Optical properties of an isotropic layer on a uniaxial crystal substrate

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Abstract. The optical properties of a homogeneous isotropic layer on an anisotropic uniaxial crystal are characterized by four reflection amplitudes \( r_{ss}, r_{sp}, r_{pp}, r_{ps} \) and four transmission amplitudes \( t_{so}, t_{se}, t_{po}, t_{pe} \). We give analytic expressions for these amplitudes. Some recent experiments relating to the geophysically important phenomenon of the surface melting of ice below 0 °C are discussed. The weak anisotropy of ice is amplified a hundredfold by index marching (the refractive indices of ice and water are not very different), but it is still qualitatively correct to interpret the experiments by assuming ice to be isotropic. An appendix gives the theory of what is measured in polarization modulation ellipsometry when anisotropy is present, and another appendix discusses the enhancement of anisotropy by refractive index matching.

1. Introduction

The optical properties of a homogeneous isotropic layer on an isotropic substrate are well known (see for example Born and Wolf (1965), section 1.6.4, or Lekner (1987), section 2-4). They may be characterized by two reflection amplitudes \( r_{s} \) and \( r_{p} \), and two transmission amplitudes \( t_{s} \) and \( t_{p} \). When the isotropic layer rests on an anisotropic substrate, the currently available 4 × 4 matrix method (see, for example, Wöhler et al (1988) or Eidner et al (1989) for recent work and further references) may be used to evaluate numerically the four reflection amplitudes \( r_{ss}, r_{sp}, r_{pp}, r_{ps} \) and the four transmission amplitudes \( t_{so}, t_{se}, t_{po}, t_{pe} \). In two recent papers (Lekner 1991, 1992a) the author has given analytic expressions for the optical coefficients of uniaxial crystals, and of crystal plates illuminated at normal incidence. Here we extend these results to give analytic expressions for the optical coefficients of an isotropic layer on a uniaxial crystal substrate.

The isotropic layer has dielectric constant \( \varepsilon = n^{2} \), and is bounded by the medium of incidence \( (\varepsilon_{1} = n_{1}^{2}) \) and the uniaxial substrate \( (\varepsilon_{o} = n_{1}^{2}, \varepsilon_{e} = n_{2}^{2}) \), at \( z = 0 \) and \( z = \Delta z \) respectively. The plane of incidence is taken as the \( zx \) plane. The direction cosines of the optic axis of the uniaxial substrate with respect to the \( x, y \) and \( z \) axes are \( \alpha, \beta \) and \( \gamma \); thus \( \mathbf{c} = (\alpha, \beta, \gamma) \) is the unit vector giving the direction of the optic axis.

We consider reflection and transmission of a plane monochromatic wave of angular frequency \( \omega \) incident from medium 1 at angle \( \theta_{1} \) to the normal. In the three media (medium of incidence, the layer, and the anisotropic substrate), all components
of the electric and magnetic vectors will have dependence on \( x \) and \( t \) contained in
the factor \( \exp i(\mathbf{K} \cdot \mathbf{r} - \omega t) \), where

\[
K = n_1(\omega/c) \sin \theta_1 = n(\omega/c) \sin \theta
\]

is the \( x \)-component of all the wavevectors, and \( \theta \) is the angle to the normal in the
isotropic layer. The \( y \)-component of all the wavevectors is zero, by choice of the
plane of incidence as the \( zx \)-plane, and by the invariance of the system with respect
to a \( y \)-translation. The \( z \)-component of the wavevector of the incident wave is

\[
q_1 = n_1(\omega/c) \cos \theta_1
\]

and it is \(-q_1\) for the reflected wave, and \( \pm q \) for the two plane waves in the layer,
where

\[
q^2 = \epsilon \omega^2/c^2 - K^2 \equiv k_\perp^2 - K^2.
\]

Within the crystal substrate two plane waves can propagate. For uniaxial crystals
these are known as the ordinary and extraordinary waves, and have \( z \)-components of
their wavevectors given by

\[
q_\parallel^2 = \epsilon_\parallel \omega^2/c^2 - K^2 \equiv k_\parallel^2 - K^2
\]

for the ordinary wave, and

\[
q_e = q - \alpha \gamma K \Delta \epsilon/\epsilon\gamma
\]

where

\[
\Delta \epsilon = \epsilon_e - \epsilon_o \quad \epsilon_\gamma = n_\gamma^2 = \epsilon_o + \gamma^2 \Delta \epsilon \quad q^2 = \epsilon_o [\epsilon_e \epsilon_\gamma \omega^2/c^2 - K^2 (\epsilon_e - \epsilon_\gamma \Delta \epsilon)]/\epsilon_\gamma^2.
\]

The electric field vector of the ordinary wave is

\[
\mathbf{E} = N_\parallel (-\beta q_\parallel, \alpha q_\parallel - \gamma K, \beta K)
\]

and is perpendicular to the optic axis and to the ordinary wavevector \((K, 0, q_\parallel)\). The
electric field of the extraordinary wave is

\[
\mathbf{E}_e = N_e (\alpha q_\parallel^2 - \gamma q_\parallel K, \beta q_\parallel^2, \gamma(k_\parallel^2 - q_\parallel^2) - \alpha q_\parallel K).
\]

\( N_\parallel \) and \( N_e \) are normalization factors: we will normalize \( \mathbf{E}_\parallel \) and \( \mathbf{E}_e \) to unit amplitude,
so that \( |\mathbf{E}_\parallel|^2 = 1 = |\mathbf{E}_e|^2 \).

The plan of the remainder of this paper is as follows. In section 2 we write
down the equations determining the reflection and transmission amplitudes, and a
2 \times 2 matrix method for their solution. In section 3 we consider the normal-incidence
case, for which the system is characterized by just two reflection and two transmission
amplitudes, which take a particularly simple form. In section 4 we consider general
oblique incidence. These results are applied in section 5 to experiments on the surface
melting of ice. In the appendices we give a theoretical analysis of what is measured
by polarization modulation ellipsometry, and of the enhancement of the anisotropy
by index matching between the overlayer and the substrate.
2. The equations for the optical coefficients

An incoming plane wave may be taken as a superposition of s- and p-polarized waves with appropriate amplitudes and phases. The s and p polarizations have $E_1$ respectively perpendicular and parallel to the plane of incidence (here the $xz$-plane). We consider the reflection and transmission of pure s and pure p incident polarizations, starting with the s polarization. The electric field components in the s-polarized case, with the common factor $\exp i(Kz - \omega t)$ suppressed, are

incident $(0, e^{iqz}, 0)$

reflected $e^{-iqz}(r_{ss} \cos \theta_1, r_{sp} \sin \theta_1)$

within layer $(\cos \theta(\alpha e^{iqz} + \beta e^{-iqz}), \alpha e^{iqz} + \beta e^{-iqz}, -\sin \theta(\alpha e^{iqz} - \beta e^{-iqz}))$

within crystal \[t_{so}E_0 e^{iq_{s}(z-\Delta z)} + t_{se}E_e e^{iq_{e}(z-\Delta z)}.\] (9)

The wavefunction within the layer has the property that the downward-propagating part has its Poynting vector (proportional to $E \times B$) along $(K, 0, q)$, while the upward-propagating part has $E \times B$ along $(K, 0, -q)$, with proportionality constants $A^2 + a^2$ and $B^2 + b^2$, respectively. These results follow on using the identity

\[
q \cos \theta + K \sin \theta = n\omega/c = k
\]

which comes from $K = k \sin \theta$, $q = k \cos \theta$.

The wavefunctions (9) contain the eight unknowns $r_{ss}$, $r_{sp}$, $A$, $B$, $a$, $b$, $t_{so}$, $t_{se}$, and the eight conditions determining them follow from the continuity of the tangential components of $E$ and $B$ at $z = 0$ and at $z = \Delta z$. The continuity of $E_y$, $E_z$, $\partial E_y/\partial z$, and $\partial E_z/\partial z - iKE_z$ at $z = 0$ gives the equations

\[
\begin{align*}
1 + r_{ss} &= A + B & r_{sp} \cos \theta_1 &= (a + b) \cos \theta \\
q_1(1 - r_{ss}) &= q(A - B) & -k_1 r_{sp} &= k(a - b).
\end{align*}
\]
(11)

The same conditions at $z = \Delta z$, with the notation

\[
A' = Ae^{iq\Delta z} \quad B' = Be^{-iq\Delta z} \quad a' = ae^{iq\Delta z} \quad b' = be^{-iq\Delta z}
\]
(12)

and with $E = (X, Y, Z)$ for the ordinary and extraordinary modes, give

\[
\begin{align*}
A' + B' &= t_{so}Y_o + t_{se}Y_e \\
(a' + b') \cos \theta &= t_{so}X_o + t_{se}X_e \\
q(A' - B') &= t_{so}q_oY_o + t_{se}q_eY_e \\
k(a' - b') &= t_{so}(q_oX_o - KZ_o) - t_{se}(q_eX_e - KZ_e).
\end{align*}
\]
(13)

We will give two solutions of this system of eight equations: a $2 \times 2$ matrix method modelled on Lekner (1992a) which will prove particularly simple at normal incidence, and an algebraic method that puts the solutions into a more physically revealing form at general incidence. The $2 \times 2$ matrix method is given here. We define the vectors

\[
u = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad r = \begin{pmatrix} r_{ss} \\ r_{sp} \end{pmatrix} \quad s = \begin{pmatrix} A + B \\ a + b \end{pmatrix} \quad d = \begin{pmatrix} A - B \\ a - b \end{pmatrix}
\]
(14)
and the diagonal cosine matrices

$$C_1 = \begin{pmatrix} 1 & 0 \\ 0 & \cos \theta_1 \end{pmatrix}, \quad C = \begin{pmatrix} 1 & 0 \\ 0 & \cos \theta \end{pmatrix}$$  \text{(15)}

Then the equation set (11) can be written as

$$u + C^{-1}C_1 r = s \quad (q_1/q)(u - CC_1^{-1}r) = d.$$  \text{(16)}

For the set of equations resulting from the continuity of the tangential components of $E$ and $B$ at $z = \Delta z$, we define the vectors

$$s' = \begin{pmatrix} A' + B' \\ a' + b' \end{pmatrix}, \quad d' = \begin{pmatrix} A' - B' \\ a' - b' \end{pmatrix}, \quad t = \begin{pmatrix} t_{so} \\ t_{se} \end{pmatrix}$$  \text{(17)}

and the matrices

$$M = \begin{pmatrix} Y_o & Y_e \\ X_o & X_e \end{pmatrix}, \quad N = \begin{pmatrix} q_o Y_o & q_e Y_e \\ q_o X_o - K Z_o & q_e X_e - K Z_e \end{pmatrix}.$$  \text{(18)}

Then the equation set (13) can be written as

$$C s' = Mt \quad qC^{-1}d' = Nt.$$  \text{(19)}

The vectors $s'$ and $d'$ are linear combinations of $s$ and $d$:

$$s' = \cos q \Delta z s + i \sin q \Delta z d \quad d' = \cos q \Delta z d + i \sin q \Delta z s.$$  \text{(20)}

The equations (19) give

$$t = M^{-1}C s' = qN^{-1}C^{-1}d'.$$  \text{(21)}

On substituting for $s'$ and $d'$ using (20) and (16), we obtain a linear equation for $r$ in terms of $u$ which has the form $Vr = Wu$, with

$$V = N^{-1}(cq_1 C_1^{-1} - isq C^{-2} C_1) + q^{-1}M^{-1}(cqC_1 - isq_1 C^2 C_1^{-1}),$$

$$W = N^{-1}C^{-1}(cq_1 + isq) - q^{-1}M^{-1}C(cq + isq_1)$$ \text{(22)}

where $c = \cos q \Delta z$ and $s = \sin q \Delta z$. Thus

$$r = V^{-1}Wu \equiv Ru$$ \text{(23)}

may be obtained by inversion and multiplication of 2 x 2 matrices. Explicit and beautifully simple results follow from this formulation at normal incidence, as will be demonstrated in the next section, but we must first discuss the case of incident $p$ polarization.

For $p$-polarized incident light, the electric field components are

incident $e^{iq \Delta z} (\cos \theta_1, 0, -\sin \theta_1)$

reflected $e^{-iq \Delta z} (r_{pp} \cos \theta_1, r_{ps}, r_{pp} \sin \theta_1)$

within layer $(\cos \theta (ae^{iq \Delta z} + be^{-iq \Delta z}), Ae^{iq \Delta z} + Be^{-iq \Delta z}, -\sin \theta (ae^{iq \Delta z} - be^{-iq \Delta z}))$

within crystal \(t_{po}E_o e^{iq \Delta z} + t_{pe}E_e e^{iq \Delta z} \). \text{(24)}
Optical properties of an isotropic layer

The continuity of $E_y$, $E_x$, $\partial E_y/\partial z$, $\partial E_x/\partial z - iKE_z$ at $z = 0$ implies

$$r_{ps} = A + B \quad (1 + r_{pp}) \cos \theta_i = (a + b) \cos \theta$$
$$q_1 r_{ps} = q(A - B) \quad k_1(1 - r_{pp}) = k(a - b). \quad (25)$$

At $z = \Delta z$ the boundary conditions give the same equations (13) as for an incoming s polarization, with $t_{po}$ replacing $t_{so}$ and $t_{pe}$ replacing $t_{se}$. A $2 \times 2$ matrix solution is as follows: we introduce the vectors

$$r' = \begin{pmatrix} r_{ps} \\ r_{pp} \end{pmatrix} \quad t' = \begin{pmatrix} t_{po} \\ t_{pe} \end{pmatrix} \quad v = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (26)$$

with all other vectors and matrices defined as above. Then the first and second pairs in (25) read

$$s = C^{-1}C_1(v + r') \quad d = q_1 q^{-1}C^2C_1^{-1}(v - r'). \quad (27)$$

The remainder of the solution proceeds as before, with the result

$$r' = V^{-1}W'v \equiv R'v \quad (28)$$

where $V$ is as defined in (22), and

$$W' = N^{-1}(cq_1C_1^{-1} + isqC^{-2}C_1) - q^{-1}M^{-1}(cqC_1 + isq_1C^2C_1^{-1}). \quad (29)$$

Equations (23) and (28) give the reflection amplitudes in terms of the $2 \times 2$ matrices $R$ and $R'$. The transmission amplitudes can be found in terms of the same two matrices: we obtain

$$t = q^{-1}M^{-1}[cq(C + C_1R) + isq_1(C - C^2C_1^{-1}R)]u \quad (30)$$
$$t' = q^{-1}M^{-1}[cq(C_1 + C_1R') + isq_1(C^2C_1^{-1} - C^2C_1^{-1}R')]v.$$

The cosine matrices, defined in (15), reduce to the identity matrix. The $M$ matrix and the $N$ matrix, defined in (18), can be written as

$$M \rightarrow \begin{pmatrix} \alpha & \beta \\ -\beta & \alpha \end{pmatrix} \begin{pmatrix} N_0 & 0 \\ 0 & N_e \end{pmatrix} \quad N \rightarrow M \begin{pmatrix} k_o & 0 \\ 0 & k_e \end{pmatrix} \quad (33)$$

3. Normal incidence

At normal incidence ($K \rightarrow 0$) we have

$$q_1 \rightarrow k_1 \quad q \rightarrow k \quad q_o \rightarrow k_o \quad q_e \rightarrow k_e = k_0 n_e / n_\gamma. \quad (31)$$

The ordinary and extraordinary modes within the uniaxial crystal also simplify (Lekner (1991), section 5.4):

$$E_o \rightarrow N_e(-\beta, \alpha, 0) \quad E_e \rightarrow N_e(\alpha, \beta, \gamma(1 - \epsilon_e/\epsilon_\gamma)). \quad (32)$$

The cosine matrices, defined in (15), reduce to the identity matrix. The $M$ matrix and the $N$ matrix, defined in (18), can be written as
We then find that the matrix $R$ in $T = Ru$ simplifies to

$$R = (\alpha^2 + \beta^2)^{-1} \begin{pmatrix} \alpha^2 r_0 + \beta^2 r_e & \alpha \beta (r_e - r_0) \\ \alpha \beta (r_e - r_0) & \alpha^2 r_e + \beta^2 r_0 \end{pmatrix} \quad (34)$$

where

$$r_0 = \frac{k(k_1 - k_o) \cos k \Delta z + i(k^2 - k_1 k_o) \sin k \Delta z}{k(k_1 + k_o) \cos k \Delta z - i(k^2 + k_1 k_o) \sin k \Delta z} \quad (35)$$

and the formula for $r_e$ is obtained by replacing $k_o$ by $k_e$ in (35). We recognize $r_o$ and $r_e$ as the normal-incidence reflection amplitudes for an isotropic layer on isotropic substrates of refractive index $n_o$ and $n_o n_e / n_e$, respectively (see Lekner (1987), equation (2.52)).

Thus

$$r_{ss} = (\alpha^2 r_0 + \beta^2 r_e) / (\alpha^2 + \beta^2) = r_o \cos^2 \phi + r_e \sin^2 \phi \quad (36)$$

$$r_{sp} = \alpha \beta (r_e - r_0) / (\alpha^2 + \beta^2) = (r_o - r_e) \cos \phi \sin \phi$$

where $\phi$ is the angle between the $E_o$ direction and the incident field $E_i$. For $p$ polarization incident, the matrix $R'$ is equal to $R$ as given in (34) for normal incidence. Thus

$$r_{ps} = \alpha \beta (r_e - r_0) / (\alpha^2 + \beta^2) = (r_o - r_e) \cos \phi \sin \phi$$

$$r_{pp} = (\alpha^2 r_e + \beta^2 r_0) / (\alpha^2 + \beta^2) = r_e \cos^2 \phi + r_o \sin^2 \phi \quad (37)$$

In the limit of zero thickness of the layer ($\Delta z \to 0$), these formulae reduce to the reflection amplitudes for a bare crystal, as given in Lekner (1991), equations (71) to (73).

Just as $r$ and $r'$, which have as components the four reflection amplitudes $r_{ss}$, $r_{sp}$, $r_{ps}$, $r_{pp}$, can be expressed (at normal incidence) in terms of the two amplitudes $r_o$ and $r_e$, so can $t$ and $t'$, which have the transmission amplitudes $t_{so}$, $t_{se}$, $t_{pe}$, $t_{pp}$, as components, be expressed in terms of $t_o$ and $t_e$, which are the transmission amplitudes for a layer of thickness $\Delta z$ on isotropic substrates of indices $n_o$ and $n_o n_e / n_e$:

$$t_o = k^{-1} [k(1 + r_o) \cos k \Delta z + ik(1 - r_o) \sin k \Delta z]$$

$$= 2k_1 k / [k(k_1 + k_o) \cos k \Delta z - i(k^2 + k_1 k_o) \sin k \Delta z] \quad (38)$$

($t_e$ is obtained by replacing $k_o$ with $k_e$ in (38)). We find that $t$ and $t'$ can be written as

$$t = Tu \quad t' = Tu \quad (39)$$

where

$$T = (\alpha^2 + \beta^2)^{-1} \begin{pmatrix} N_o^{-1} & 0 \\ 0 & N_e^{-1} \end{pmatrix} \begin{pmatrix} t_o & 0 \\ 0 & t_e \end{pmatrix} \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} = (\alpha^2 + \beta^2)^{-1} \begin{pmatrix} \alpha N_o^{-1} t_o & -\beta N_o^{-1} t_e \\ \beta N_e^{-1} t_e & \alpha N_e^{-1} t_e \end{pmatrix} \quad (40)$$
Thus
\begin{align}
  t_{so} &= \alpha N_o^{-1} t_o / (\alpha^2 + \beta^2) \\
  t_{so} &= \beta N_e^{-1} t_e / (\alpha^2 + \beta^2) \\
  t_{po} &= -\beta N_o^{-1} t_o / (\alpha^2 + \beta^2) \\
  t_{pe} &= \alpha N_e^{-1} t_e / (\alpha^2 + \beta^2).
\end{align}

(41)

In the limit of zero thickness of the layer, the formulae (41) reduce to the direct transmission amplitudes into a uniaxial crystal, as given in Lekner (1991), equations (78) and (79).

Since the reflection and transmission properties at normal incidence are entirely determined by the amplitudes \( r_o, r_e, t_o, t_e \), we will note the behaviour of the latter as a function of the layer thickness \( \Delta z \). Let
\begin{align}
  f_1 &= (k_1 - k) / (k_1 + k) \\
  f_o &= (k - k_o) / (k + k_o) \\
  f_e &= (k - k_e) / (k + k_e)
\end{align}

(42)

be the Fresnel s-wave reflection amplitudes at the \( z = 0 \) and \( z = \Delta z \) faces of the isotropic layer, in the latter case for substrates of refractive index \( n_o \) and \( n_o n_e / n_r \). Then \( r_o \) and \( r_e \) can be written as
\begin{align}
  r_o &= (f_1 + f_o Z) / (1 + f_1 f_o Z) \\
  r_e &= (f_1 + f_e Z) / (1 + f_1 f_e Z)
\end{align}

(43)

where \( Z = \exp(2i k \Delta z) \). As \( \Delta z \) increases, \( Z \) moves on the unit circle in the complex plane, and since \( r_o \) and \( r_e \) are related to \( Z \) by a bilinear transformation, they also move on circles in the complex plane. The period in \( \Delta z \) of all the motions is \( \pi / k \). (If the isotropic layer were absorbing, the motions would not be periodic, but spirals converging onto the origin.) The properties of the loci of \( r_o, r_e, t_o, t_e \), are as follows (cf Lekner (1992a), sections 4 and 5): when all the media are non-absorbing, the circles \( r_o \) and \( r_e \) are symmetric with respect to reflection in the real axis. Thus their radii and centres may be found from the intersections with the real axis at \( Z = \pm 1 \). At \( Z = +1 \), \( r_o \) and \( r_e \) take the zero-thickness values
\begin{align}
  r_o^+ &= (k_1 - k_o) / (k_1 + k_o) \\
  r_e^+ &= (k_1 - k_e) / (k_1 + k_e)
\end{align}

(44)

while at \( Z = -1 \), \( r_o \) becomes
\begin{align}
  r_o^- &= (f_1 - f_o) / (1 - f_1 f_o) = (k_1 k_o - k^2) / (k_1 k_o + k^2)
\end{align}

(45)

(we omit the \( e \) versions for the remainder of this section—they are obtained by replacing \( k_o \) by \( k_e \) in the formulae). Thus the centre and radius of the locus of \( r_o \) are given by
\begin{align}
  c_o = (r_o^+ + r_o^-) / 2 \\
  a_o = (r_o^+ - r_o^-) / 2.
\end{align}

(46)

The transmission amplitude \( t_o \) can be written as
\begin{align}
  t_o &= (1 + f_1)(1 + f_o) \zeta / (1 + f_1 f_o \zeta^2)
\end{align}

(47)

where \( \zeta = \exp(i k \Delta z) \). As \( \Delta z \) increases, \( t_o \) moves on a quartic in the complex plane, repeating with period \( 2\pi / k \) in \( \Delta z \). The equation of the quartic is found by eliminating \( \zeta \) from (47), using \( \zeta^4 = 1 \). If we write \( t_o = X + i Y \), the quartic is
\begin{align}
  (X^2 + Y^2)^2 = (t_o^+ X)^2 + (t_o^+ Y)^2
\end{align}

(48)
where \( \pm t_0^+ \) is the value of \( t_0 \) at \( \zeta = \pm 1 \), and \( \pm it_0^- \) is the value at \( \zeta = \pm i \):

\[
t_0^+ = \frac{2k_1}{(k_1 + k_0)} \quad t_0^- = \frac{2k_1k}{(k_1k_0 + k^2)}.
\]

The reciprocal \( t_0^{-1} \) moves on an ellipse, with semiaxes \( (t_0^+)^{-1} \) and \( (t_0^-)^{-1} \). These results are closely analogous to those for a uniaxial crystal plate upon an isotropic substrate, discussed in Lekner (1992a).

4. Oblique incidence

Although the 2x2 matrix solution gives beautifully simple results at normal incidence, I have found it more fruitful to work directly with the original boundary condition equations (11) and (13) at general incidence. Consider the equations expressing the continuity of \( E_y \) and \( \partial E_y / \partial z \) at \( z = 0 \), namely

\[
1 + r_{ss} = A + B \quad 1 - r_{ss} = q_1^{-1}q(A - B).
\]

These may be solved for \( r_{ss} \) in terms of \( B/A \):

\[
r_{ss} = \frac{q_1 - q + (q_1 + q)B/A}{q_1 + q + (q_1 - q)B/A} = \frac{f_1 + B/A}{1 + f_1B/A}.
\]

where \( f_1 = (q_1 - q)/(q_1 + q) \) is the oblique incidence Fresnel s-wave reflection amplitude for the boundary between the medium of incidence and the layer. The continuity of \( E_y \) and \( \partial E_y / \partial z \) at \( \Delta z \) gives a pair of equations (the first and third of (13)) which may be solved for \( B/A \):

\[
\frac{B}{A} = g \exp(2iq\Delta z) \quad g = \frac{(q - q_e)\iota_{so}Y_o + (q - q_o)\iota_{so}Y_e}{(q + q_o)\iota_{so}Y_o + (q + q_e)\iota_{so}Y_e}.
\]

Thus the expression for \( r_{ss} \) may be put into the form of the s-wave reflection amplitude \( r_s \) for a layer on an isotropic substrate (medium 2):

\[
r_s = (f_1 + f_2Z)/(1 + f_1f_2Z) \quad r_{ss} = (f_1 + gZ)/(1 + f_1gZ)
\]

where \( f_2 = (q - q_2)/(q + q_2) \) and \( Z = \exp(2iq\Delta z) \) (compare Lekner (1987), equation (2.58)). Note that \( g \to f_2 \) when the substrate becomes isotropic \( (\epsilon_o, \epsilon_e \to \epsilon_2) \), and then \( r_{ss} \to r_s \).

To evaluate \( g \) we need the ratio of transmission amplitudes, \( \tau_s = \iota_{sc}/\iota_{so} \). From the two equations involving the coefficients \( a \) and \( b \) in (11) we find

\[
a/b = (Q_1 - Q)/(Q_1 + Q) = -F_1
\]

where \( Q_1 = q_1/\epsilon_1 \), \( Q = q/\epsilon \) and \( F_1 \) is the Fresnel p-wave reflection amplitude at the \( z = 0 \) boundary of the layer. From the second and third equations of (13) we find

\[
(a/b)Z = a'/b' = (S_o + \tau_sS_e)/(D_o + \tau_sD_e)
\]
where

\[ S_o = (k^2 + q_{o})X_o - qKZ_o \quad D_o = (k^2 - q_{o})X_o + qKZ_o \quad (56) \]

with \( S_o \) and \( D_o \) similarly defined. From (54) and (55) we obtain \( \tau_s = \tau_{ss}/\tau_{so} \):

\[ \tau_s = -(S_o + D_oF_1Z)/(S_e + D_eF_1Z) \quad (57) \]

and hence \( g \) in terms of known quantities:

\[ g = [(q - q_{o})Y_o + (q - q_{e})Y_e\tau_s]/[(q + q_{o})Y_o + (q + q_{e})Y_e\tau_s]. \quad (58) \]

Just as \( r_{ss} \) can be put into the form that \( r_s \) takes for an isotropic substrate, so \( r_{pp} \) can be put into the form that \( r_p \) takes in that case:

\[ r_p = (F_1 + F_2Z)/(1 + F_1F_2Z) \quad r_{pp} = (F_1 + GZ)/(1 + F_1GZ) \quad (59) \]

where \( F_1 \) and \( F_2 \) are the Fresnel reflection amplitudes for p waves at the \( z = 0 \) and \( z = \Delta z \) interfaces. \( (F_1 \) was defined in (54) and \( F_2 = (Q_2 - Q)/(Q_2 + Q) \) where \( Q_2 = q_2/\epsilon_2 \), \( \epsilon_2 \) being the dielectric constant of the isotropic substrate.) The form (59) for \( r_{pp} \) follows from the second and fourth equations (25), with

\[ G = b'/a' = (b/a)Z^{-1} = (D_o + \tau_pD_e)/(S_o + \tau_pS_e). \quad (60) \]

From the other p-wave equations we find the value of \( \tau_p = t_{pe}/t_{po} \):

\[ \tau_p = -\{(q + q_{o} + (q - q_{o})f_{1}Z)Y_o\} / \{(q + q_{e} + (q - q_{e})f_{1}Z)Y_e\} \quad (61) \]

having used the fact that

\[ B/A = -f_{1}^{-1} = g'Z \quad (62) \]

where \( g' \) has the same form as \( g \) in (58), with \( \tau_p \) replacing \( \tau_s \). For an isotropic substrate we have \( G = F_2 \), and thus \( r_{pp} \rightarrow r_p \).

Figure 1 shows the paths of \( \tau_{ss} \), \( r_{pp} \), \( r_{sp} \) and \( \tau_{ps} \) in the complex plane, for fixed angle of incidence and variable thickness \( \Delta z \) of the isotropic layer. The paths repeat after thickness \( \pi/\omega \), since all the reflection amplitudes are functions of the thickness via \( Z = \exp(2i\omega \Delta z) \). As the thickness increases, \( Z \) moves on the unit circle in the complex plane. The loci are close to circles, which indicates that the functions \( g(Z) \) and \( G(Z) \) are nearly independent of the layer thickness. (For an isotropic substrate \( g \rightarrow f_2 \) and \( G \rightarrow F_2 \), and \( r_{ss} \rightarrow r_s = (f_1 + f_2Z)/(1 + f_1f_2Z) \), \( r_{pp} \rightarrow r_p = (F_1 + F_2Z)/(1 + F_1F_2Z) \), \( r_{sp} \) and \( r_{ps} \rightarrow 0 \); the \( r_s \) and \( r_p \) loci are then exact circles.) Note that the \( r_{pp} \) locus moves across the origin as the angle of incidence increases. This implies that there are two angles at which \( r_{pp} \) can be zero: the Brewster angle of the substrate, for which \( F_1 + G(1) = 0 \), and another angle at
Figure 1. Loci of $r_{ss}$, $r_{pp}$, $r_{sp}$, and $r_{ps}$ in the complex plane, for variable thickness $\Delta z$ of the isotropic layer. The curves are drawn for air/water/calcite at $30^\circ$ and $60^\circ$ angle of incidence. The calcite optic axis is taken to make equal angles with $x$, $y$, and $z$ axes ($\alpha$, $\beta$, and $\gamma$ all take the value $1/\sqrt{3}$). The refractive indices (at 633 nm) are $n = 1.3327$, $n_o = 1.655$, $n_e = 1.485$. The paths repeat with period $\pi/q$ in $\Delta z$. This is 256 nm at $30^\circ$ and 312 nm at $60^\circ$ for 633 nm light incident on water from air. Zero-thickness values are indicated by a dot; arrows indicate the direction of increasing thickness.

which $F_1 - G(-1) = 0$. The corresponding values that $\Delta z$ must have for $r_{pp}$ to be zero are integer $\times \pi/q$ and odd integer $\times \pi/2q$, respectively.

The cross-reflection amplitudes $r_{sp}$ and $r_{ps}$ may be obtained from the boundary conditions on using the values for $r_{ss}$, $r_s$ and $r_{pp}$, $r_p$ given above. We find, after some reduction,

$$r_{sp} = \frac{8k_1Q_1q^2k_0^2}{(q_1 + q)(Q_1 + Q)} \frac{\beta(\alpha q_o + \gamma K)(q_e - q_o)N_oN_eZ}{(1 + f_1GZ)D_{sp}}$$

$$r_{ps} = \frac{8k_1Q_1q^2k_0^2}{(q_1 + q)(Q_1 + Q)} \frac{\beta(\alpha q_o - \gamma K)(q_e - q_o)N_oN_eZ}{(1 + f_1GZ)D_{ps}}$$

(63)

where the denominators $D_{sp}$ and $D_{ps}$ are linear in $Z$:

$$D_{sp} = (q + q_o)Y_eS_o - (q + q_o)Y_oS_e + F_1Z[(q + q_o)Y_eD_o - (q + q_o)Y_oD_e]$$

$$D_{ps} = (q + q_o)Y_eS_o - (q + q_o)Y_oS_e + f_1Z[(q - q_e)Y_eS_o - (q - q_o)Y_oS_e].$$

(64)
When \( Z = \exp(2i q \Delta z) \) is unity, these formulae reduce to the bare crystal values (denoted by a bar in this paper)

\[
\begin{align*}
\bar{r}_{sp} &= 2\beta(\alpha q_o + \gamma K)(q_e - q_o)k_1 k_o^2 N_o N_e / D \\
\bar{r}_{ps} &= 2\beta(\alpha q_o - \gamma K)(q_e - q_o)k_1 k_o^2 N_o N_e / D
\end{align*}
\]

where \( D \) is the common denominator of the reflection and transmission amplitudes (Lekner (1991), formulae (35) and (47)). Similarly \( r_{ss} \) and \( r_{pp} \) reduce to \( \bar{r}_{ss} \) and \( \bar{r}_{pp} \) as given by Lekner (1991), equations (34) and (42), when \( Z = 1 \).

At normal incidence the formulae of the previous section are regained.

It is interesting that the ratio of the s to p and p to s reflection amplitudes is not affected by the presence of the isotropic layer on the crystal. This follows from the identity

\[(1 + f_1 g Z)D_{sp} = (1 + F_1 G Z)D_{ps}.\]  

Thus the two complex numbers \( r_{sp} \) and \( r_{ps} \) have a real ratio (and so lie on a common radius in the complex plane). From (66) and (63) we have that

\[
\frac{r_{sp}}{r_{ps}} = \frac{(\alpha q_o + \gamma K)}{(\alpha q_o - \gamma K)}
\]

which is the same ratio that is obtained on reflection from the bare crystal. Note that \( r_{sp} = r_{ps} \) at normal incidence, and also when the optic axis lies in the reflecting plane \( (\gamma = 0) \).

At grazing incidence \( q_1 \) and \( Q_1 \) tend to zero. Thus \( f_1 = (q_1 - q)/(q_1 + q) \to -1 \) and \( F_1 = (Q - Q_1)/(Q + Q_1) \to 1 \). It follows from (53) and (59) that \( r_{ss} \to -1 \) and \( r_{pp} \to 1 \) at grazing incidence. (For isotropic media it is a general theorem that \( r_s \to -1 \) and \( r_p \to 1 \); see Lekner (1987), section 2-3.) From (63) we see that the cross-reflection amplitudes \( r_{sp} \) and \( r_{ps} \) both tend to zero as \( \theta_1 \to 90^\circ \).

At normal incidence \( r_{sp} = r_{ps} \), but the result that \( r_p = r_s \) at \( \theta_1 = 0^\circ \) for isotropic media does not generalize to \( r_{pp} = r_{ss} \); see section 3.

The transmission amplitudes are obtained in a similar way to the reflection amplitudes. We will just state the results:

\[
\begin{align*}
t_{so} &= -2q(S_o + D_o F_1 Z)A_s e^{iq \Delta z} / D_{sp} \quad t_{se} = 2q(S_o + D_o F_1 Z)A_s e^{iq \Delta z} / D_{sp} \\
t_{po} &= 2k_1 q[q + q_e + (q - q_o)f_1 Z]Y_e A_p e^{iq \Delta z} / D_{ps} \\
t_{pe} &= -2k_1 q[q + q_o + (q - q_o)f_1 Z]Y_e A_p e^{iq \Delta z} / D_{ps}
\end{align*}
\]

where \( A_s \) is the value of the coefficient \( A \) in (11) and (13),

\[
A_s = 2q_1/[(q_1 + q)(1 + f_1 g Z)].
\]  

The transmission amplitudes for the p wave incident are

\[
\begin{align*}
t_{po} &= 2k_1 q[q + q_o + (q - q_e)f_1 Z]Y_e A_p e^{iq \Delta z} / D_{ps} \\
t_{pe} &= -2k_1 q[q + q_e + (q - q_o)f_1 Z]Y_e A_p e^{iq \Delta z} / D_{ps}
\end{align*}
\]

where

\[
A_p = 2Q_1/[(Q_1 + Q)(1 + F_1 G Z)].
\]
5. Application to experiments on the premelting of ice

The premelting of ice, that is, the existence of a layer of water on the surface of ice below 0°C, has considerable geophysical importance. The compaction of snow, frost heave, rock fracture, water transport at subzero temperatures, and charge transfer in the electrification of thunder clouds are some of the topics discussed in a recent review (Dash 1989). We will discuss some recent optical studies of the surface of melting of ice. We begin with the Elbaum reflectivity experiment (Elbaum 1991, Elbaum et al. 1992), since this is simpler to analyse than the ellipsometry work to be discussed later in this section.

Elbaum interpreted his data by treating the ice as an isotropic substrate. He measured the p to p reflected intensity, \( R_{pp} = |r_{pp}|^2 \), at the Brewster angle, which was obtained by locating the minimum in \( R_{pp} \) at temperatures well below 0°C, when no water layer covered his ice crystals. As the temperature was raised to the melting point, an increased reflectivity was interpreted as being caused by a growing water layer, as follows. On the isotropic substrate model, the reflection amplitude is approximated by the first equation of (59):

\[
\begin{align*}
F_1 &= \frac{Q_1 - Q}{Q + Q_1} \\
F_2 &= \frac{Q_2 - Q}{Q_2 + Q} \\
Z &= \exp(2iQ\Delta z) \\
R_p(\theta_b) &= F_b(1 - Z)/(1 - F_b^2 Z) \\
R_p(\theta_b) &= 4F_b^2 \sin^2 q_b \Delta z/(1 - 2F_b^2 \cos 2q_b \Delta z + F_b^4)
\end{align*}
\]

where \( q_b \) is the value taken by \( q \) at the substrate Brewster angle \( \theta_b = \arctan(\epsilon_2/\epsilon_1)^{1/2} \):

\[
q_b = (\omega/c)[\epsilon - \epsilon_1 \epsilon_2/(\epsilon_1 + \epsilon_2)]^{1/2}.
\]

We see that (73) gives a quadratic dependence of the reflectance on the thickness \( \Delta z \) of the water layer, provided \( q_b \Delta z \ll 1 \). This is in accord with the general theory of reflection by thin layers on isotropic substrates, which gives (Lekner 1987), chapter 3)

\[
R_p(\theta_b) = [(\omega/c)I_1]^2/[4(\epsilon_1 + \epsilon_2)]
\]

as the leading term in the p reflectance at the Brewster angle, with the integral invariant \( I_1 \) taking the value

\[
I_1 = \Delta z (\epsilon_1 - \epsilon)(\epsilon - \epsilon_2)/\epsilon
\]

for a uniform layer (Lekner 1987), table 3-1).

To estimate \( R_p(\theta_b) \) we will use the refractive indices of Furukawa et al. (1987) for ice at 3°C and 633 nm:

\[
n_o = 1.30763 \quad n_e = 1.30903
\]
and $n = 1.3327$ for the water layer (this is the measured value at $0^\circ\text{C}$ and 633 nm). We need $\epsilon_2$, the dielectric constant of the effectively isotropic substrate, and we obtain this from $\epsilon_o = n_o^2$ and $\epsilon_\| = n_\|^2$ by using the formula

$$\epsilon_2 = (2\epsilon_o + \epsilon_\|)/3.$$  

(78)

Then (73) gives $R_p(\theta_B) \simeq 7.3 \times 10^{-7}$ when $\Delta z = 10 \text{ nm}$. Although this is a small reflectivity, it is well above Elbaum's noise level. Using the isotropic substrate model, Elbaum interpreted his reflectivity data as indicating premelting on the basal face of ice crystals, with $\Delta z \simeq 10 \text{ nm}$ at about $0.5^\circ\text{C}$.

We now consider the effect of anistropy of the substrate on the $p$ to $p$ reflectivity. Could the one part per thousand anistropy produce any measurable effect? The surprising answer is that it does, as we shall now see. The $r_{pp}$ reflection amplitude is given in (59). We see that it is zero for the base crystalline substrate when $G(Z = 1) = -F_1$, and this equation defines the Brewster $\theta_B$ angle for the crystal, which now depends on the crystal orientation. At this angle $F_1 = F_B$, and for thin layers

$$r_{pp} \to [(G_B' - F_B)/(1 - F_B^2)]^{2\pi q_B} \Delta z$$  

$$G' = (\partial G/\partial Z)_{Z=1}$$  

(79)

to first order in the layer thickness. From (73) we see that the analogous formula for an isotropic substrate has $G'$ missing. The derivative of $G(Z)$ at $Z = 1$ can be found from the defining relations (60) and (61):

$$G' = (q^2 - q_\|^2)k_L^2k_T^2(q_o - q_\|)^2\beta^2(\alpha q_o - \gamma K)(\alpha q_o + \gamma K)N_o^2N_\|^2/[((q_1 + q_o)Y_oS_o - (q_1 + q_\|)Y_oS_\|)^2].$$  

(80)

We see that it is zero in the isotropic limit, and zero also when $\beta = 0$ or $\alpha q_o = \pm \gamma K$. Numerically we have found it to be small compared to $F_B$ when ice is the substrate. This does not mean that anisotropy has no effect: since $\theta_B$ varies with crystal orientation, so do $F_B$ and $q_B$. Upper and lower bounds on $\theta_B$ have been found (Lekner 1992b); these occur when $\alpha^2 = 1$ (optic axis parallel to $x$, as for example in reflection from a prism face of ice with the optic axis in the plane of incidence), and $\gamma^2 = 1$ (optic axis parallel to $z$, as in reflection from a basal face of ice). The formulae giving $\theta_B$ for $\alpha^2 = 1$ and for $\gamma^2 = 1$ are, respectively,

$$\tan^2 \theta_B = \frac{\epsilon_o(\epsilon_o - \epsilon_\|)}{\epsilon_\|(\epsilon_o - \epsilon_\|)}$$  

$$\tan^2 \theta_B = \frac{\epsilon_\|(\epsilon_o - \epsilon_\|)}{\epsilon_\|(\epsilon_o - \epsilon_\|)}.$$  

(81)

For ice the Brewster angle upper and lower bounds are $52.66^\circ$ and $52.55^\circ$, a variation of only $0.1^\circ$. However, the multiplier of $\Delta z$ in (79) increases by a factor of 1.25 in going from the $\alpha^2 = 1$ to the $\gamma^2 = 1$ reflection. This enormous amplification, of parts per thousand to one in four, is due to index matching: the refractive index of the water layer is close to both indices of ice. To see how it works, consider the isotropic case again. The value of $F_B$ in (73) is

$$F_B = (r - 1)/(r + 1)$$  

$$r = \sqrt{(\epsilon_1 + \epsilon_\|)/\epsilon - \epsilon_\|(\epsilon_1 - \epsilon_\|)/\epsilon_\|}.$$  

(82)

This is zero (and $r = 1$) when $\epsilon$ is equal to $\epsilon_1$ or $\epsilon_\|$. In the air–water–ice case $\epsilon$ is close to $\epsilon_\|$, and $r$ is close to unity ($r \simeq 0.902$). Thus the two parts per thousand
difference provided by anisotropy in the effective value of \( \epsilon_2 \) is to be compared to eight parts per thousand in \(|r - 1|\): hence the one in four change in the multiplier of \( \Delta z \). Closer index matching would give still greater effect to anisotropy, but at the expense of a decrease in reflectivity at the Brewster angle. A more detailed discussion of anisotropy enhancement by index matching is given in appendix B.

For reflection from the basal plane there is azimuthal symmetry, and the reflectance is independent of the plane of incidence. For thin layers the reflectivity at the Brewster angle (given by the second formula in (81)) has a form like (75) with

\[
I_1 = \Delta z \left\{ \left( \frac{\epsilon_o \epsilon_e - \epsilon_i^2}{\epsilon_o - \epsilon_i} \right) - \left( \frac{(\epsilon_e - \epsilon_i) \epsilon - \epsilon_e \epsilon_i}{\epsilon_o - \epsilon_i} \right) \right\}.
\]

Details may be found in section 7-3 of Lekner (1987), which also takes into account possible layer anisotropy.

Elbaum observed surface melting only on the basal face. The above factor of 1.25 applies to the greatest possible change in the factor multiplying \( \Delta z \) between the prism and the basal faces. For the basal face, \( R_{pp}(\theta_B) \) with \( \theta_B \) given by the second part of (81) is \( 8.4 \times 10^{-7} \) for \( \Delta z = 10 \) nm, compared to \( 7.3 \times 10^{-7} \) for isotropic ice using the \( \epsilon_2 \) found from (78). This 20\% difference in reflectance implies that Elbaum's thickness estimates are likely to be about 10\% high.

We now turn to the ellipsometric experiments, which have the advantage that the ellipsometric signal is proportional to the thickness of the layer resting on the substrate, as opposed to the \( R_{pp} \) reflectivity at the substrate Brewster angle, which we saw is proportional to the square of the small quantity \( \omega \Delta z / c \). What polarization modulation ellipsometry measures in the presence of anisotropy is discussed in appendix A. In the absence of this theory, the experiments of Beaglehole and Nason (1980) and of Furukawa et al (1987) on the premelting of ice had been analysed by assuming ice to be isotropic. In the isotropic case, polarization modulation ellipsometry measures the imaginary part of \( r_p / r_s \) at the angle where the real part of \( r_p / r_s \) is zero. (This follows also as a limit from the anisotropic case: see the discussion following (A11) in appendix A.) For thin layers we have (see, for example, Lekner (1987), chapter 3)

\[
r_p / r_s = f_p / f_s - 2i Q_1 K^2 I_1 / [(Q_1 + Q_2)^2 \epsilon_1 \epsilon_2] + \ldots
\]

where \( f_p \) and \( f_s \) are the Fresnel reflection amplitudes for the bare substrate, and \( I_1 \) is given by (76). To the lowest order in \( \omega \Delta z / c \), the real part of \( r_p / r_s \) is zero at the substrate Brewster angle, \( \theta_B = \text{atan}(n_2/n_1) \). At this angle

\[
\text{Im}(r_p / r_s) = [\sqrt{\epsilon_1 + \epsilon_2 / (\epsilon_2 - \epsilon_1)}(\omega / c) I_1 + \ldots
\]

How much error in the deduced thickness of the water layer is caused by assuming ice to be isotropic? Since the difference between the ordinary and extraordinary indices of ice is about one part in a thousand, the error might be expected to be of this order. In fact we found from (A11) that the factor multiplying \( \Delta z \) varied by 25\% as the crystal substrate took on different orientations. This was the total variation, with values being calculated that were both larger and smaller than predicted by (85). As in the reflectivity case, a reason for the amplification is index matching: the refractive index of water is close to both refractive indices of ice. (For more detail, see appendix B.) In addition to index matching, there is the presence of the s to p and
p to s reflection amplitudes: instead of \( r_p/r_s \), polarization modulation ellipsometry now measures \( (r_{pp} \pm r_{ps})/(r_{ss} \pm r_{sp}) \), and (85) becomes only a guide to order of magnitude. Nevertheless, for water on ice the analysis assuming isotropy is correct to within about \( \pm 10\% \).

Appendix A. Polarization modulation ellipsometry of anisotropic media

Jasperson and Schnatterly (1969) introduced the technique of sinusoidally varying the polarization of the incident beam in an ellipsometer, with synchronous detection of the intensity modulations. The method is currently extensively used by Beaglehole and collaborators. This appendix gives the theory of what is measured by polarization modulation ellipsometry when anisotropy is present. In the Beaglehole (1980) ellipsometer, the incident beam passes through a polarizer which gives equal amplitudes of s and p polarization, and then through a birefringent modulator in which the s and p waves get a (periodically modulated) phase shift relative to each other. The beam then reflects from the sample, and passes through an analyser to the detector. The analyser is cycled through two positions, parallel and perpendicular to the polarizer direction. The amplitudes of the p- and s-polarized waves after reflection are given by

\[
E_p = r_{pp}E_p^i + r_{sp}E_s^i \quad E_s = r_{ps}E_p^i + r_{ss}E_s^i
\]

where \( E_p^i \) and \( E_s^i \) are the amplitudes of the incident waves after passing through the polarizer and birefringent modulator. On removing a common factor, these can be written as 1 and \( e^{i\delta} \), respectively, where

\[
\delta(t) = A \sin(\Omega t)
\]

in which \( \Omega/2\pi \) is the frequency of the modulator. After reflection the p and s components are thus

\[
r_{pp} + r_{sp}e^{i\delta} \quad r_{ps} + r_{ss}e^{i\delta}.
\]

The signal detected after passing through the analyser is thus proportional to

\[
|r_{pp} + r_{sp}e^{i\delta} \pm (r_{ps} + r_{ss}e^{i\delta})|^2
\]

where the two signs correspond to the two positions of the analyser. We will write (A4) as

\[
|u + e^{i\delta}v|^2 = |u|^2 + |v|^2 + 2(u_r v_r + u_i v_i) \cos \delta - 2(u_r v_i - u_i v_r) \sin \delta
\]

where

\[
u = u_r + i u_i, \quad v = v_r + i v_i
\]

and \( u = u_r + i u_i, \ v = v_r + i v_i \).
The terms $\cos \delta$ and $\sin \delta$ are sinusoidal functions of sinusoidal argument, which we may expand using the Jacobi formulae (Watson (1966), section 2.22)

\[
\begin{align*}
\cos(A \sin \Omega t) &= J_0(A) + 2 \sum_{n=1}^{\infty} J_{2n}(A) \cos(2n \Omega t) \\
\sin(A \sin \Omega t) &= 2 \sum_{n=0}^{\infty} J_{2n+1}(A) \sin((2n + 1) \Omega t).
\end{align*}
\]

It is usual to adjust the voltage on the birefringent modulator so as to make $J_0(A) = 0$ (this requires $A \approx 2.4048$ radians or about $138^\circ$, for the lowest root of $J_0$). The DC component of (A5) is then

\[ \text{DC: } |u|^2 + |v|^2 \]  

(A8)

For any value of the $A$ the $\Omega$ and $2\Omega$ components (measured by lock-in amplifiers) are

\[
\begin{align*}
\Omega: & \quad -4J_1(A)(u_r v_i - u_i v_r) \\
2\Omega: & \quad 4J_2(A)(u_r v_r + u_i v_i).
\end{align*}
\]

(A9)

Note that

\[ u/v = [u_r v_r + u_i v_i - i(u_r v_i - u_i v_r)]/|u|^2 \]  

(A10)

so the $2\Omega$ and $\Omega$ signals are proportional to the real and imaginary parts of

\[ (u/v)_\pm = (r_{pp} \pm r_{ps})/(r_{sp} \pm r_{ss}) = \pm(r_{pp} \pm r_{ps})/(r_{ss} \pm r_{sp}). \]  

(A11)

In the isotropic case $(u/v)_\pm \rightarrow \pm r_p/r_s$, and the Beaglehole measurements are of $\text{Im}(r_p/r_s)$ at the ellipsometric Brewster angle where $\text{Re}(r_p/r_s) = 0$. In the anisotropic case one may (for example) define the ellipsometric Brewster angle by the zero of the difference of the $(2\Omega/\text{DC})_\pm$ signals.

Appendix B. Enhancement of anisotropy by index matching

We consider the $p$ to $p$ reflection first. The dominant factor in $r_{pp}$ for thin layers is, from (79),

\[
F_B = [(Q - Q_1)/(Q + Q_1)]_{\delta_B} \equiv (R - 1)/(R + 1).
\]

(B1)

For an isotropic substrate the corresponding factor is

\[
F_b = (r - 1)/(r + 1) \quad r^2 = (\epsilon_1 + \epsilon_2)/\epsilon - \epsilon_1 \epsilon_2/\epsilon_2.
\]

(B2)

The ratio $R = (Q/Q_1)_{\delta_B}$ depends on the Brewster angle, which varies between the extremes given in (81). At any angle

\[ R^2 = [\epsilon - (cK/\omega)^2]/[\epsilon_1 - (cK/\omega)^2] \epsilon_1^2/\epsilon_2. \]  

(B3)
For $\alpha^2 = 1$ (optic axis parallel to $x$), we have

$$(eK_B/\omega)^2 = \epsilon_1\epsilon_0(\epsilon_0 - \epsilon_1)/(\epsilon_0\epsilon_0 - \epsilon_1^2)$$

(B4)

$$R^2 = \frac{\epsilon(\epsilon_0\epsilon_0 - \epsilon_1^2) - \epsilon_1\epsilon_0(\epsilon_0 - \epsilon_1)}{\epsilon^2(\epsilon_0 - \epsilon_1)} = r_r^2 + \frac{(\epsilon - \epsilon_1)(2\epsilon_1 + 2\epsilon_2)\Delta\epsilon}{3\epsilon^2(\epsilon_2 - \epsilon_1)} + O(\Delta\epsilon)^2.$$ \hspace{1cm} (B5)

For $\gamma^2 = 1$ (optic axis parallel to $z$), the corresponding values are

$$(eK_B/\omega)^2 = \epsilon_1\epsilon_0(\epsilon_0 - \epsilon_1)/(\epsilon_0\epsilon_0 - \epsilon_1^2)$$

(B6)

$$R^2 = \frac{\epsilon(\epsilon_0\epsilon_0 - \epsilon_1^2) - \epsilon_1\epsilon_0(\epsilon_0 - \epsilon_1)}{\epsilon^2(\epsilon_0 - \epsilon_1)} = r_r^2 - \frac{(\epsilon - \epsilon_1)(2\epsilon_1 + 2\epsilon_2)\Delta\epsilon}{3\epsilon^2(\epsilon_2 - \epsilon_1)} + O(\Delta\epsilon)^2.$$ \hspace{1cm} (B7)

The change in $F_B$ between the $x$ and $z$ orientations of the optic axis of the substrate is

$$\Delta F_B = F_B(\alpha^2 = 1) - F_B(\gamma^2 = 1)$$

$$= (\epsilon - \epsilon_1)(\epsilon_1 + \epsilon_2)\Delta\epsilon/[\epsilon^2(\epsilon_2 - \epsilon_1)(r + 1)^2] + O(\Delta\epsilon)^2.$$ \hspace{1cm} (B8)

Thus the fractional change in the multiplier of $\Delta z$ in the reflection amplitude $r_{pp}$ is approximately

$$\Delta F_B/F_B = (\epsilon_1 + \epsilon_2)\Delta\epsilon/[(\epsilon_2 - \epsilon_1)(\epsilon_2 - \epsilon)\epsilon] + O(\Delta\epsilon)^2.$$ \hspace{1cm} (B9)

(The exact change can be found from (79). We have omitted the factor $q_B(1 - G_B/F_B)/(1 - F_B^2)$; for water on ice this has small variation compared to that of $F_B$.)

We see from (B9) that the enhancement of the effect of the anisotropy $\Delta\epsilon = \epsilon_2 - \epsilon_0$ is achieved in direct proportion that the dielectric constant $\epsilon$ of the overlayer is matched to the average dielectric constant $\epsilon_2 = (2\epsilon_0 + \epsilon_e)/3$ of the crystal substrate. When $\epsilon = \epsilon_2$, $r = 1$ and $F_B$ is zero: thus for close matching we obtain a large enhancement of anisotropy, at the expense of weak reflectivity. Conversely, if the ratio given in (B9) is small compared to unity, anisotropy in the substrate can be neglected. For air–water–ice the ratio in (B9) $\simeq -0.22$ (left-hand side $-0.2165$, right-hand side $-0.2167$); thus anisotropy is appreciable but not dominant for this system.

We now briefly discuss the enhancement of anisotropy by index matching in ellipsometric measurement. The reflection amplitude $r_{pp}$ at the substrate Brewster angle $\theta_B$ is given by (79). It is of first order in the overlayer thickness, and pure imaginary in the thin-film limit. The other reflection amplitudes are $\bar{r}_{ss}, \bar{r}_{sp}$ and $\bar{r}_{ps}$ (all real), plus imaginary parts that are first order in the layer thickness. For $r_{sp}$ and $r_{ps}$ the magnitude follows from (79) that the $\Omega$ signal (see appendix A) which is proportional to the imaginary part of $(r_{pp} \pm r_{ps})/(r_{ss} \pm r_{sp})$, is approximately $\pm \text{Im}(r_{pp})/\bar{r}_{ss}$; provided $\bar{r}_{ps}$ and $\bar{r}_{sp}$ are small in magnitude compared to $F_B$. It then follows from the arguments given earlier in this appendix that the fractional change in $\text{Im}(r_{pp})$ as $\theta_B$ varies between its extremes is given approximately by (B9). Thus the magnitude of (B9) also provides a guide to the importance of anisotropy on the $\Omega$ component of polarization modulation ellipsometry: if $\Delta F_B/F_B$ is small, anisotropy is unimportant, provided also that $\bar{r}_{sp}$ and $\bar{r}_{ps}$ are small in magnitude compared to $F_B$. 

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