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OPTICAL PROPERTIES OF MEMBRANE MODELS AT ARBITRARY ANGLES OF INCIDENCE

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SUMMARY

In a previous paper several methods of calculating the reflectance of a model bimolecular lipid membrane were compared. In this paper, several other approximations are derived and assessed, and the calculations are extended to oblique incidence. Brewster angles are calculated from a particularly simple equation. For several particular models, the polarization properties are most unusual, in that the P-component has a larger reflectance than the S-component.

INTRODUCTION

Interest in the optical properties of thin films derives partly from the fact that a knowledge of the reflectivity and Brewster angle can, for model refractive index profiles, lead to estimates of film thickness.

In the case of ultra-thin films such as monolayers, black soap films and black lipid membranes, there is evidence suggestive of the presence of regions of significant thickness in which the refractive index undergoes a continuous variation[1,2]. Moreover this variation might extend into the adjacent media[1].

In a recent consideration of this problem expressions were derived for the reflectivity of a membrane having two outside regions where the refractive index varies continuously and an inner region where the refractive index is constant[1].

The treatment utilized the transition layer theory of DRUDE[3,4]. The more exact expression was shown to yield results for symmetric trilayers which were in excellent agreement with those obtained by multilayer theory. The agreement was inferior in the case of the simpler, more approximate expressions.

In the above work the treatment was limited to the case of normal incidence. In the present paper we have extended the investigation of the validity of the more exact treatment (Eqn. 26 of ref. 1) to the case of oblique incidence. We have also examined the form of the expressions when the entire membrane is regarded as constituting a single transition. In this case particularly simple, yet fairly reliable formulae, are obtained for the reflection at normal incidence and for the Brewster angle of the membrane.

* This work was completed while R. Simons was on study leave at the Weizmann Institute of Science, Rehovot, Israel.

THEORY

Approximation to DRUDE'*s theory for reflectance of a transition layer*

DRUDE's theory[3,4] derives the reflectance of a transition layer of thickness l, bounded by media of dielectric constants ε_1 and ε_2, in terms of the quantities

$$p = \int \varepsilon(z)\mathrm{d}z, \qquad q = \int \mathrm{d}z/\varepsilon(z) \tag{1}$$

where $\varepsilon(z)$ is the dielectric constant of the layer as a function of depth z (Fig. 1).

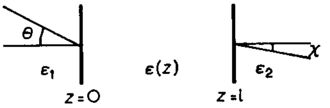


Fig. 1. A single transition layer.

SIMONS[1] derived, for a transition layer, equations for the complex reflectances and transmittances ρ_p, τ_p and ρ_s, τ_s in parallel and perpendicular polarizations (Eqns. 15 and 16 of ref. 1), under the conditions of normal incidence and very small thickness of the transition layer. If we now relax the requirement of normal incidence, we obtain from Eqns. 3 of ref. 1 the following generalizations of the previous expressions in which θ is the angle of incidence in Medium 1, χ is the angle of refraction in Medium 2, and we neglect terms of order higher than the first in l/λ.

$$\begin{aligned}
\rho_{1,2\mathrm{p}} &= \frac{\cos\theta\sqrt{\varepsilon_2} - \cos\chi\sqrt{\varepsilon_1}}{\cos\theta\sqrt{\varepsilon_2} + \cos\chi\sqrt{\varepsilon_1}}\,\mathrm{e}^{j\delta_\mathrm{p}} \\
\rho_{1,2\mathrm{s}} &= \frac{\cos\theta\sqrt{\varepsilon_1} - \cos\chi\sqrt{\varepsilon_2}}{\cos\theta\sqrt{\varepsilon_1} + \cos\chi\sqrt{\varepsilon_2}}\,\mathrm{e}^{j\delta_\mathrm{s}} \\
\tau_{1,2\mathrm{p}} &= \frac{2\sqrt{\varepsilon_1}\cos\theta}{\cos\theta\sqrt{\varepsilon_2} + \cos\chi\sqrt{\varepsilon_1}}\,\mathrm{e}^{j\delta'_\mathrm{p}} \\
\tau_{1,2\mathrm{s}} &= \frac{2\sqrt{\varepsilon_2}\cos\theta}{\cos\theta\sqrt{\varepsilon_2} + \cos\chi\sqrt{\varepsilon_2}}\,\mathrm{e}^{j\delta'_\mathrm{s}}
\end{aligned} \tag{2}$$

where

$$\begin{aligned}
\tan\delta_\mathrm{p} &= \frac{4\pi}{\lambda}\,\frac{\sqrt{\varepsilon_1}p\cos\theta\cos^2\chi - (l - q\varepsilon_2\sin^2\chi)\varepsilon_2\sqrt{\varepsilon_1}\cos\theta}{\varepsilon_2\cos^2\theta - \varepsilon_1\cos^2\chi} \\
\tan\delta_\mathrm{s} &= \frac{4\pi}{\lambda}\,\frac{\sqrt{\varepsilon_1}\cos\theta(l\varepsilon_2\sin^2\chi - p) + l\cos\theta\cos^2\chi\varepsilon_2\sqrt{\varepsilon_1}}{\varepsilon_1\cos^2\theta - \varepsilon_2\cos^2\chi} \\
\tan\delta'_\mathrm{p} &= -\frac{2\pi}{\lambda}\,\frac{(l - q\varepsilon_2\sin^2\chi)\sqrt{\varepsilon_1\varepsilon_2} + p\cos\theta\cos\chi}{\cos\theta\sqrt{\varepsilon_2} + \cos\chi\sqrt{\varepsilon_1}} \\
\tan\delta'_\mathrm{s} &= -\frac{2\pi}{\lambda}\,\frac{l\cos\theta\cos\chi\sqrt{\varepsilon_1\varepsilon_2} - l\varepsilon_2\sin^2\chi + p}{\cos\theta\sqrt{\varepsilon_1} + \cos\chi\sqrt{\varepsilon_2}}
\end{aligned} \tag{3}$$

Application of theory to thin films

Suppose that in a thin film (approx. 100 Å) the profile for the dielectric constant is symmetrically disposed about the centre of the membrane and varies from a value of ε_1 in the outside media to a value of ε_2 in the film interior (Fig. 2). The regions lying between the loci of those points where ε first attains the values ε_1 and ε_2 constitute optically inhomogeneous regions of thickness l. Let d_c denote the distance measured perpendicular to the surface of the film over which $\varepsilon = \varepsilon_2$.

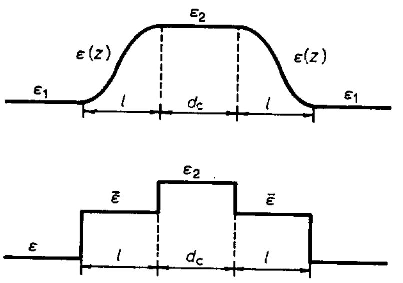


Fig. 2. Membrane model comprising two transition layers and a core.

If light is incident at an angle θ from the medium ε_1 then the angle of incidence on the transition regions will be χ from the medium ε_2 and the corresponding angle of refraction θ. In this latter case Eqns. 2 and 3 apply but it is necessary to interchange θ and χ and the suffixes 1 and 2.

Writing

$$\beta = \frac{4\pi}{\lambda} \sqrt{\varepsilon_2}\, d_c \cos\chi \tag{4}$$

the complex reflectance of the film for the components in (ρ_p) and perpendicular to (ρ_s) the plane of incidence satisfy

$$\rho_p = \rho_{1,2p} + \tau_{1,2p}\tau_{2,1p} \frac{\rho_{2,1p} e^{j\beta}}{1 - \rho_{2,1p}^2 e^{j\beta}} \tag{5a}$$

$$\rho_s = \rho_{1,2s} + \tau_{1,2s}\tau_{2,1s} \frac{\rho_{2,1s} e^{j\beta}}{1 - \rho_{2,1s}^2 e^{j\beta}} \tag{5b}$$

Eqns. 5 appear to be the most exact expressions for the complex reflectance of a thin film which may be derived using the DRUDE theory and ignoring terms of order higher than the first in l/λ.

Simplified expressions for the complex reflectance may be obtained by applying the DRUDE equations (Eqns. 2 of ref. 1) directly to the film treated as a single transition layer of length l. For this case the equations yield, since $\varepsilon_2 = \varepsilon_1$ and $\theta = \chi$

$$\rho_p = \frac{\frac{4\pi^2}{\lambda^2}[p^2\cos^4\theta - (l - q\varepsilon_1\sin^2\theta)^2\varepsilon_1^2] + j\frac{4\pi}{\lambda}[p\sqrt{\varepsilon_1}\cos^3\theta - (l - q\varepsilon_1\sin^2\theta)\varepsilon_1\sqrt{\varepsilon_1}\cos\theta]}{4\varepsilon_1\cos^2\theta + \frac{4\pi^2}{\lambda^2}[p\cos^2\theta + (l - q\varepsilon_1\sin^2\theta)\varepsilon_1]^2} \tag{6a}$$

$$\rho_s = \frac{\frac{4\pi^2}{\lambda^2}[l^2\varepsilon_1^2 \cos^4\theta - (p - l\varepsilon_1 \sin^2\theta)^2] + j\frac{4\pi}{\lambda}[l\varepsilon_1\sqrt{\varepsilon_1}\cos^3\theta - (p - l\varepsilon_1 \sin^2\theta)\sqrt{\varepsilon_1}\cos\theta]}{4\varepsilon_1\cos^2\theta + \frac{4\pi^2}{\lambda^2}[l\varepsilon_1\cos^2\theta + p - l\varepsilon_1\sin^2\theta]^2} \qquad (6b)$$

where l, p and q now refer to the entire thickness of the membrane.

Multiplying Eqns. 6 by their complex conjugates and ignoring higher order terms in l/λ leads to the following expressions for the energy reflectances

$$R_p = |\rho_p|^2 = \frac{\pi^2[p\cos^3\theta - (l - q\varepsilon_1\sin^2\theta)\varepsilon_1\cos\theta]^2}{\lambda^2\varepsilon_1\cos^4\theta} \qquad (7a)$$

$$R_s = |\rho_s|^2 = \frac{\pi^2[l\varepsilon_1\cos^3\theta - (p - l\varepsilon_1\sin^2\theta)\cos\theta]^2}{\lambda^2\varepsilon_1\cos^4\theta} \qquad (7b)$$

At normal incidence $|\rho_p|^2 = |\rho_s|^2 = |\rho|^2$ and the equations simplify to

$$|\rho|^2 = \frac{\pi^2 l^2(\bar{\varepsilon} - \varepsilon_1)^2}{\lambda^2\varepsilon_1} \qquad (8)$$

where $\bar{\varepsilon} = p/l$ is the mean value of the dielectric constant in the reflecting system.

The approximate treatment also leads to a simple expression for the angle θ_B for which ρ_p is zero. From Eqn. 7a

$$p\cos^2\theta_B - (l - q\varepsilon_1\sin^2\theta_B)\varepsilon_1 = 0$$

whence

$$\tan^2\theta_B = \frac{p - l\varepsilon_1}{l\varepsilon_1 - q\varepsilon_1^2} \qquad (9)$$

Recalling that $q = \int dz/\varepsilon = l\overline{\varepsilon^{-1}}$, Eqn. 9 yields

$$\tan^2\theta_B = \frac{\bar{\varepsilon}}{\varepsilon_1}\left[\frac{\varepsilon_1 - \varepsilon_1^2/\bar{\varepsilon}}{\varepsilon_1 - \varepsilon_1^2\overline{\varepsilon^{-1}}}\right] \qquad (10)$$

which for a uniform refracting medium reduces to the usual Brewster angle relation.

RESULTS

Numerical comparison of various formulae for case of normal incidence

In this part of the paper, we shall present numerical comparisons of the results of the various computational procedures which have been described. As a reference method, we shall use standard multilayer theory[6], with each transition layer replaced by a uniform film with dielectric constant $\bar{\varepsilon}$. The two exact formulations of the method of DRUDE (Eqns. 3 and 26 of ref. 1) and the multilayer method were programmed in FORTRAN for a CDC 3200 computer at National Standards Laboratory using complex arithmetic routines where necessary, and in some cases using double precision arithmetic to check on rounding errors. Independent calculations were made at the Weizmann Institute using multilayer theory, Eqn. 26 of ref. 1, the SMART AND SENIOR[5] formula (ref. 1, p. 218) and Eqn. 8 of this paper.

TABLE Ia

NORMAL REFLECTANCES OF A MODEL MEMBRANE BY VARIOUS METHODS

Calculations were performed for $n_1 = \sqrt{\varepsilon_1} = 1.33$, $\bar{n} = \sqrt{\bar{\varepsilon}} = 1.51$, $l = 20$ Å, $d_c = 100$ Å, $\lambda = 6328$ Å. R_0 is found from multilayer theory. R_1 is from Eqn. 26 of ref. 1 (the DRUDE formula for each transition layer combined with interference across the core). R_2 is from Eqn. 8 of this paper (the DRUDE formula applied to the entire membrane, to order l/λ). R_3 is from Eqn. 3 of ref. 1. (This is the exact form from which Eqn. 8 is derived by approximation.) R_{ss} is from SMART AND SENIOR (as extended in ref. 1).

n_2	R_0	R_1	R_2	R_3	R_{ss}
1.00	$0.445 \cdot 10^{-3}$	$0.444 \cdot 10^{-3}$	$0.444 \cdot 10^{-3}$	$0.432 \cdot 10^{-3}$	$0.568 \cdot 10^{-3}$
1.20	$0.221 \cdot 10^{-4}$	$0.220 \cdot 10^{-4}$	$0.216 \cdot 10^{-4}$	$0.209 \cdot 10^{-4}$	$0.321 \cdot 10^{-4}$
1.26*	$0.624 \cdot 10^{-6}$	$0.620 \cdot 10^{-6}$	$0.724 \cdot 10^{-6}$	$0.749 \cdot 10^{-6}$	$0.247 \cdot 10^{-7}$
1.40	$0.214 \cdot 10^{-3}$	$0.211 \cdot 10^{-3}$	$0.218 \cdot 10^{-3}$	$0.210 \cdot 10^{-3}$	$0.214 \cdot 10^{-3}$
1.60	$0.136 \cdot 10^{-2}$	$0.136 \cdot 10^{-2}$	$0.138 \cdot 10^{-2}$	$0.135 \cdot 10^{-2}$	$0.137 \cdot 10^{-2}$
1.80	$0.384 \cdot 10^{-2}$	$0.384 \cdot 10^{-2}$	$0.391 \cdot 10^{-2}$	$0.369 \cdot 10^{-3}$	$0.379 \cdot 10^{-2}$
2.00	$0.806 \cdot 10^{-2}$	$0.807 \cdot 10^{-2}$	$0.826 \cdot 10^{-2}$	$0.768 \cdot 10^{-2}$	$0.775 \cdot 10^{-2}$

* Predicted $R = 0$ (Eqn. 11).

TABLE Ib

NORMAL REFLECTANCES OF A MODEL MEMBRANE BY VARIOUS METHODS

Calculations were performed for $n_1 = \sqrt{\varepsilon_1} = 1.33$, $\bar{n} = \sqrt{\bar{\varepsilon}} = 1.51$, $l = 10$ Å, $d_c = 30$ Å, $\lambda = 6328$ Å. For the meaning of the symbols R_0, R_1, R_2, R_3, R_{ss}, see Table Ia.

n_2	R_0	R_1	R_2	R_3	R_{ss}
1.00	$0.230 \cdot 10^{-4}$	$0.230 \cdot 10^{-4}$	$0.230 \cdot 10^{-4}$	$0.229 \cdot 10^{-4}$	$0.355 \cdot 10^{-4}$
1.20*	$0.166 \cdot 10^{-7}$	$0.163 \cdot 10^{-7}$	$0.178 \cdot 10^{-7}$	$0.177 \cdot 10^{-7}$	$0.883 \cdot 10^{-7}$
1.40	$0.354 \cdot 10^{-4}$	$0.353 \cdot 10^{-4}$	$0.355 \cdot 10^{-4}$	$0.353 \cdot 10^{-5}$	$0.348 \cdot 10^{-4}$
1.60	$0.160 \cdot 10^{-3}$	$0.160 \cdot 10^{-3}$	$0.161 \cdot 10^{-3}$	$0.160 \cdot 10^{-3}$	$0.160 \cdot 10^{-3}$
1.80	$0.411 \cdot 10^{-3}$	$0.411 \cdot 10^{-3}$	$0.412 \cdot 10^{-3}$	$0.409 \cdot 10^{-3}$	$0.396 \cdot 10^{-3}$
2.00	$0.827 \cdot 10^{-3}$	$0.827 \cdot 10^{-3}$	$0.829 \cdot 10^{-3}$	$0.822 \cdot 10^{-3}$	$0.768 \cdot 10^{-3}$

* Predicted $R = 0$ (Eqn. 11).

TABLE Ic

NORMAL REFLECTANCES OF A MODEL MEMBRANE BY VARIOUS METHODS

Calculations were performed for $n_1 = \sqrt{\varepsilon_1} = 1.00$, $\bar{n} = \sqrt{\bar{\varepsilon}} = 1.51$, $l = 50$ Å, $d_c = 100$ Å, $\lambda = 6328$ Å. For the meaning of the symbols R_0, R_1, R_2, R_3, R_{ss}, see Table Ia.

n_2	R_0	R_1	R_2	R_3	R_{ss}
1.00*	$0.389 \cdot 10^{-2}$	$0.385 \cdot 10^{-2}$	$0.404 \cdot 10^{-2}$	$0.378 \cdot 10^{-2}$	$0.325 \cdot 10^{-2}$
1.20	$0.702 \cdot 10^{-2}$	$0.652 \cdot 10^{-2}$	$0.729 \cdot 10^{-2}$	$0.675 \cdot 10^{-2}$	$0.684 \cdot 10^{-2}$
1.40	$0.119 \cdot 10^{-1}$	$0.117 \cdot 10^{-1}$	$0.124 \cdot 10^{-1}$	$0.113 \cdot 10^{-2}$	$0.121 \cdot 10^{-1}$
1.60	$0.189 \cdot 10^{-1}$	$0.189 \cdot 10^{-1}$	$0.199 \cdot 10^{-1}$	$0.178 \cdot 10^{-1}$	$0.194 \cdot 10^{-1}$
1.80	$0.288 \cdot 10^{-1}$	$0.288 \cdot 10^{-1}$	$0.305 \cdot 10^{-1}$	$0.268 \cdot 10^{-2}$	$0.290 \cdot 10^{-1}$
2.00	$0.418 \cdot 10^{-1}$	$0.418 \cdot 10^{-1}$	$0.451 \cdot 10^{-1}$	$0.386 \cdot 10^{-2}$	$0.409 \cdot 10^{-1}$

* No predicted minimum for R (Eqn. 11).

Tables Ia, Ib, Ic show the results of these calculations for three hypothetical membranes. In each case a range of dielectric constants was used for the central layer, and the calculations were restricted to the case of normal incidence. The agreement between the multilayer theory and the more conservative DRUDE method (Eqn. 26 of ref. 1) is excellent. The application of the method of DRUDE to the entire membrane, considered as one transition layer (Eqn. 3 of ref. 1), is less successful, but still agrees to within 5 % in most cases with the multilayer theory.

Tables Ia, Ib and Ic also show the results from Eqn. 8, which is an approximation to Eqn. 3 of ref. 1, and from SIMONS' generalization (ref. 1, p. 218) of Eqn. 11 of SMART AND SENIOR[5].

It will be noticed that in each of Tables Ia and Ib there is one entry for which R is almost zero. An explanation of this feature was obtained by using a first order expansion in the phase-thickness $2\pi nd/\lambda$ of each layer in the multilayer calculations. In Appendix 1 it is shown that the reflectance should be zero when

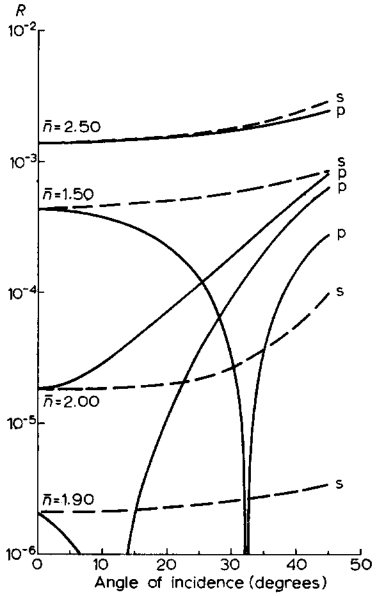
$$\bar{n}^2 = n_1^2 + \frac{d_c}{2l}(n_1^2 - n_2^2) \tag{11}$$

The entries in Tables Ia and Ib for which R is nearly zero satisfy this equation. For Table Ic, the equation has no real solution for n_2, and this accounts for the absence of a minimum value in that Table. Eqn. 11 corresponds exactly to the condition $\bar{n} = \sqrt{\varepsilon_1}$ in SIMONS' generalization of the formula of SMART AND SENIOR[5], from which it follows that this condition cannot arise when $\varepsilon_1 = 1$ unless both $\bar{\varepsilon}$ and ε_2 are also equal to 1.

Behaviour at oblique incidence: Brewster's angle

The calculations by the DRUDE method and by multilayer theory were extended to the case of oblique incidence. In general the membranes show a normal variation of R_s and R_p with angle of incidence, including an angle at which $R_p = 0$ (Brewster angle). Fig. 3 shows the behaviour of the system corresponding to the first entry in Table Ia, but with various values of $\bar{n}$, the mean refractive index of the transition layers. The values plotted were calculated from multilayer theory. Because of the enormous range of reflectances which occur, a logarithmic scale is used for R. (At any angle of incidence beyond 48.6°, the Snell law predicts a complex angle of refraction in the core. Total internal reflection would then occur, were it not for the presence of the second transition layer, which provides coupling to the outer medium. To avoid reprogramming to deal with this situation, we terminated the calculations at 45°.) Brewster angles are illustrated for $\bar{n} = 1.50$ and 1.90. Beyond the value $\bar{n} = 1.92$ at which $R = 0$ according to Eqn. 11, a striking change in behaviour occurs. The perpendicularly polarized component R_s becomes relatively independent of the angle of incidence, whereas the parallel polarized component R_p rises rapidly, far exceeding R_s. This unusual behaviour reaches its peak at $\bar{n} = 2.00$, and then the two curves draw together. For $\bar{n}$ greater than 2.50, R_s again exceeds R_p, but there is no sign of a Brewster angle. This behaviour is particularly surprising because of the very small thicknesses of the individual films. It is well known that, for reflection at any boundary, R_s must exceed or equal R_p. It is unexpected that the small phase differences between the waves reflected from each of the boundaries in the multilayer should be sufficiently different in the two polarizations to outweigh the inherent dominance of R_s over R_p.

Somewhat similar behaviour occurs in the system shown in Fig. 4, which corresponds to the first entry in Table Ib. The critical value of $\bar{n}$ is here 1.71 ($R = 0$). The curves labelled $\bar{n} = 2.20$ in Fig. 4 are particularly interesting. For P-polarization, R is practically independent of the angle of incidence.



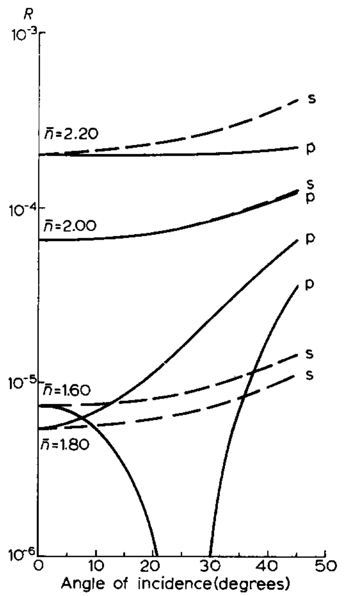


Fig. 3. Reflectance of parallel (P) and perpendicularly (S) polarized components as a function of angle of incidence, for a series of multilayers based on the first entry in Table Ia, but with various values of $\bar{n}$. ($n_1 = 1.33$, $n_2 = 1.00$, $l = 20$ Å, $d_c = 100$ Å, $\lambda = 6328$ Å).

Fig. 4. Reflectance of parallel (P) and perpendicularly (S) polarized components as a function of angle of incidence, for a series of multilayers based on the first entry in Table Ib, but with various values of $\bar{n}$. ($n_1 = 1.33$, $n_2 = 1.00$, $l = 10$ Å, $d_c = 30$ Å, $\lambda = 6328$ Å).

This intriguing behaviour has not been explored more extensively because of its marginal relevance to the present paper. It would be interesting to obtain experimental confirmation of the predicted behaviour, but the present situation of the authors makes this impracticable. Because of the inconvenient values of refractive index which are required, and the very small thicknesses, it may be worth scaling the whole structure up to microwave wavelengths. Alternatively, a systematic search would probably discover other combinations of films with similar behaviour, and possibly more convenient parameters.

Comparison of various methods of calculation for oblique incidence

An extensive series of calculations of reflectance as a function of angle of incidence was made, by each of the methods described earlier, for a representative sample of the systems tabulated in Tables Ia–Ic. In all cases the relative accuracies of the methods were the same for oblique incidence as for normal incidence. To illustrate this, we show in Tables IIa–IIc the results corresponding to the entries with $n_2 = 1.60$

TABLE IIa

REFLECTANCES AT OBLIQUE INCIDENCE BY VARIOUS METHODS

Calculations were performed for $n_1 = \sqrt{\varepsilon_1} = 1.33$, $\bar{n} = \sqrt{\bar{\varepsilon}} = 1.51$, $n_2 = 1.60$, $l = 20$ Å, $d_c = 100$ Å, $\lambda = 6328$ Å. R_1 is from Eqn. 26 of ref. 1 (*cf.* Table Ia). R_2 is from Eqns. 7a and b of this paper. R_3 is from Eqn. 3 of ref. 1 (R_3 is therefore an approximation to R_2. *cf.* Table Ia).

θ	R_0	R_1	R_2	R_3
S-polarization				
0°	$0.136 \cdot 10^{-2}$	$0.136 \cdot 10^{-2}$	$0.138 \cdot 10^{-2}$	$0.132 \cdot 10^{-2}$
15°	$0.146 \cdot 10^{-2}$	$0.146 \cdot 10^{-2}$	$0.148 \cdot 10^{-2}$	$0.141 \cdot 10^{-2}$
30°	$0.182 \cdot 10^{-2}$	$0.182 \cdot 10^{-2}$	$0.184 \cdot 10^{-2}$	$0.177 \cdot 10^{-2}$
45°	$0.273 \cdot 10^{-2}$	$0.273 \cdot 10^{-2}$	$0.276 \cdot 10^{-2}$	$0.267 \cdot 10^{-2}$
P-polarization				
0°	$0.136 \cdot 10^{-2}$	$0.136 \cdot 10^{-2}$	$0.138 \cdot 10^{-2}$	$0.132 \cdot 10^{-2}$
15°	$0.114 \cdot 10^{-2}$	$0.114 \cdot 10^{-2}$	$0.116 \cdot 10^{-2}$	$0.111 \cdot 10^{-2}$
30°	$0.597 \cdot 10^{-3}$	$0.597 \cdot 10^{-3}$	$0.604 \cdot 10^{-3}$	$0.581 \cdot 10^{-3}$
45°	$0.582 \cdot 10^{-4}$	$0.582 \cdot 10^{-4}$	$0.587 \cdot 10^{-4}$	$0.570 \cdot 10^{-4}$

TABLE IIb

REFLECTANCES AT OBLIQUE INCIDENCE BY VARIOUS METHODS

Calculations were performed for $n_1 = \sqrt{\varepsilon_1} = 1.33$, $\bar{n} = \sqrt{\bar{\varepsilon}} = 1.51$, $n_2 = \sqrt{\varepsilon_2} = 1.60$, $l = 10$ Å, $d_c = 30$ Å, $\lambda = 6328$ Å. For the meaning of the symbols R_0, R_1, R_2, R_3, see Table IIa.

θ	R_0	R_1	R_2	R_3
S-polarization				
0°	$0.160 \cdot 10^{-3}$	$0.160 \cdot 10^{-3}$	$0.161 \cdot 10^{-3}$	$0.160 \cdot 10^{-3}$
15°	$0.172 \cdot 10^{-3}$	$0.172 \cdot 10^{-3}$	$0.172 \cdot 10^{-3}$	$0.171 \cdot 10^{-3}$
30°	$0.214 \cdot 10^{-3}$	$0.214 \cdot 10^{-3}$	$0.214 \cdot 10^{-3}$	$0.213 \cdot 10^{-3}$
45°	$0.321 \cdot 10^{-3}$	$0.321 \cdot 10^{-3}$	$0.321 \cdot 10^{-3}$	$0.320 \cdot 10^{-3}$
P-polarization				
0°	$0.160 \cdot 10^{-3}$	$0.160 \cdot 10^{-3}$	$0.161 \cdot 10^{-3}$	$0.160 \cdot 10^{-3}$
15°	$0.135 \cdot 10^{-3}$	$0.135 \cdot 10^{-3}$	$0.135 \cdot 10^{-3}$	$0.134 \cdot 10^{-3}$
30°	$0.697 \cdot 10^{-4}$	$0.697 \cdot 10^{-4}$	$0.698 \cdot 10^{-4}$	$0.695 \cdot 10^{-4}$
45°	$0.645 \cdot 10^{-5}$	$0.645 \cdot 10^{-5}$	$0.646 \cdot 10^{-5}$	$0.643 \cdot 10^{-5}$

TABLE IIc

REFLECTANCES AT OBLIQUE INCIDENCE BY VARIOUS METHODS

Calculations were performed for $n_1 = \sqrt{\varepsilon_1} = 1.00$, $\bar{n} = \sqrt{\bar{\varepsilon}} = 1.51$, $n_2 = \sqrt{\varepsilon_2} = 1.60$, $l = 50$ Å, $d_c = 100$ Å, $\lambda = 6328$ Å. For the meaning of the symbols R_0, R_1, R_2, R_3, see Table IIa.

θ	R_0	R_1	R_2	R_3
S-polarization				
0°	$0.195 \cdot 10^{-1}$	$0.194 \cdot 10^{-1}$	$0.199 \cdot 10^{-1}$	$0.184 \cdot 10^{-1}$
15°	$0.203 \cdot 10^{-1}$	$0.201 \cdot 10^{-1}$	$0.213 \cdot 10^{-1}$	$0.191 \cdot 10^{-1}$
30°	$0.252 \cdot 10^{-1}$	$0.250 \cdot 10^{-1}$	$0.265 \cdot 10^{-1}$	$0.238 \cdot 10^{-1}$
45°	$0.374 \cdot 10^{-1}$	$0.372 \cdot 10^{-1}$	$0.398 \cdot 10^{-1}$	$0.356 \cdot 10^{-1}$
P-polarization				
0°	$0.195 \cdot 10^{-1}$	$0.194 \cdot 10^{-1}$	$0.199 \cdot 10^{-1}$	$0.184 \cdot 10^{-1}$
15°	$0.167 \cdot 10^{-1}$	$0.166 \cdot 10^{-1}$	$0.175 \cdot 10^{-1}$	$0.157 \cdot 10^{-1}$
30°	$0.107 \cdot 10^{-1}$	$0.106 \cdot 10^{-1}$	$0.111 \cdot 10^{-1}$	$0.101 \cdot 10^{-1}$
45°	$0.334 \cdot 10^{-2}$	$0.333 \cdot 10^{-2}$	$0.343 \cdot 10^{-2}$	$0.318 \cdot 10^{-2}$

in each of Tables Ia–Ic. The results for normal incidence are repeated from Table I for ease of reference.

Calculation of Brewster angle for some typical membrane models

Because of the usefulness of the Brewster angle in assessing various models, Eqn. 10 was applied to several proposed membrane structures. For comparison, the results of multilayer theory were interpolated to obtain Brewster angles. The results

TABLE IIIa

BREWSTER ANGLES CALCULATED FROM Eqn. 10 AND MULTILAYER THEORY

Calculated for $n_1 = \sqrt{\varepsilon_1} = 1.00$, $n_2 = \sqrt{\varepsilon_2} = 1.51$, $l = 10$ Å, $d_c = 30$ Å, $\lambda = 6328$ Å. θ_B is from Eqn. 10. θ_0 is from multilayer theory by interpolation to $\pm$ 0.1 degree.

$\bar{n} = \sqrt{\bar{\varepsilon}}$:	*1.00*	*1.20*	*1.40*	*1.60*	*1.80*	*2.00*	*2.20*	*2.40*	*2.60*
θ_B	56.48	55.11	55.78	57.14	58.74	60.37	61.95	63.44	64.84
θ_0	56.4				58.8				64.8

TABLE IIIb

BREWSTER ANGLES CALCULATED FROM Eqn. 10 AND MULTILAYER THEORY

Calculated for $n_1 = \sqrt{\varepsilon_1} = 1.00$, $n_2 = \sqrt{\varepsilon_2} = 1.51$, $l = 20$ Å, $d_c = 100$ Å, $\lambda = 6328$ Å. θ_B and θ_0 are defined in Table IIIa.

$\bar{n} = \sqrt{\bar{\varepsilon}}$:	*1.00*	*1.20*	*1.40*	*1.60*	*1.80*	*2.00*	*2.20*	*2.40*	*2.60*
θ_B	56.49	55.58	56.00	56.96	58.18	59.49	60.81	62.11	63.36
θ_0	56.5				58.2				63.3

TABLE IIIc

BREWSTER ANGLES CALCULATED FROM Eqn. 10 AND MULTILAYER THEORY

Calculated for $n_1 = \sqrt{\varepsilon_1} = 1.33$, $n_2 = \sqrt{\varepsilon_2} = 1.00$, $l = 10$ Å, $d_c = 30$ Å, $\lambda = 6328$ Å. θ_B and θ_0 are defined in Table IIIa.

$\bar{n} = \sqrt{\bar{\varepsilon}}$:	*1.00*	*1.20*	*1.40*	*1.60*	*1.70*
θ_B	36.94	37.91	35.67	26.22	9.12
θ_0	37.2		37.2	25.8	9.0

TABLE IIId

BREWSTER ANGLES CALCULATED FROM Eqn. 10 AND MULTILAYER THEORY

Calculated for $n_1 = \sqrt{\varepsilon_1} = 1.33$, $n_2 = \sqrt{\varepsilon_2} = 1.00$, $l = 20$ Å, $d_c = 100$ Å, $\lambda = 6328$ Å. θ_B and θ_0 are defined in Table IIIa.

$\bar{n} = \sqrt{\bar{\varepsilon}}$:	*1.00*	*1.20*	*1.40*	*1.60*	*1.80*	*1.90*
θ_B	36.94	37.57	36.22	32.19	22.63	10.22
θ_0	36.9			32.2	22.8	11.0

are given in Tables IIIa–IIId. In the majority of cases the agreement is within the interval of interpolation. The worst cases, which still agree to within 0.8 degree, occur when $\bar{n}$ is large compared with n_2. This is just the condition for which the DRUDE method might be expected to be inaccurate, because it assumes smooth variations in refractive index. We conclude that Eqn. 10 is a useful approximate expression for the Brewster angle.

DISCUSSION

The present work has confirmed the validity of the DRUDE theory for light at oblique incidence on a membrane separating identical media.

In the case of black lipid films the optical properties of primary interest are the reflectivity at near normal incidence and the Brewster angle, these being used to evaluate the membrane thickness for an assumed profile for the dielectric constant. Except for the case where the dielectric constant is assumed to be uniform within the membrane, such calculations are complicated, recourse to numerical methods generally being required[2].

In the present treatment, Eqns. 8 and 10, though approximate, have been shown to provide reasonably reliable predictions for the reflectivity and Brewster angle which possess the advantage of simplicity. These show the normal reflectance as depending on the thickness of the transition region and the mean dielectric constant therein and the Brewster angle as being determined by both the mean and inverse mean dielectric constants in the transition region. Their simplicity renders them useful for obtaining a fair idea, by hand calculations, of the dependence of membrane thickness on the assumed model for the membrane.

We wish to comment on ref. 1. In the first of Eqns. 2, the factor $\sqrt{\varepsilon_1\varepsilon_2}$ should read $\sqrt{\varepsilon_2}$. Also the first entry in Table III deserves comment. The extremely small values of R_1 and R_2 ($0.282 \cdot 10^{-14}$) arise from the failure of Assumption 2 since in this case $\varepsilon_1 = \varepsilon_2$ and $\tan \delta_{12}$ (Eqns. 17, 18, 29) is infinite, rather than small. R_3, which does not depend on Assumption 2, is in error; it should be $0.385 \cdot 10^{-2}$.

APPENDIX I

The matrix formulation of multilayer theory[6] describes each film by a matrix

$$Q_i = \begin{Vmatrix} \cos\theta_i & j\sin\theta_i/y_i \\ jy_i\sin\theta_i & \cos\theta_i \end{Vmatrix}$$

where $\theta_i = 2\pi n_i d_i \cos\Phi_i/\lambda$, Φ_i = angle of refraction, $j = \sqrt{-1}$ and $y_i = n_i/\cos\Phi_i$ for P-polarization or $y_i = n_i\cos\Phi_i$ for S-polarization.

For very thin films, the approximations $\cos\theta_i = 1$ and $\sin\theta_i = \theta_i$ are reasonably accurate, and Q_i reduces to

$$Q_i \simeq \begin{Vmatrix} 1 & j\theta_i/y_i \\ jy_i\theta_i & 1 \end{Vmatrix}$$

The matrix corresponding to three films and the medium beyond the multilayer is described by the column matrix

$$\begin{Vmatrix}\alpha\\ \beta\end{Vmatrix} = Q_3Q_2Q_1\begin{Vmatrix}1\\ y_0\end{Vmatrix}$$

where $y_0 = n_0/\cos\Phi_0$ or $n_0\cos\Phi_0$ according to the polarization. The complex coefficient of reflection in the medium of incidence (y_4) is

$$\rho = \frac{y_4\alpha - \beta}{y_4\alpha + \beta}$$

Carrying through the matrix operations, using the approximation for Q_i, for the special case $y_3 = y_1$ (symmetrical system), we obtain

$$R = \rho^*\rho = \frac{[2(y_0^2\theta_1/y_1 - y_1\theta_1) + (y_0^2\theta_2/y_2 - y_2\theta_2)]^2}{4y_0^2 + [(2y_0^2\theta_1/y_1 + y_1\theta_1) + (y_0^2\theta_2/y_2 + y_2\theta_2)]^2}$$

The numerator of this expression vanishes when

$$\frac{\theta_2}{\theta_1} = 2\frac{y_2}{y_1}\frac{(y_0^2 - y_1^2)}{(y_2^2 - y_0^2)}$$

For normal incidence (all $\Phi_i = 0$) this reduces to

$$\frac{d_2}{d_1} = 2\frac{(n_0^2 - n_1^2)}{(n_2^2 - n_0^2)}$$

or

$$n_1^2 = n_0^2 + \frac{d_2}{2d_c}(n_0^2 - n_2^2)$$

To convert this expression to the notation used in the body of the paper, we substitute as follows: $\bar{n}$ and l for n_1 and d_1 (outer layer), n_1 for n_0 (medium), n_2 and d_c for n_2 and d_2 (central layer). Thus $\bar{n}^2 = n_1^2 + d_c\,(n_1^2 - n_2^2)/2l$, which is Eqn. 11.

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