1+ss'Z^2)}\,. \tag{116}$$

We note that the first-order amplitude corrections proportional to the layer thickness (i.e. those with superscript Δ) are not singular at the critical angle, because they all have the factor c_0 cancelling the c_0^{-1} in Δ.

4.5. Optical properties near the critical angles

Enhancement of chirality effects in the vicinity of the critical angles has been noted in [15, 16, 18]. Here we give the reflection amplitudes, first for a bulk chiral medium, and then for a chiral layer.

If the medium of incidence has refractive index greater than one or both of the indices of the chiral layer, there will be an angle of incidence at which only one of the helicities can propagate within the chiral medium. Suppose $\gamma > 0$, i.e. $n_+ > n_-$. Then the negative helicity wave will be the first to decay exponentially within the bulk chiral medium, at angles of incidence greater than the critical angle θ_1^- given by

$$\sin\theta_1^- = \frac{n_-}{n_1} \,. \tag{117}$$

At this critical angle of incidence $c_- = \cos\theta_-$ is zero, and

$$c_+ = \cos\theta_+ = \frac{2}{n_+}(\gamma n)^{1/2} \approx 2\left(\frac{\gamma}{n}\right)^{1/2} \tag{118}$$

where $n = (n_+ + n_-)/2$ as before. The reflection amplitudes for the bulk medium have the following form at θ_1^-:

$$\begin{aligned} r_{ss} &= \frac{2mc_1 + c_+(1-m^2)}{2mc_1 + c_+(1+m^2)} = 1 - \frac{mc_+}{c_1} + \mathrm{O}(c_+^2) \\ r_{pp} &= -\frac{2mc_1 - c_+(1-m^2)}{2mc_1 + c_+(1+m^2)} = -1 + \frac{c_+}{mc_1} + \mathrm{O}(c_+^2) \\ r_{ps} = r_{sp} &= \frac{-2\mathrm{i}mc_+}{2mc_1 + c_+(1+m^2)} = -\frac{\mathrm{i}c_+}{c_1} + \mathrm{O}(c_+^2) \,. \end{aligned} \tag{119}$$

Similar formulae hold at θ_1^+: c_- replaces c_+ in the above formulae, and the sign of the r_{ps} and r_{sp} resulting expression is changed. Thus r_{ps} and r_{sp} are proportional to the square root of the small chirality parameter γ. Since $c_1(\theta_1^-) = \sqrt{1-(n_-/n_1)^2}$, index matching will increase the coefficient of $\sqrt{\gamma}$ in r_{sp} and r_{ps}.

The corresponding positive and negative helicity reflection amplitudes are (at θ_1^-)

$$\begin{aligned} r_{+-} = r_{-+} &= \frac{c_+(m^2-1)}{2mc_1 + c_+(1+m^2)} = \frac{(m^2-1)c_+}{2mc_1} + \mathrm{O}(c_+^2) \\ r_{++} &= \frac{2m(c_1 - c_+)}{2mc_1 + c_+(1+m^2)} = 1 - \frac{(m+1)^2 c_+}{2mc_1} + \mathrm{O}(c_+^2) \\ r_{--} &= \frac{2m(c_1 + c_+)}{2mc_1 + c_+(1+m^2)} = 1 - \frac{(m-1)^2 c_+}{2mc_1} + \mathrm{O}(c_+^2) \,. \end{aligned} \tag{120}$$

We now look at the amplitudes for a chiral layer at the critical angle θ_1^- for waves of negative helicity. We shall give r_{++} etc, since the helicity classification gives somewhat simpler results than the p and s polarization characterization. We give the results to zeroth order in c_+, which is equal to $2(\gamma n)^{1/2}/n_+$ at θ_1^-:

$$\begin{aligned} r_{+-} = r_{-+} &= \frac{-m'(m^2-1)c_2}{2\mathrm{i}mm'c_1c_2k_+d - [mc_1 + m'c_2 + mm'(m'c_1 + mc_2)]} + \mathrm{O}(c_+) \\ r_{++}, r_{--} &= \frac{m[2\mathrm{i}m'c_1c_2k_+d - c_1(1+m'^2) \pm 2m'c_2]}{2\mathrm{i}mm'c_1c_2k_+d - [mc_1 + m'c_2 + mm'(m'c_1 + mc_2)]} + \mathrm{O}(c_+) \end{aligned} \tag{121}$$

where $k_+ = n_+\omega/c$, so that $k_+d = 2\pi n_+ d/\lambda$. For thick films for which k_+d is large but c_+k_+d is still small compared to unity, r_{+-} and r_{-+} are small compared to r_{++} and r_{--}, which tend to 1 (compare with (120)). The corresponding transmission amplitudes are

$$\begin{pmatrix} t_{++} \\ t_{+-} \\ t_{-+} \\ t_{--} \end{pmatrix} = -\frac{c_1 m'}{D_-} \begin{pmatrix} (1+m)(1+m') \\ (1+m)(1-m') \\ (1-m)(1+m') \\ (1-m)(1-m') \end{pmatrix} + \mathrm{O}(c_+) \tag{122}$$

where D_- is the denominator appearing in (121). We see that the strongest transmission amplitude when $c_- = 0$ is t_{++}, and the weakest is t_{--}, but that no amplitude is zero at the critical angle for waves of negative helicity. However, only t_{++} and t_{-+} give amplitudes of waves propagating through the chiral slab; inside the slab the waves of negative helicity propagate along the surface at θ_1^-.

4.6. Thin chiral layer

We consider the optical properties of a thin chiral layer between achiral media with constants ϵ_1, μ_1 and ϵ_2, μ_2. By 'thin' we mean that the dimensionless quantity $\omega d/c = 2\pi d/\lambda$ is small compared to unity. We find that the reflection amplitudes have the following expansions to order $\omega d/c$:

$$
\begin{aligned}
r_{\rm ss} &= \frac{m'c_1 - mc_2}{m'c_1 + mc_2} + \frac{\mathrm{i}mc_1[m'^2(n_+c_+^2 + n_-c_-^2 - c_2^2(n_+ + n_-)]\omega d/c}{(m'c_1 + mc_2)^2} + \mathrm{O}\left(\frac{\omega d}{c}\right)^2 \\
r_{\rm pp} &= \frac{m'c_2 - mc_1}{m'c_2 + mc_1} - \frac{\mathrm{i}mc_1[n_+c_+^2 + n_-c_-^2 - (m'c_2)^2(n_+ + n_-)]\omega d/c}{(mc_1 + m'c_2)^2} + \mathrm{O}\left(\frac{\omega d}{c}\right)^2 \\
r_{\rm sp} &= r_{\rm ps} = -\frac{mm'c_1[n_+c_+^2 - n_-c_-^2 - c_2^2(n_+ - n_-)]\omega d/c}{(mc_1 + m'c_2)(m'c_1 + mc_2)} + \mathrm{O}\left(\frac{\omega d}{c}\right)^2 .
\end{aligned}
\tag{123}
$$

We note $m = (\epsilon\mu_1/\epsilon_1\mu)^{1/2}$ and $m' = (\epsilon\mu_2/\epsilon_2\mu)^{1/2}$ have the common factor $(\epsilon/\mu)^{1/2}$, so that the properties of the chiral layer cancel out in the zero-thickness limit, as they must. The same applies to the transmission amplitudes, which have the expansions

$$
\begin{aligned}
t_{\rm ss} &= \frac{2m'c_1}{m'c_1 + mc_2} + \frac{\mathrm{i}m'c_1[mm'(n_+c_+^2 + n_-c_-^2) + c_1c_2(n_+ + n_-)]\omega d/c}{(m'c_1 + mc_2)^2} + \mathrm{O}\left(\frac{\omega d}{c}\right)^2 \\
t_{\rm pp} &= \frac{2m'c_1}{mc_1 + m'c_2} + \frac{\mathrm{i}m'c_1[n_+c_+^2 + n_-c_-^2 + mm'c_1c_2(n_+ + n_-)]\omega d/c}{(mc_1 + m'c_2)^2} + \mathrm{O}\left(\frac{\omega d}{c}\right)^2 \\
t_{\rm sp} &= \frac{m'c_1[m'(n_+c_+^2 - n_-c_-^2) + mc_1c_2(n_+ - n_-)]\omega d/c}{(mc_1 + m'c_2)(m'c_1 + mc_2)} + \mathrm{O}\left(\frac{\omega d}{c}\right)^2 \\
t_{\rm ps} &= -\frac{m'c_1[m(n_+c_+^2 - n_-c_-^2) + m'c_1c_2(n_+ - n_-)]\omega d/c}{(mc_1 + m'c_2)(m'c_1 + mc_2)} + \mathrm{O}\left(\frac{\omega d}{c}\right)^2 .
\end{aligned}
\tag{124}
$$

Note that

$$
n_+c_+^2 - n_-c_-^2 = (n_+ - n_-)[1 + (n_1\sin\theta_1)^2/n_+n_-] . \tag{125}
$$

Thus all the polarization-switching reflection and transmission amplitudes (i.e. all those with subscripts sp or ps) have first-order thickness terms which are proportional to the chirality parameter $\gamma = (n_+ - n_-)/2$.

5. Ellipsometry of chiral media

5.1. Ellipsometric ratios

The usual ellipsometric configurations measure the ratios [19]

$$
\rho_P = \frac{r_{\rm pp} + r_{\rm sp}\tan P}{r_{\rm ps} + r_{\rm ss}\tan P} \qquad \text{or} \qquad \rho_A = \frac{r_{\rm pp} + r_{\rm ps}\tan A}{r_{\rm sp} + r_{\rm ss}\tan A} \tag{126}
$$

where P is the angle between the polarizer easy direction and $\boldsymbol{p}$, while A is the angle between the analyser easy direction and $\boldsymbol{p}'$.

We will consider polarization modulation ellipsometry, which avoids the null ellipsometry problems of stray light and shot noise. In the polarizer–modulator–sample–analyser configuration, when the modulation angular frequency is Ω, the DC, Ω and 2Ω parts of the intensity are, up to a common constant of proportionality [19]

$$\begin{aligned}
&\mathrm{DC} : |\rho_A|^2 \cos^2 P + 2\mathrm{Re}(\rho_A) J_0(M) \sin P \cos P + \sin^2 P \\
&\Omega : 4\,\mathrm{Im}(\rho_A) J_1(M) \sin P \cos P \sin \Omega t \\
&2\Omega : 4\,\mathrm{Re}(\rho_A) J_2(M) \sin P \cos P \cos 2\Omega t\,.
\end{aligned} \tag{127}$$

In the polarizer–sample–modulator–analyser configuration, the intensity components take the same form, with ρ_P replacing ρ_A and A replacing P in (127). M is the maximum phase shift between s and p components induced by the modulator; $J_0(M)$, $J_1(M)$ and $J_2(M)$ are Bessel functions.

Information about chirality is carried mainly by the off-diagonal amplitudes r_{sp} and r_{ps} (we saw that these are equal in the cases considered here), which are zero for isotropic achiral media. By selecting zero P or zero A we measure

$$\rho_{P=0} = \frac{r_{\mathrm{pp}}}{r_{\mathrm{ps}}} \qquad \text{or} \qquad \rho_{A=0} = \frac{r_{\mathrm{pp}}}{r_{\mathrm{sp}}}\,. \tag{128}$$

By selecting P or A equal to $\pm 90^\circ$, we measure

$$\rho_{P=\pm 90^\circ} = \frac{r_{\mathrm{sp}}}{r_{\mathrm{ss}}} \qquad \text{or} \qquad \rho_{A=\pm 90^\circ} = \frac{r_{\mathrm{ps}}}{r_{\mathrm{ss}}}\,. \tag{129}$$

In the polarizer–modulator–sample–analyser configuration we measure ρ_A. In this arrangement the polarizer easy axis should not be set with easy axis along the $\boldsymbol{p}$ or $\boldsymbol{s}$ directions, because for $P = 0$ or $\pm 90^\circ$ only the DC part of the signal is non-zero. In the polarizer–sample–modulator–analyser configuration we measure ρ_P, and then the analyser easy axis should not be set along the $\boldsymbol{s}$ or $\boldsymbol{p}'$ directions.

Henceforth we assume that $r_{\mathrm{sp}} = r_{\mathrm{ps}}$, as is the case for reflection from a bulk isotropic chiral medium, or from an isotropic chiral layer. Then the ellipsometric ratios in (128) take the common value

$$\rho_{/\!/} = \frac{r_{\mathrm{pp}}}{r_{\mathrm{sp}}} = \frac{r_{\mathrm{pp}}}{r_{\mathrm{ps}}} \tag{130}$$

(where // stands for polarization parallel to the plane of incidence). The magnitude of $\rho_{/\!/}$ can be very large, since r_{pp} is being divided by the small amplitudes $r_{\mathrm{sp}} = r_{\mathrm{ps}}$. The ellipsometric ratios in (129) likewise take the common value

$$\rho_{\perp} = \frac{r_{\mathrm{sp}}}{r_{\mathrm{ss}}} = \frac{r_{\mathrm{ps}}}{r_{\mathrm{ss}}} \tag{131}$$

where $\perp$ stands for polarization perpendicular to the plane of incidence.

It appears at first sight that one should measure the large value of $\rho_{/\!/}$, but when ρ is large the ratio of the Ω or 2Ω signals to the DC signal is proportional to $\mathrm{Im}(\rho)/|\rho|^2$ or $\mathrm{Re}(\rho)/|\rho|^2$, respectively. (Taking the ratio to the DC signal eliminates unknown calibration factors.) Thus there is usually no advantage to a ρ of very large magnitude.

5.2. Achiral–chiral interface

We saw in section 4.5 that $r_{\mathrm{sp}} = r_{\mathrm{ps}}$ are proportional to the square root of the small chirality parameter γ when the angle of incidence is near the critical angles $\theta_1^{\pm} = \arcsin(n_{\pm}/n_1)$ for a bulk chiral medium. These critical angles are generally very close together: $n_{\pm} = n \pm \gamma$ and γ is small. (For natural turpentine at the sodium D wavelength, $\gamma = -0.606 \times 10^{-6}$.)

The critical angle for the average refractive index is $\theta_c = \arcsin(n/n_1)$, and at this angle we find that $\rho_\perp$ takes the value

$$\rho_\perp(\theta_c) = -(1+\mathrm{i})n_1 \left[\frac{2|\gamma|}{n(n_1^2 - n^2)}\right]^{1/2} \mathrm{sgn}(\gamma) + \mathrm{O}(\gamma)\,. \tag{132}$$

Note that index matching increases the effect of chirality, already maximized in the neighbourhood of the critical angles. (Index matching is likewise known to increase the effect of anisotropy: see [28, 29].) For example, if the medium of incidence is glass with refractive index 1.50, and the chiral medium is turpentine (with index 1.47), $\rho_\perp(\theta_c) \approx 0.004\,56(1+\mathrm{i})$, which is of a magnitude that would be easily measurable, were it not for the fact that this relatively large magnitude is confined to a very narrow angular range. This angular range is essentially the difference between the two critical angles,

$$\theta_1^+ - \theta_1^- = \arcsin(n_+/n_1) - \arcsin(n_-/n_1) = \frac{2\gamma}{(n_1^2 - n^2)^{1/2}} + \mathrm{O}(\gamma^2)\,. \tag{133}$$

We see that this difference is enhanced by index matching, but that it would take a very close match with $n_1 - n$ of order $|\gamma|^{1/2}$ to make the angular range of order $|\gamma|^{1/2}$, which is still small. We conclude that reflection ellipsometry is not a viable way of measuring the chirality of non-absorbing bulk weakly chiral media. Silverman and Badoz [24] have however shown that for absorbing chiral layers, the ellipticity and differential circular reflectance (DCR) are strongly enhanced. Measurements of DCR are presented in [17], and discussed in [3].

5.3. *Ellipsometry of a chiral layer*

We now look at the ellipsometry of a non-absorbing chiral layer. When the substrate is optically identical to the medium of incidence (as for unsupported or embedded films, for example), the zero-thickness value of all the reflection amplitudes is zero. From equation (123) we find, with $c_2 = c_1$ and $m' = m$, that the leading terms are independent of the film thickness:

$$\begin{aligned}
\rho_\perp &= \frac{r_{\mathrm{sp}}}{r_{\mathrm{ss}}} = \frac{\mathrm{i}m\big[n_+c_+^2 - n_-c_-^2 - c_1^2(n_+ - n_-)\big]}{m^2\big(n_+c_+^2 + n_-c_-^2\big) - c_1^2(n_+ + n_-)} + \mathrm{O}\left(\frac{\omega d}{c}\right) \\
\rho_{//} &= \frac{r_{\mathrm{pp}}}{r_{\mathrm{sp}}} = \frac{\mathrm{i}\big[(n_+c_+^2 + n_-c_-^2 - (mc_1)^2(n_+ + n_-)\big]}{m\big[n_+c_+^2 - n_-c_-^2 - c_1^2(n_+ - n_-)\big]} + \mathrm{O}\left(\frac{\omega d}{c}\right).
\end{aligned} \tag{134}$$

As noted below (125), the r_{sp} amplitude leading term is proportional to the chirality parameter $\gamma = (n_+ - n_-)/2$. Thus $\rho_{//}$ can be very large for thin films. We saw in the discussion following (131) that a large ellipsometric ratio is not usually an advantage, and here we shall concentrate on $\rho_\perp$. From equation (134) we find, using (43) and (75), that

$$\rho_\perp = \frac{\mathrm{i}n_1\left(n_1^2 + n^2\right)s_1^2\gamma}{n^2\left(n^2 - n_1^2\right)} + \mathrm{O}\left(\frac{\omega d}{c}\right) + \mathrm{O}(\gamma^3)\,. \tag{135}$$

We see that matching the (equal) indices of the medium of incidence and of the substrate to the average index of the chiral layer enhances the ellipsometric ratio $\rho_\perp$, and that the leading term of $\rho_\perp$ increases with angle of incidence as $\sin^2\theta_1$. We know from (A4) that r_{sp} is zero at grazing incidence, so that finite-thickness corrections must bring $\rho_\perp$ to zero as $s_1 = \sin\theta_1 \to 1$. Figures 1–3 show the real and imaginary parts of $\rho_\perp$ for thin films of turpentine ($n = 1.47, \gamma = -0.606 \times 10^{-6}$ at the sodium D wavelength) between glass

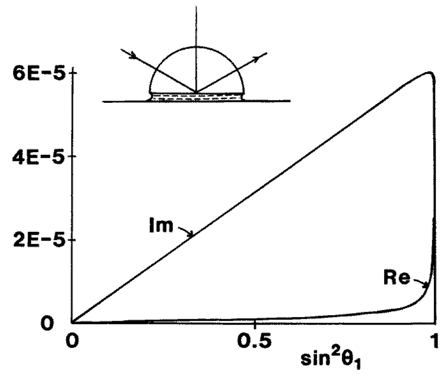

Figure 1. Real and imaginary parts of $\rho_\perp = r_{sp}/r_{ss}$ for a turpentine layer between glass of index 1.48, versus $\sin^2\theta_1$. The curves are drawn for layer thickness $d = \lambda/\pi$, index 1.47 and chirality $\gamma = -0.606 \times 10^{-6}$. The inset shows a possible experimental configuration.

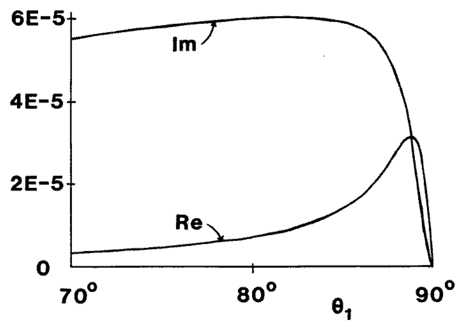

Figure 2. Detail, near grazing incidence, of figure 1. Note that the horizontal scale is θ_1 rather than $\sin^2\theta_1$.

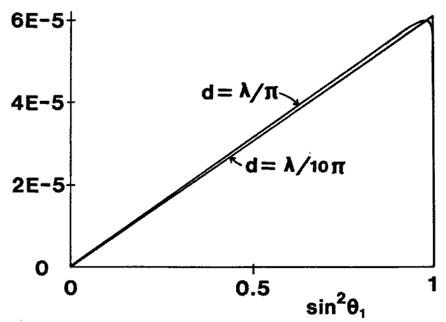

Figure 3. $\mathrm{Im}(\rho_\perp)$ for turpentine layers of thicknesses $\lambda/10\pi$ and λ/π (other parameters as in figure 1). Thinner layers have $\mathrm{Im}(\rho_\perp)$ indistinguishable on this scale from the $\lambda/10\pi$ curve. The straight line given by the leading term of (135) is also indistinguishable from the $d \leqslant \lambda/10\pi$ curves, up to the maximum near grazing incidence.

plates of index 1.48. We see that $\mathrm{Im}(\rho_\perp)$ is accurately given by the leading term in (135) up to quite appreciable film thicknesses, except very close to grazing incidence.

We thus have a method for the measurement of the chirality parameter γ: determination of the imaginary part of $\rho_\perp$ for thin films held between (for example) a half-cylinder and a plate made from the same glass. This method is insensitive to the film thickness, provided the thickness remains small compared to the wavelength. Index matching enhances the ellipsometric signal, but at the expense of the light intensity. The measurement of the ellipsometric reflection signal provides a method of obtaining the chirality parameter for very small volumes of sample, in contrast to the usual method of measurement of the rotation of the plane of polarization on transmission through the sample.

Appendix. General formulae for a chiral layer

We give the reflection and transmission amplitudes which characterize the optical properties of a chiral layer (with indices $n_\pm$) between non-chiral media 1 and 2, medium 1 being the medium of incidence. Let the factors

$$Z_\pm = \exp(\mathrm{i}q_\pm d) \tag{A1}$$

give the phase increments in a single transit of the layer for the two helicities, and define the quantities

$$\begin{aligned}
F_1^\pm &= 2m(c_1^2 + c_+c_-) \pm (m^2+1)(c_+ + c_-)c_1 \\
F_2^\pm &= 2m'(c_2^2 + c_+c_-) \pm (m'^2+1)(c_+ + c_-)c_2 \\
G_1^\pm &= 2m(c_1^2 + c_+c_-) \pm (m^2-1)(c_+ + c_-)c_1 \\
G_2^\pm &= 2m'(c_2^2 + c_+c_-) \pm (m'^2-1)(c_+ + c_-)c_2 \\
f_1^\pm &= 2m(c_1^2 - c_+c_-) \pm (m^2+1)(c_+ - c_-)c_1 \\
f_2^\pm &= 2m'(c_2^2 - c_+c_-) \pm (m'^2+1(c_+ - c_-)c_2 \\
g_1^\pm &= 2m(c_1^2 + c_+c_-) \pm (m^2-1)(c_+ - c_-)c_1 \\
g_2^\pm &= 2m'(c_2^2 + c_+c_-) \pm (m'^2-1)(c_+ - c_-)c_2
\end{aligned} \tag{A2}$$

where $c_1 = \cos\theta_1$, $c_2 = \cos\theta_2$, $c_\pm = \cos\theta_\pm$, and $m = (\epsilon\mu_1/\epsilon_1\mu)^{1/2}$, $m' = (\epsilon\mu_2/\epsilon_2\mu)^{1/2}$. The reflection and transmission amplitudes share a common denominator,

$$D = F_1^+F_2^+ - 8c_1c_2c_+c_-(m^2-1)(m'^2-1)Z_+Z_- - f_1^-f_2^-Z_+^2 - f_1^+f_2^+Z_-^2 + F_1^-F_2^-Z_+^2Z_-^2\,. \tag{A3}$$

The reflection amplitudes are given by

$$\begin{aligned}
Dr_{\mathrm{ss}} &= G_1^-F_2^+ + 8c_1c_2c_+c_-(m^2+1)(m'^2-1)Z_+Z_- - g_1^+f_2^-Z_+^2 - g_1^-f_2^+Z_-^2 + G_1^+F_2^-Z_+^2Z_-^2 \\
-Dr_{\mathrm{pp}} &= G_1^+F_2^+ - 8c_1c_2c_+c_-(m^2+1)(m'^2-1)Z_+Z_- - g_1^-f_2^-Z_+^2 \\
&\quad - g_1^+f_2^+Z_-^2 + G_1^-F_2^-Z_+^2Z_-^2 \\
Dr_{\mathrm{sp}} &= Dr_{\mathrm{ps}} = -2\mathrm{i}mc_1\{(c_+ - c_-)[F_2^+ - F_2^-Z_+^2Z_-^2] + (c_+ + c_-)[f_2^-Z_+^2 - f_2^+Z_-^2]\}\,.
\end{aligned} \tag{A4}$$

The transmission amplitude numerators are

$$\begin{aligned}
Dt_{\mathrm{ss}} &= 8m'c_1\{c_+(mc_1 + c_-)(m'c_2 + c_-)Z_+ + c_-(mc_1 + c_+)(m'c_2 + c_+)Z_- \\
&\quad - c_+(mc_1 - c_-)(m'c_2 - c_-)Z_+Z_-^2 - c_-(mc_1 - c_+)(m'c_2 - c_+)Z_+^2Z_-\} \\
Dt_{\mathrm{pp}} &= 8m'c_1\{c_+(c_1 + mc_-)(c_2 + m'c_-)Z_+ + c_-(c_1 + mc_+)(c_2 + m'c_+)Z_- \\
&\quad - c_+(c_1 - mc_-)(c_2 - m'c_-)Z_+Z_-^2 - c_-(c_1 - mc_+)(c_2 - m'c_+)Z_+^2Z_-\} \\
Dt_{\mathrm{sp}} &= 8\mathrm{i}m'c_1\{-c_+(mc_1 + c_-)(m'c_- + c_2)Z_+ + c_-(mc_1 + c_+)(m'c_+ + c_2)Z_- \\
&\quad - c_+(mc_1 - c_-)(m'c_- - c_2)Z_+Z_-^2 + c_-(mc_1 - c_+)(m'c_+ - c_2)Z_+^2Z_-\} \\
Dt_{\mathrm{ps}} &= 8\mathrm{i}m'c_1\{c_+(c_1 + mc_-)(m'c_2 + c_-)Z_+ - c_-(c_1 + mc_+)(m'c_2 + c_+)Z_- \\
&\quad - c_+(c_1 - mc_-)(m'c_2 - c_-)Z_+Z_-^2 + c_-(c_1 - mc_+)(m'c_2 - c_+)Z_+Z_-^2\}\,.
\end{aligned} \tag{A5}$$

Note that r_{sp}, r_{ps} and all the transmission amplitudes go to zero at grazing incidence, where $c_1 \to 0$. The conservation laws (20) are satisfied for a non-absorbing layer.

The formulae simplify considerably when the chiral layer lies between optically identical media (so that $m' = m$ and $c_2 = c_1$). Then $F_1^{\pm} = F_2^{\pm}, \ldots, g_1^{\pm} = g_2^{\pm}$, and the common denominator factors

$$D \to (F^+ + f^- Z_+ + f^+ Z_- + F^- Z_+ Z_-)(F^+ - f^- Z_+ - f^+ Z_- + F^- Z_+ Z_-) \tag{A6}$$

where F^+ is the common value of F_1^+ and F_2^+, etc. In the expressions for the reflection and transmission amplitudes we can drop the subscripts 1 and 2 on $F_1^{\pm}, \ldots, g_2^{+}$, and set $m' = m$ and $c_2 = c_1$. The ss and pp transmission amplitude numerators simplify to

$$\begin{aligned} Dt_{\mathrm{ss}} &\to 8mc_1\{c_+ Z_+[(mc_1+c_-)^2-(mc_1-c_-)^2 Z_-^2]+c_- Z_-[(mc_1+c_+)^2-(mc_1-c_+)^2 Z_+^2]\} \\ Dt_{\mathrm{pp}} &\to 8mc_1\{c_+ Z_+[(c_1+mc_-)^2-(c_1-mc_-)^2 Z_-^2]+c_- Z_-[(c_1+mc_+)^2-(c_1-mc_+)^2 Z_+^2]\}\,. \end{aligned} \tag{A7}$$

When $n_2 < n_1$, $c_2 = \cos\theta_2$ is imaginary for angle of incidence greater than the critical angle $\theta_c = \arcsin(n_2/n_1)$. At the critical angle $c_2 = 0$, and the reflection amplitude formulae simplify to

$$\begin{aligned} D_0 r_{\mathrm{ss}} &= G_1^- + g_1^+ Z_+^2 + g_1^- Z_-^2 + G_1^+ Z_+^2 Z_-^2 \\ -D_0 r_{\mathrm{pp}} &= G_1^+ + g_1^- Z_+^2 + g_1^+ Z_-^2 + G_1^- Z_+^2 Z_-^2 \\ D_0 r_{\mathrm{sp}} &= D_0 r_{\mathrm{ps}} = -2\mathrm{i}mc_1\{(c_+ - c_-)(1 - Z_+^2 Z_-^2) - (c_+ + c_-)(Z_+^2 - Z_-^2)\} \\ D_0 &= F_1^+ + f_1^- Z_+^2 + f_1^+ Z_-^2 + F_1^- Z_+^2 Z_-^2\,. \end{aligned} \tag{A8}$$

These reflection amplitudes satisfy the energy conservation law

$$|r_{\mathrm{ss}}|^2 + |r_{\mathrm{sp}}|^2 = 1 \qquad |r_{\mathrm{pp}}|^2 + |r_{\mathrm{ps}}|^2 = 1 \tag{A9}$$

because light of either s or p polarization is totally reflected at the critical angle. (The same conservation law is satisfied when $\theta_1 > \theta_c$: no energy propagates into the substrate when the angle of incidence exceeds the critical angle.)

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