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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 matching (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 $\epsilon = n^2$, and is bounded by the medium of incidence ($\epsilon_1 = n_1^2$) and the uniaxial substrate ($\epsilon_o = n_o^2$, $\epsilon_e = n_e^2$), 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 α , β and γ ; thus $c = (\alpha, \beta, \gamma)$ is the unit vector giving the direction of the optic axis.

We consider reflection and transmission of a plane monochromatic wave of angular frequency ω , incident from medium 1 at angle θ_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 $\exp i(Kx - \omega t)$, where

$$K = n_1(\omega/c) \sin \theta_1 = n(\omega/c) \sin \theta \tag{1}$$

is the x -component of all the wavevectors, and θ 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 xz -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

$$q_1 = n_1(\omega/c) \cos \theta_1 \tag{2}$$

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

$$q^2 = \epsilon\omega^2/c^2 - K^2 \equiv k^2 - K^2. \tag{3}$$

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

$$q_o^2 = \epsilon_o\omega^2/c^2 - K^2 \equiv k_o^2 - K^2 \tag{4}$$

for the ordinary wave, and

$$q_e = \bar{q} - \alpha\gamma K \Delta\epsilon/\epsilon_\gamma \tag{5}$$

where

$$\Delta\epsilon = \epsilon_e - \epsilon_o \quad \dots \quad \epsilon_\gamma = n_\gamma^2 = \epsilon_o + \gamma^2 \Delta\epsilon \quad \bar{q}^2 = \epsilon_o[\epsilon_e\epsilon_\gamma\omega^2/c^2 - K^2(\epsilon_e - \beta^2 \Delta\epsilon)]/\epsilon_\gamma^2. \tag{6}$$

The electric field vector of the ordinary wave is

$$\mathbf{E} = N_o(-\beta q_o, \alpha q_o - \gamma K, \beta K) \tag{7}$$

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

$$\mathbf{E}_e = N_e(\alpha q_o^2 - \gamma q_e K, \beta k_o^2, \gamma(k_o^2 - q_e^2) - \alpha q_e K). \tag{8}$$

N_o and N_e are normalization factors: we will normalize \mathbf{E}_o and \mathbf{E}_e to unit amplitude, so that $|\mathbf{E}_o|^2 = 1 = |\mathbf{E}_e|^2$.

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 2×2 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 $\exp i(Kx - \omega t)$ suppressed, are

$$\begin{aligned}
 \text{incident} & \quad (0, e^{iq_1z}, 0) \\
 \text{reflected} & \quad e^{-iq_1z}(r_{sp} \cos \theta_1, r_{ss}, r_{sp} \sin \theta_1) \\
 \text{within layer} & \quad (\cos \theta (ae^{iqz} + be^{-iqz}), Ae^{iqz} + Be^{-iqz}, -\sin \theta (ae^{iqz} - be^{-iqz})) \\
 \text{within crystal} & \quad t_{so}E_o e^{iq_o(z-\Delta z)} + t_{se}E_e e^{iq_e(z-\Delta z)}. \tag{9}
 \end{aligned}$$

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

$$q \cos \theta + K \sin \theta = n\omega/c = k \tag{10}$$

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 $E_y, E_x, \partial E_y/\partial z$, and $\partial E_x/\partial z - iKE_z$ at $z = 0$ gives the equations

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

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

$$A' = Ae^{iq\Delta z} \quad B' = Be^{-iq\Delta z} \quad a' = ae^{iq\Delta z} \quad b' = be^{-iq\Delta z} \tag{12}$$

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

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

We will give two solutions of this system of eight equations: a 2×2 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 2×2 matrix method is given here. We define the vectors

$$u = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad r = \begin{pmatrix} r_{ss} \\ r_{sp} \end{pmatrix} \quad s = \begin{pmatrix} A + B \\ a + b \end{pmatrix} \quad d = \begin{pmatrix} A - B \\ a - b \end{pmatrix} \tag{14}$$

and the diagonal cosine matrices

$$\mathbf{C}_1 = \begin{pmatrix} 1 & 0 \\ 0 & \cos \theta_1 \end{pmatrix} \quad \mathbf{C} = \begin{pmatrix} 1 & 0 \\ 0 & \cos \theta \end{pmatrix} \quad (15)$$

Then the equation set (11) can be written as

$$\mathbf{u} + \mathbf{C}^{-1}\mathbf{C}_1\mathbf{r} = \mathbf{s} \quad (q_1/q)(\mathbf{u} - \mathbf{C}\mathbf{C}_1^{-1}\mathbf{r}) = \mathbf{d}. \quad (16)$$

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

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

and the matrices

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

Then the equation set (13) can be written as

$$\mathbf{C}\mathbf{s}' = \mathbf{M}\mathbf{t} \quad q\mathbf{C}^{-1}\mathbf{d}' = \mathbf{N}\mathbf{t}. \quad (19)$$

The vectors \mathbf{s}' and \mathbf{d}' are linear combinations of \mathbf{s} and \mathbf{d} :

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

The equations (19) give

$$\mathbf{t} = \mathbf{M}^{-1}\mathbf{C}\mathbf{s}' = q\mathbf{N}^{-1}\mathbf{C}^{-1}\mathbf{d}'. \quad (21)$$

On substituting for \mathbf{s}' and \mathbf{d}' using (20) and (16), we obtain a linear equation for \mathbf{r} in terms of \mathbf{u} which has the form $\mathbf{V}\mathbf{r} = \mathbf{W}\mathbf{u}$, with

$$\begin{aligned} \mathbf{V} &= \mathbf{N}^{-1}(c q_1 \mathbf{C}_1^{-1} - i s q \mathbf{C}^{-2} \mathbf{C}_1) + q^{-1} \mathbf{M}^{-1}(c q \mathbf{C}_1 - i s q_1 \mathbf{C}^2 \mathbf{C}_1^{-1}) \\ \mathbf{W} &= \mathbf{N}^{-1} \mathbf{C}^{-1}(c q_1 + i s q) - q^{-1} \mathbf{M}^{-1} \mathbf{C}(c q + i s q_1) \end{aligned} \quad (22)$$

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

$$\mathbf{r} = \mathbf{V}^{-1} \mathbf{W} \mathbf{u} \equiv \mathbf{R} \mathbf{u} \quad (23)$$

may be obtained by inversion and multiplication of 2×2 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	$e^{iq_1 z} (\cos \theta_1, 0, -\sin \theta_1)$
reflected	$e^{-iq_1 z} (r_{pp} \cos \theta_1, r_{ps}, r_{pp} \sin \theta_1)$
within layer	$(\cos \theta (ae^{iqz} + be^{-iqz}), Ae^{iqz} + Be^{-iqz}, -\sin \theta (ae^{iqz} - be^{-iqz}))$
within crystal	$t_{po} E_o e^{iq_o(z-\Delta z)} + t_{pe} E_e e^{iq_e(z-\Delta z)}.$

(24)

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

$$\begin{aligned} r_{ps} &= A + B & (1 + r_{pp}) \cos \theta_1 &= (a + b) \cos \theta \\ -q_1 r_{ps} &= q(A - B) & k_1(1 - r_{pp}) &= k(a - b). \end{aligned} \quad (25)$$

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 2×2 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

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

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

$$W' = N^{-1}(cq_1 C_1^{-1} + isqC^{-2}C_1) - q^{-1}M^{-1}(cqC_1 + isq_1 C^2 C_1^{-1}). \quad (29)$$

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

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

We shall next use these results to obtain simple formulae for the reflection and transmission amplitudes at normal incidence.

3. Normal incidence

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

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

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

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

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

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

We then find that the matrix \mathbf{R} in $\mathbf{r} = \mathbf{R}\mathbf{u}$ simplifies to

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

where

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

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 $n_o n_e / n_\gamma$, respectively (see Lekner (1987), equation (2.52)).

Thus

$$\begin{aligned} r_{ss} &= (\alpha^2 r_o + \beta^2 r_e) / (\alpha^2 + \beta^2) = r_o \cos^2 \phi + r_e \sin^2 \phi \\ r_{sp} &= \alpha\beta(r_e - r_o) / (\alpha^2 + \beta^2) = (r_o - r_e) \cos \phi \sin \phi \end{aligned} \quad (36)$$

where ϕ is the angle between the E_o direction and the incident field E_1 . For p polarization incident, the matrix \mathbf{R}' is equal to \mathbf{R} as given in (34) for normal incidence. Thus

$$\begin{aligned} r_{ps} &= \alpha\beta(r_e - r_o) / (\alpha^2 + \beta^2) = (r_o - r_e) \cos \phi \sin \phi \\ r_{pp} &= (\alpha^2 r_e + \beta^2 r_o) / (\alpha^2 + \beta^2) = r_e \cos^2 \phi + r_o \sin^2 \phi. \end{aligned} \quad (37)$$

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

Just as \mathbf{r} and \mathbf{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 \mathbf{t} and \mathbf{t}' , which have the transmission amplitudes t_{so} , t_{se} , t_{po} , t_{pe} as components, be expressed in terms of t_o and t_e , which are the transmission amplitudes for a layer of thickness Δz on isotropic substrates of indices n_o and $n_o n_e / n_\gamma$:

$$\begin{aligned} t_o &= k^{-1} [k(1 + r_o) \cos k \Delta z + i k_1 (1 - r_o) \sin k \Delta z] \\ &= 2k_1 k / [k(k_1 + k_o) \cos k \Delta z - i(k^2 + k_1 k_o) \sin k \Delta z] \end{aligned} \quad (38)$$

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

$$\mathbf{t} = \mathbf{T}\mathbf{u} \quad \mathbf{t}' = \mathbf{T}\mathbf{v} \quad (39)$$

where

$$\begin{aligned} \mathbf{T} &= (\alpha^2 + \beta^2)^{-1} \begin{pmatrix} N_o^{-1} & 0 \\ 0 & N_e^{-1} \end{pmatrix} \begin{pmatrix} t_o & 0 \\ 0 & t_e \end{pmatrix} \begin{pmatrix} \alpha & -\beta \\ \beta & \alpha \end{pmatrix} \\ &= (\alpha^2 + \beta^2)^{-1} \begin{pmatrix} \alpha N_o^{-1} t_o & -\beta N_o^{-1} t_o \\ \beta N_e^{-1} t_e & \alpha N_e^{-1} t_e \end{pmatrix}. \end{aligned} \quad (40)$$

Thus

$$\begin{aligned} t_{so} &= \alpha N_o^{-1} t_o / (\alpha^2 + \beta^2) & t_{se} &= \beta N_e^{-1} t_e / (\alpha^2 + \beta^2) \\ t_{po} &= -\beta N_o^{-1} t_o / (\alpha^2 + \beta^2) & t_{pe} &= \alpha N_e^{-1} t_e / (\alpha^2 + \beta^2). \end{aligned} \quad (41)$$

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 and t_o , t_e , we will note the behaviour of the latter as a function of the layer thickness Δz . Let

$$f_1 = (k_1 - k) / (k_1 + k) \quad f_o = (k - k_o) / (k + k_o) \quad f_e = (k - k_e) / (k + k_e) \quad (42)$$

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 $n_o n_e / n_\gamma$. Then r_o and r_e can be written as

$$r_o = (f_1 + f_o Z) / (1 + f_1 f_o Z) \quad r_e = (f_1 + f_e Z) / (1 + f_1 f_e Z) \quad (43)$$

where $Z = \exp(2ik\Delta z)$. As Δz 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 Δz of all the motions is π/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 and 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

$$r_o^+ = (k_1 - k_o) / (k_1 + k_o) \quad r_e^+ = (k_1 - k_e) / (k_1 + k_e) \quad (44)$$

while at $Z = -1$, r_o becomes

$$r_o^- = (f_1 - f_o) / (1 - f_1 f_o) = (k_1 k_o - k^2) / (k_1 k_o + k^2) \quad (45)$$

(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

$$c_o = (r_o^+ + r_o^-) / 2 \quad a_o = (r_o^+ - r_o^-) / 2. \quad (46)$$

The transmission amplitude t_o can be written as

$$t_o = (1 + f_1)(1 + f_o)\zeta / (1 + f_1 f_o \zeta^2) \quad (47)$$

where $\zeta = \exp(ik\Delta z)$. As Δz increases, t_o moves on a quartic in the complex plane, repeating with period $2\pi/k$ in Δz . The equation of the quartic is found by eliminating ζ from (47), using $\zeta\zeta^* = 1$. If we write $t_o = X + iY$, the quartic is

$$(X^2 + Y^2)^2 = (t_o^+ X)^2 + (t_o^+ Y)^2 \quad (48)$$

where $\pm t_o^\pm$ is the value of t_o at $\zeta = \pm 1$, and $\pm i t_o^i$ is the value at $\zeta = \pm i$:

$$t_o^+ = 2k_1/(k_1 + k_o) \quad t_o^i = 2k_1 k/(k_1 k_o + k^2). \tag{49}$$

The reciprocal t_o^{-1} moves on an ellipse, with semiaxes $(t_o^+)^{-1}$ and $(t_o^i)^{-1}$. 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 2×2 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

$$1 + r_{ss} = A + B \quad 1 - r_{ss} = q_1^{-1} q(A - B). \tag{50}$$

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

$$r_{ss} = \frac{q_1 - q + (q_1 + q)B/A}{q_1 + q + (q_1 - q)B/A} = \frac{f_1 + B/A}{1 + f_1 B/A} \tag{51}$$

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 Δz gives a pair of equations (the first and third of (13)) which may be solved for B/A :

$$\frac{B}{A} = g \exp(2iq \Delta z) \quad g = \frac{(q - q_o)t_{so}Y_o + (q - q_e)t_{se}Y_e}{(q + q_o)t_{so}Y_o + (q + q_e)t_{se}Y_e}. \tag{52}$$

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):

$$r_s = (f_1 + f_2 Z)/(1 + f_1 f_2 Z) \quad r_{ss} = (f_1 + g Z)/(1 + f_1 g Z) \tag{53}$$

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

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

$$a/b = (Q_1 - Q)/(Q_1 + Q) = -F_1 \tag{54}$$

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

$$(a/b)Z = a'/b' = (S_o + \tau_s S_e)/(D_o + \tau_s D_e) \tag{55}$$

where

$$S_o = (k^2 + q q_o) X_o - q K Z_o \quad D_o = (k^2 - q q_o) X_o + q K Z_o \quad (56)$$

with S_e and D_e similarly defined. From (54) and (55) we obtain $\tau_s = t_{se}/t_{so}$:

$$\tau_s = -(S_o + D_o F_1 Z)/(S_e + D_e F_1 Z) \quad (57)$$

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:

$$r_p = (F_1 + F_2 Z)/(1 + F_1 F_2 Z) \quad r_{pp} = (F_1 + G Z)/(1 + F_1 G Z) \quad (59)$$

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 $Q_2 = q_2/\epsilon_2$, ϵ_2 being the dielectric constant of the isotropic substrate.) The form (59) for r_{pp} follows from the second and fourth equations (25), with

$$G = b'/a' = (b/a) Z^{-1} = (D_o + \tau_p D_e)/(S_o + \tau_p S_e). \quad (60)$$

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 τ_p replacing τ_s . For an isotropic substrate we have $G \rightarrow F_2$, and thus $r_{pp} \rightarrow r_p$.

Figure 1 shows the paths of r_{ss} , r_{pp} , r_{sp} and r_{ps} in the complex plane, for fixed angle of incidence and variable thickness Δz of the isotropic layer. The paths repeat after thickness π/q , since all the reflection amplitudes are functions of the thickness via $Z = \exp(2iq\Delta z)$. 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 $r_{ss} \rightarrow r_s = (f_1 + f_2 Z)/(1 + f_1 f_2 Z)$, $r_{pp} \rightarrow r_p = (F_1 + F_2 Z)/(1 + F_1 F_2 Z)$, 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

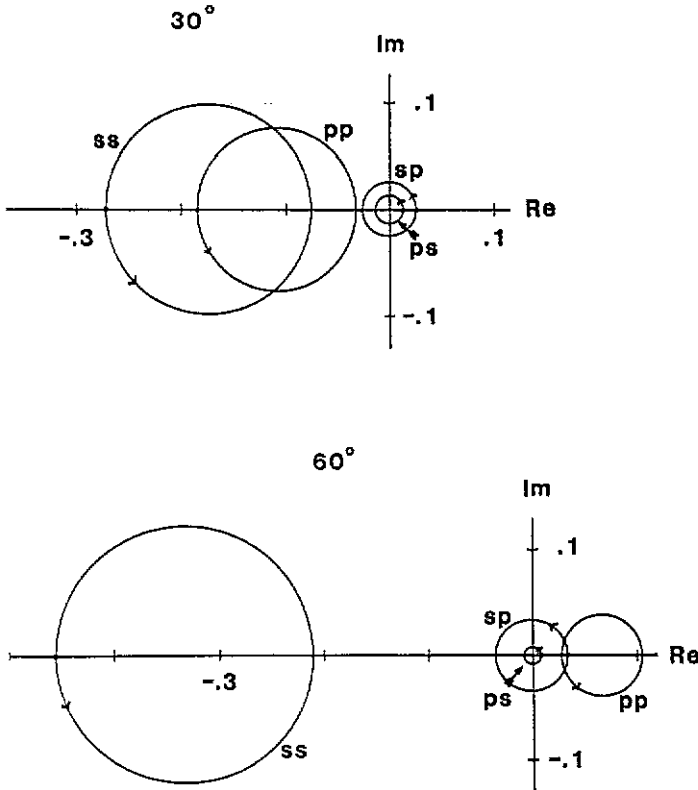


Figure 1. Loci of r_{ss} , r_{pp} , r_{sp} and r_{ps} in the complex plane, for variable thickness Δz of the isotropic layer. The curves are drawn for air/water/calcite at 30° and 60° angle of incidence. The calcite optic axis is taken to make equal angles with x , y and z axes (α , β and γ all take 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 π/q in Δz . This is 256 nm at 30° and 312 nm at 60° 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 Δz 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} , τ_s and r_{pp} , τ_p given above. We find, after some reduction,

$$r_{sp} = \frac{8k_1 Q_1 q^2 k_o^2}{(q_1 + q)(Q_1 + Q)} \frac{\beta(\alpha q_o + \gamma K)(q_e - q_o) N_o N_e Z}{(1 + f_1 g Z) D_{sp}} \quad (63)$$

$$r_{ps} = \frac{8k_1 Q_1 z^2 k_o^2}{(q_1 + q)(Q_1 + Q)} \frac{\beta(\alpha q_o - \gamma K)(q_e - q_o) N_o N_e Z}{(1 + F_1 G Z) D_{ps}}$$

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

$$D_{sp} = (q + q_e) Y_e S_o - (q + q_o) Y_o S_e + F_1 Z [(q + q_e) Y_e D_o - (q + q_o) Y_o D_e] \quad (64)$$

$$D_{ps} = (q + q_e) Y_e S_o - (q + q_o) Y_o S_e + f_1 Z [(q - q_e) Y_e S_o - (q - q_o) Y_o S_e].$$

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

$$\begin{aligned} \bar{r}_{sp} &= 2\beta(\alpha q_o + \gamma K)(q_e - q_o)k_1 k_o^2 N_o N_e / D \\ \bar{r}_{ps} &= 2\beta(\alpha q_o - \gamma K)(q_e - q_o)k_1 k_o^2 N_o N_e / D \end{aligned} \tag{65}$$

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

$$(1 + f_1 g Z) D_{sp} = (1 + F_1 G Z) D_{ps}. \tag{66}$$

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

$$r_{sp} / r_{ps} = (\alpha q_o + \gamma K) / (\alpha q_o - \gamma K) \tag{67}$$

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 $f_1 = (q_1 - q) / (q_1 + q) \rightarrow -1$ and $F_1 = (Q - Q_1) / (Q + Q_1) \rightarrow 1$. It follows from (53) and (59) that $r_{ss} \rightarrow -1$ and $r_{pp} \rightarrow 1$ at grazing incidence. (For isotropic media it is a general theorem that $r_s \rightarrow -1$ and $r_p \rightarrow 1$: 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 $\theta_1 \rightarrow 90^\circ$.

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:

$$t_{so} = -2q(S_e + D_e F_1 Z) A_s e^{iq \Delta z} / D_{sp} \quad t_{se} = 2q(S_o + D_o F_1 Z) A_s e^{iq \Delta z} / D_{sp} \tag{68}$$

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

$$A_s = 2q_1 / [(q_1 + q)(1 + f_1 g Z)]. \tag{69}$$

The transmission amplitudes for the p wave incident are

$$\begin{aligned} t_{po} &= 2k_1 q [q + q_e + (q - q_e) f_1 Z] Y_e A_p e^{iq \Delta z} / D_{ps} \\ t_{pe} &= -2k_1 q [q + q_o + (q - q_o) f_1 Z] Y_o A_p e^{iq \Delta z} / D_{ps} \end{aligned} \tag{70}$$

where

$$A_p = 2Q_1 / [(Q_1 + Q)(1 + F_1 G Z)]. \tag{71}$$

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):

$$r_p = \frac{F_1 + F_2 Z}{1 + F_1 F_2 Z} \quad \dots \quad F_1 = \frac{Q - Q_1}{Q + Q_1} \quad \dots \quad F_2 = \frac{Q_2 - Q}{Q_2 + Q} \quad \dots \quad Z = \exp(2iq \Delta z). \quad (72)$$

At the Brewster angle for the substrate, $Q_1 = Q_2 = (\omega/c)(\epsilon_1 + \epsilon_2)^{-1/2}$ and $F_1 = -F_2 = F_b$, so

$$r_p(\theta_b) = F_b(1 - Z)/(1 - F_b^2 Z) \quad (73)$$

$$R_p(\theta_b) = 4F_b^2 \sin^2 q_b \Delta z / (1 - 2F_b^2 \cos 2q_b \Delta z + F_b^4)$$

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

$$q_b = (\omega/c)[\epsilon - \epsilon_1 \epsilon_2 / (\epsilon_1 + \epsilon_2)]^{1/2}. \quad (74)$$

We see that (73) gives a quadratic dependence of the reflectance on the thickness Δz 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)

$$R_p(\theta_b) = [(\omega/c)I_1]^2 / [4(\epsilon_1 + \epsilon_2)] \quad (75)$$

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

$$I_1 = \Delta z (\epsilon_1 - \epsilon)(\epsilon - \epsilon_2) / \epsilon \quad (76)$$

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:

$$n_o = 1.30763 \quad n_e = 1.30903 \quad (77)$$

and $n = 1.3327$ for the water layer (this is the measured value at 0°C and 633 nm). We need ϵ_2 , the dielectric constant of the effectively isotropic substrate, and we obtain this from $\epsilon_o = n_o^2$ and $\epsilon_e = n_e^2$ by using the formula

$$\epsilon_2 = (2\epsilon_o + \epsilon_e)/3. \tag{78}$$

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°C .

We now consider the effect of anisotropy of the substrate on the p to p reflectivity. Could the one part per thousand anisotropy 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 θ_B angle for the crystal, which now depends on the crystal orientation. At this angle $F_1 = F_B$, and for thin layers

$$r_{pp} \rightarrow [(G'_B - F_B)/(1 - F_B^2)]2iq_B \Delta z \quad G' = (\partial G/\partial Z)_{Z=1} \tag{79}$$

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):

$$G' = \frac{(q^2 - q_1^2)k^2 k_o^4 (q_e - q_o)^2 \beta^2 (\alpha q_o - \gamma K)(\alpha q_o + \gamma K) N_o^2 N_e^2}{[(q_1 + q_e)Y_e S_o - (q_1 + q_o)Y_o S_e]^2}. \tag{80}$$

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 θ_B varies with crystal orientation, so do F_B and q_B . Upper and lower bounds on θ_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 θ_B for $\alpha^2 = 1$ and for $\gamma^2 = 1$ are, respectively,

$$\tan^2 \theta_B = \frac{\epsilon_o(\epsilon_e - \epsilon_1)}{\epsilon_1(\epsilon_o - \epsilon_1)} \quad \tan^2 \theta_B = \frac{\epsilon_e(\epsilon_o - \epsilon_1)}{\epsilon_1(\epsilon_e - \epsilon_1)}. \tag{81}$$

For ice the Brewster angle upper and lower bounds are 52.66° and 52.55° , a variation of only 0.1° . However, the multiplier of Δz 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

$$F_b = (r - 1)/(r + 1) \quad r = \sqrt{(\epsilon_1 + \epsilon_2)/\epsilon - \epsilon_1 \epsilon_2/\epsilon_2}. \tag{82}$$

This is zero (and $r = 1$) when ϵ is equal to ϵ_1 or ϵ_2 . In the air-water-ice case ϵ is close to ϵ_2 , and r is close to unity ($r \simeq 0.992$). Thus the two parts per thousand

difference provided by anisotropy in the effective value of ϵ_2 is to be compared to eight parts per thousand in $|r - 1|$: hence the one in four change in the multiplier of Δz . 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

$$I_1 = \Delta z \{ (\epsilon_o \epsilon_e - \epsilon_1^2) / (\epsilon_o - \epsilon_1) - [(\epsilon_e - \epsilon_1) / (\epsilon_o - \epsilon_1)] \epsilon - \epsilon_e \epsilon_1 / \epsilon \}. \quad (83)$$

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 Δz between the prism and the basal faces. For the basal face, $R_{pp}(\theta_B)$ with θ_B given by the second part of (81) is 8.4×10^{-7} for $\Delta z = 10$ nm, compared to 7.3×10^{-7} for isotropic ice using the ϵ_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)

$$r_p/r_s = f_p/f_s - 2iQ_1K^2I_1/[(Q_1 + Q_2)^2\epsilon_1\epsilon_2] + \dots \quad (84)$$

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, $\theta_B = \text{atn}(n_2/n_1)$. At this angle

$$\text{Im}(r_p/r_s) = [\sqrt{\epsilon_1 + \epsilon_2}/(\epsilon_2 - \epsilon_1)](\omega/c)I_1 + \dots \quad (85)$$

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 Δz 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

$$E_p = r_{pp} E_p^i + r_{sp} E_s^i \quad E_s = r_{ps} E_p^i + r_{ss} E_s^i \quad (\text{A1})$$

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

$$\delta(t) = A \sin(\Omega t) \quad (\text{A2})$$

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

$$r_{pp} + r_{sp} e^{i\delta} \quad r_{ps} + r_{ss} e^{i\delta}. \quad (\text{A3})$$

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

$$|r_{pp} + r_{sp} e^{i\delta} \pm (r_{ps} + r_{ss} e^{i\delta})|^2 \quad (\text{A4})$$

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

$$|u + e^{i\delta} v|^2 = |u|^2 + |v|^2 + 2(u_r v_r + u_i v_i) \cos \delta - 2(u_r v_i - u_i v_r) \sin \delta \quad (\text{A5})$$

where

$$u_{\pm} = r_{pp} \pm r_{ps} \quad v_{\pm} = r_{sp} \pm r_{ss} \quad (\text{A6})$$

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)

$$\begin{aligned}\cos(A \sin \Omega t) &= J_0(A) + 2 \sum_{n=1}^{\infty} J_{2n}(A) \cos(2n\Omega t) \\ \sin(A \sin \Omega t) &= 2 \sum_{n=0}^{\infty} J_{2n+1}(A) \sin((2n+1)\Omega t).\end{aligned}\tag{A7}$$

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

$$\text{DC: } |u|^2 + |v|^2 \tag{A8}$$

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

$$\Omega: -4J_1(A)(u_r v_i - u_i v_r) \quad 2\Omega: 4J_2(A)(u_r v_r + u_i v_i).\tag{A9}$$

Note that

$$u/v = [u_r v_r + u_i v_i - i(u_r v_i - u_i v_r)]/|v|^2 \tag{A10}$$

so the 2Ω and Ω signals are proportional to the real and imaginary parts of

$$(u/v)_\pm = (r_{pp} \pm r_{ps})/(r_{sp} \pm r_{ss}) = \pm(r_{pp} \pm r_{ps})/(r_{ss} \pm r_{sp}). \tag{A11}$$

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),

$$F_B = [(Q - Q_1)/(Q + Q_1)]_{\theta_B} \equiv (R - 1)/(R + 1).\tag{B1}$$

For an isotropic substrate the corresponding factor is

$$F_b = (r - 1)/(r + 1) \quad r^2 = (\epsilon_1 + \epsilon_2)/\epsilon - \epsilon_1 \epsilon_2/\epsilon_2.\tag{B2}$$

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

$$R^2 = [\epsilon - (cK/\omega)^2]/[\epsilon_1 - (cK/\omega)^2] \epsilon_1^2/\epsilon^2.\tag{B3}$$

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

$$(cK_B/\omega)^2 = \epsilon_1\epsilon_o(\epsilon_e - \epsilon_1)/(\epsilon_o\epsilon_e - \epsilon_1^2) \quad (\text{B4})$$

$$R^2 = \frac{\epsilon(\epsilon_o\epsilon_e - \epsilon_1^2) - \epsilon_1\epsilon_o(\epsilon_e - \epsilon_1)}{\epsilon^2(\epsilon_o - \epsilon_1)} = r^2 + \frac{(\epsilon - \epsilon_1)(\epsilon_1 + 2\epsilon_2)\Delta\epsilon}{3\epsilon^2(\epsilon_2 - \epsilon_1)} + O(\Delta\epsilon)^2. \quad (\text{B5})$$

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

$$(cK_B/\omega)^2 = \epsilon_1\epsilon_e(\epsilon_o - \epsilon_1)/(\epsilon_o\epsilon_e - \epsilon_1^2) \quad (\text{B6})$$

$$R^2 = \frac{\epsilon(\epsilon_o\epsilon_e - \epsilon_1^2) - \epsilon_1\epsilon_e(\epsilon_o - \epsilon_1)}{\epsilon^2(\epsilon_e - \epsilon_1)} = r^2 - \frac{(\epsilon - \epsilon_1)(2\epsilon_1 + \epsilon_2)\Delta\epsilon}{3\epsilon^2(\epsilon_2 - \epsilon_1)} + O(\Delta\epsilon)^2. \quad (\text{B7})$$

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

$$\begin{aligned} \Delta F_B &= F_B(\alpha^2 = 1) - F_B(\gamma^2 = 1) \\ &= (\epsilon - \epsilon_1)(\epsilon_1 + \epsilon_2)\Delta\epsilon/[\epsilon^2(\epsilon_2 - \epsilon_1)r(r+1)^2] + O(\Delta\epsilon)^2. \end{aligned} \quad (\text{B8})$$

Thus the fractional change in the multiplier of Δz in the reflection amplitude r_{pp} is approximately

$$\Delta F_B/F_b = (\epsilon_1 + \epsilon_2)\Delta\epsilon/[(\epsilon_2 - \epsilon_1)(\epsilon_2 - \epsilon)r] + O(\Delta\epsilon)^2. \quad (\text{B9})$$

(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 $\Delta\epsilon = \epsilon_e - \epsilon_o$ is achieved in direct proportion that the dielectric constant ϵ of the overlayer is matched to the average dielectric constant $\epsilon_2 = (2\epsilon_o + \epsilon_e)/3$ 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 θ_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 of the imaginary part is proportional to the real part (see figure 1). It follows from (79) that the Ω signal (see appendix A) which is proportional to the imaginary part of $\pm(r_{pp} \pm r_{ps})/(r_{ss} \pm r_{sp})$, 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 θ_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 Ω 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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