Optical reflectivity of thin rough films: Application to ellipsometric measurements on liquid films

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Equations to calculate the optical properties of a flat but rough interface are given. This interface is supposed to be much thinner than the wavelength of the light, and made of $N-1$ layers of refractive indices n_m (for layer m) between two media of refractive indices n_0 and n_N. The interfaces separating two layers are rough. The roughness is supposed to have weak slopes ($|\nabla Z|(z) \ll 1$). These equations can be solved very simply for any N values. The explicit solution for $N=2$ (one rough layer) is given for the incidence angle equal to the Brewster angle in order to apply the result to ellipsometric measurements, specially on liquid interfaces whose roughness originates from thermal fluctuations and is depending on a small number of parameters.

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I. INTRODUCTION

Ellipsometry is a very sensitive optical technique to characterize flat interfaces [1]. The ellipsometer allows the determination of the change of the state of polarization of a beam reflected from the studied interface. From this change, one deduces the ratio of the reflectivity r_p of the interface for the waves of polarization p, i.e., a polarization in the plane of incidence, over the reflectivity r_s for the waves of polarization s, i.e., a polarization perpendicular to the plane of incidence.

For Fresnel interfaces (i.e., ideal flat interfaces for which the refractive index changes abruptly from that of the incidence medium, n_0, to that of the second medium, n_N at $z=0$) this ratio, r_p/r_s, is a real number which vanishes at the Brewster incidence θ_B (given by $\tan\theta_B = n_N/n_0$). However, for real interfaces this ratio is a complex number ($r_p/r_s, = \rho + i\bar{\rho}$) because the phase change at the reflection is different for the s and p polarizations. Only the real part of the signal vanishes at the Brewster angle for real interfaces between two nonabsorbing media.

In the following the interfaces are supposed much thinner than the wavelength of the light. Consequently ρ, the real part of r_p/r_s, is very close to the value given by Fresnel's equations. To a good approximation the imaginary part, $\bar{\rho}$ (called ellipticity) is a number independent of the incidence angle in the vicinity of the Brewster angle where it is measurable. Consequently, for interfaces much thinner than the wavelength of the light, the ellipsometry gives only one item of information, the ellipticity $\bar{\rho}$ which measures the deviation of the real interface from a Fresnel interface. It is so sensitive that it gives information on interfaces as thin as 1 Å.

However, the interpretation of the ellipsometric signal needs models. For interfaces much thinner than the wavelength of the light ($\ell \ll \lambda$) the most currently used model (and historically the first which was proposed) is the Drude's model that attributes the ellipsometric signal to a flat layer of thickness ℓ at the interface where the refractive index $n(z)$ is different from those of the two media on the two sides of the interface, n_0 and n_N [2]. The ellipticity is given by

$$\bar{\rho} = \frac{\pi}{\lambda}\frac{\sqrt{n_0^2+n_N^2}}{n_0^2-n_N^2}\int_{-\infty}^{+\infty}\frac{n_0^2-n(z)^2}{n(z)^2}dz.$$

Many authors deduce the interfacial thickness from a measurement of $\bar{\rho}$ and this equation. However, this needs the knowledge of the refractive index through the interfacial film. In many cases $n(z)$ is taken as a constant and estimated. This is a good approximation for thick wetting films since their refractive indices are generally close to that of the bulk wetting liquid [7,8]. In some cases, it can be given by theory. For instance, it results from a continuous variation of the density or the composition for liquid-vapor or liquid-liquid interfaces. Close to the liquid-gas or liquid-liquid critical point the profile is well described by a van der Waals–Landau theory [3–6]. In these examples the interfacial layer is homogenous. However, the Drude's equation applies also to interfacial layers constituted by an agglomerate of domains of different refractive indices much smaller than the wavelength of the light. In this case, the refractive index $n(z)$ of the interfacial layer is an effective one deduced from the composition of the film and the refractive indices of the different domains [9]. Moreover, an optical anisotropy of the interfacial film can be taken into account in this model [1,10–12].

A second and more recent model attributes the ellipsometric signal to the interfacial roughness [Fig. 2(a)]. Crossing the interface $Z[x,y]$, the refractive index changes abruptly from the refractive index of the incidence medium, n_0, to that of the second medium, n_N. When the mean slope of the interface is very large, $\overline{|\nabla Z(x,y)|} \gg 1$ the ellipticity can be calculated with the Drude's model in which $n(z)$ is an effective refractive index [13]. When the interfacial slope is small $|\nabla Z(z)| \ll 1$ the Drude's model does not apply since the ellipticity becomes a function of the scale of the roughness and necessitates a second model [13–16]. This model was first applied to the calculation of the ellipticity induced by thermally excited waves on liquid-liquid [14–18] and liquid-liquid interfaces covered with a surfactant film lowering the interfacial tension. The model allows the determination of the cutoff at high frequency for the capillary waves which is a function of the bending elasticity of the surfactant film [12,18,19].

These two models are two limits of a more general model describing the interface as a rough film with a constant thickness [12,18–20] [Fig. 2(b)]. The two faces of the film have

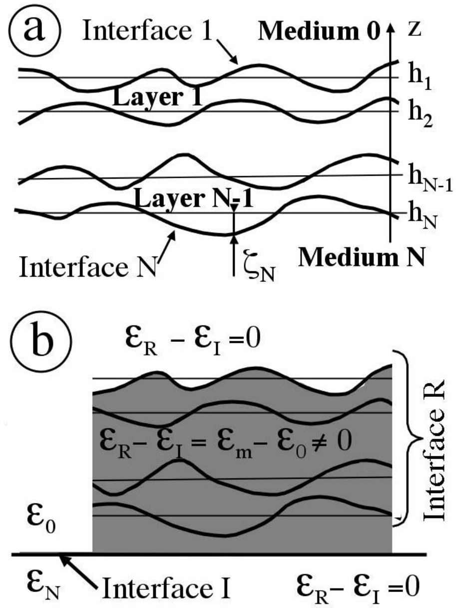

FIG. 1. (a) Model of interface made of $N-1$ rough layers separating the incidence medium of dielectric constant ε_0 from a medium of dielectric constant ε_N. This interface is called real interface in the following. (b) Ideal interface I (Fresnel interface between media of dielectric constant ε_0 and ε_N) and region of the space (grey zone) where the dipolar moments that intervene in the calculation of the reflected light are localized.

the same roughness. The ellipticity is the sum of the ellipticity due to the thickness of the layer and that due to the roughness [21],

$$\bar{\rho} = \bar{\rho}^{\ell} + \bar{\rho}^{R}.$$

One can find thin interfaces not described by the above models. This happens for wetting films on a liquid when the interfacial tension between the liquid of the film and the liquid beneath is very low while the interfacial tension between the liquid film and the vapor is large. The amplitude of the thermal fluctuations of one face of the film are large and comparable to the film thickness while the second face of the film is flat since its surface tension is large [Fig. 2(c)]. Such films are obtained when a surfactant film covers the liquid-film interface [22,23] or when the liquid-film interface is close to a critical point [24,25]. Up to now, the film thickness has been deduced from ellipsometric measurements supposing that the Drude's equation gives the mean value of the film thickness without proof of the validity of this assumption. Bedeaux and Vlieger have given an extensive study of the optical properties of thin film [26]. However, their approach is more adapted to specialists of ellipsometry on solid surfaces than to specialists of physical chemistry working on liquid interfaces.

In the following we give a method to calculate the ellipsometric signal for a general model, a thin multilayered rough film [Fig. 1(a)] constituted by $N-1$ films separated by N rough interfaces. The roughness considered has small amplitude such that it can be considered as a superposition of independent modes of wave vector $\mathbf{q}$ and amplitude $\zeta_{m,q}$ (for the interface m) with $q|\zeta_{mq}| \ll 1$. In previous calculations, it was shown that modes with wavelengths larger than the wavelength of the light, λ ($q\lambda > 1$), do not contribute to the imaginary part of the ellipsometric signal [13]. Consequently, in the following calculation, one takes into account only modes with large wave vectors q ($q\lambda > 1$). The decomposition in modes is well adapted to liquid surfaces since the mean square amplitude of each mode of the roughness of these surfaces due to thermal fluctuations can be deduced from the hydrodynamics and the thermodynamics with a small number of parameter (for instance surface tension, and surface rigidity).

In a second part, one solves the case $N=2$ and gives explicitly the equation for this case: a rough film of dielectric constant ε_1 between two media of dielectric constants ε_0 and ε_2. Then one applies the result to the analysis of ellipsometric signals obtained from wetting films on liquid and surfactant films at liquid interfaces.

In our general model [Fig. 1(a)], the interface is made of $N-1$ thin and rough layers between the semi-infinite incident medium 0 (dielectric constant ε_0) and the semi-infinite medium N (dielectric constant ε_N). The layer m has a dielectric constant ε_m and stretches from the interface m to the interface $m+1$. These dielectric constants are those at the frequency of the light, i.e., equal to the square of the refractive index. The coordinates of the interface m are given by

$$Z_m(\mathbf{r}) = h_m + \zeta_m(\mathbf{r}), \tag{1}$$

where h_m is the mean z coordinate of the interface m and $\zeta_m(\mathbf{r})$ its roughness whose mean value is zero. $\mathbf{r}$ is a vector of the plane x,y. This roughness can be written as a sum of modes,

$$\zeta_m(\mathbf{r}) = \sum_{|q|>1/\lambda} \zeta_{m,q} \exp(i\mathbf{q} \cdot \mathbf{r}), \tag{2}$$

with $q|\zeta_{mq}| \ll 1$ and one supposes that two modes of wave vectors $\mathbf{q_1}$ and $\mathbf{q_2}$ are not correlated if $\mathbf{q_1} \neq \mathbf{q_2}$. Moreover, $\zeta_{m-q} = (\zeta_{m,q})^*$ since $\zeta_m(\mathbf{r})$ is real.

The method to calculate the field reflected by the interface was developed by Croce and co-workers [14,27–30]. The distribution of matter forming the interface is called R for real. A simpler distribution I (for ideal) is substituted for R. I is such that the reflectivity of the interface in this new ideal distribution is easy to calculate. Moreover, the distribution I is chosen such that the difference between the two distributions I and R is limited to a small region of the space. In our case I is a Fresnel interface below the real one but close to and parallel to this one [Fig. 1(b)]. The electromagnetic field reflected in the real case R is obtained by adding to the electromagnetic field reflected in the ideal case I, the electromagnetic field radiated by dipolar sources located in the small region of the space where the distributions of matter I and R are different.

The ellipticity can be written $\mathrm{Im}[(r_p^F + \delta r_p)/(r_s^F + \delta r_s)]$, where r^F is the reflectivity of the Fresnel interface and δr, the correction corresponding to the light radiated by the dipolar sources. The indices s and p indicate the polarization (respectively, perpendicular and in the plane of incidence). For thin interfaces $r_s^F \gg \delta r_s$. Moreover, at the Brewster angle, $r_p^F=0$ and consequently $\bar{\rho} \approx \mathrm{Im}(\delta r_p / r_s^F)$.

The dipolar sources in a volume dv around the point P are given by the equation

$$\frac{(\varepsilon_R - \varepsilon_I)}{4\pi} \boldsymbol{\mathcal{E}}_R(P) dv, \tag{3}$$

where ε_R and ε_I are the dielectric constant at the point P in the cases R and I, respectively, $\boldsymbol{\mathcal{E}}_R(P)$ is the electromagnetic field at the same point in the real case R.

The dipolar sources [Eq. (3)] vanish except in a thin and flat region of the space whose thickness is $\ell \ll \lambda$. One can imagine that this region of the space is constituted of a collection of patches whose dimensions are Δx, Δy (with $\Delta x < \lambda$) and $\Delta y < \lambda$ and thickness ℓ. Moreover, the roughness being at small scale ($q\lambda > 1$), the patches are similar and consequently, the intensity of the electromagnetic field radiated by a patch is independent of its position in the plane x, y. The calculation of the field radiated by dipoles [Eq. (3)], reduces to the calculation of the field radiated by one patch (which does not take into account the phase of the waves because the size of a patch is much smaller than λ^3) followed by a summation on the fields radiated by the different patches (which is only a summation on the phase because the intensity of the field radiated by one patch is independent of its position x, y) [13]. In addition, as the phase variation of the electromagnetic field inside a patch is neglected, this field satisfies electrostatic laws (electrostatic approximation [31–33]). After summation on the phase, the field radiated by dipoles [Eq. (3)] is given by

$$\delta E_u = \frac{i}{2Ak_{0Z}} \sum_{m=1}^{N} \int_{V_m} (k_m^2 - k_0^2) \mathbf{W}_u \cdot \mathbf{E}_R(P) dv, \tag{4a}$$

where V_m is the illuminated volume of the layer m of the interface and $\mathbf{E}_R(P)$ the electrostatic field, i.e., the field $\boldsymbol{\mathcal{E}}_R(P)$ without its phase term.

The electrostatic field $\mathbf{E}_R(P)$ derives from a potential $V_R(P)$. The integration (4a) on volumes V_m becomes an integration on the surfaces of volumes V_m [9],

$$\delta E_u = \frac{i}{2Ak_{0Z}} \sum_{m=1}^{N} \int_{S_m} (k_m^2 - k_0^2) V_R(P) \mathbf{W}_u \cdot d\mathbf{S}, \tag{4b}$$

$d\mathbf{S}=\mathbf{N}\, dS$, where $\mathbf{N}$ is the vector normal to the surface S_m of the volume V_m. $\mathbf{W}_u$ is a vector depending upon the polarization u (s or p), k_m is the amplitude of the wave vector of the light in the layer m. In the following one takes $u=p$ since the calculation of $\bar{\rho}$ needs only the calculation of δE_p. The components of the vector $\mathbf{W}_p$ are functions of the components of the wave vector of the incident light $\mathbf{k}_0$ $(\mathbf{k}_{0x}, \mathbf{k}_{0z})$ and that of the transmitted light $\mathbf{k}_N$ (k_{Nx}, k_{Nz}) [14]:

$$(\mathbf{W}_p)_x = \frac{2k_{0z}k_{Nz}k_0}{k_{Nz}k_0^2 + k_{0z}k_N^2},$$

$$(\mathbf{W}_p)_y = 0, \tag{5}$$

$$(\mathbf{W}_p)_z = -2\frac{k_{0,x}}{k_0}\frac{k_{0,z}k_N^2}{k_{N,z}k_0^2 + k_{0,z}k_N^2}.$$

The exact value of the field $\mathbf{E}_R$ or the potential V_R in the real configuration R is unknown. However, it can be obtained by a development in the series. In the following we calculate the reflected field to second order in $(q\zeta_q)^2$. It can be shown that a development of the potential V_R to first order is sufficient to get the reflected field to second order using Eqs. (4a) or (4b).

Moreover the modes q being uncorrelated, the reflected light is calculated for one mode and a summation over the modes is performed at the end of the calculation.

To first order in $q\zeta_{m,q}$, $V_{\mathbf{R}}(P)$ inside the layer m can be written as

$$\begin{aligned} V_R^{(m)}(P) &= V_0^{(m)}(P) + V_1^{(m)}(P) \\ &= -\frac{\varepsilon_0}{\varepsilon_m} E_{0,z}\, z - \mathbf{E}_{0,x}\, \mathbf{r} + \sum_{|\mathbf{q}|>1/\lambda} [U_{1,q}^{(m)} \exp(|q|z) \\ &\quad + V_{1,q}^{(m)} \exp(-|q|z)] \exp(i\mathbf{q}\cdot\mathbf{r}), \end{aligned} \tag{6}$$

where $(E_{0,x}, E_{0,z})$ are the components of the field $\mathbf{E}_0$ to order zero in the incident medium, far from the interface. It is the sum of the incident field and the reflected field to order zero (Fresnel equations),

$$\begin{aligned} E_{0,x} &= 2\frac{k_{0,z}k_{N,z}k_0}{k_{N,z}k_0^2 + k_{0,z}k_N^2} \boldsymbol{\mathcal{E}}_0, \\ E_{0,z} &= 2\frac{k_{0,x}}{k_0}\frac{k_{0,z}k_N^2}{k_{N,z}k_0^2 + k_{0,z}k_N^2} \boldsymbol{\mathcal{E}}_0, \end{aligned} \tag{7}$$

$\boldsymbol{\mathcal{E}}_0$ is the amplitude of the electric field of the incident light beam. The coefficients $U_{1,q}^{(m)}$ and $V_{1,q}^{(m)}$ in Eq. (6) are deduced from electrostatic equations, i.e., the continuity of the potential at the interface between the layer m and the layer $m-1$ and the continuity of the component of the displacement normal to the interface to first order in $q\zeta_{mq}$,

$$V_R^{(m)}(\mathbf{r}, Z_m(\mathbf{r})) = V_R^{(m-1)}(\mathbf{r}, Z_m(\mathbf{r})), \tag{8a}$$

$$\varepsilon_m \mathbf{N} \cdot \boldsymbol{\nabla} V_R^{(m)}(\mathbf{r}, Z_m(\mathbf{r})) = \varepsilon_{m-1} \mathbf{N} \cdot \boldsymbol{\nabla} V_R^{(m-1)}(\mathbf{r}, Z_m(\mathbf{r})), \tag{8b}$$

where $\mathbf{N}$ is the vector normal to the interface at the point $(\mathbf{r}, Z_m(\mathbf{r}))$. Taking into account Eqs. (1), (2), (6), (8a), and (8b) one obtains

$$\begin{aligned} &-\left(\frac{1}{\varepsilon_{m-1}} - \frac{1}{\varepsilon_m}\right)\varepsilon_0 E_{0,z}\zeta_{m,q} + (U_{1,\mathbf{q}}^{(m)} - U_{1,\mathbf{q}}^{(m-1)})\exp(|q|h_m) \\ &\quad + (V_{1,\mathbf{q}}^{(m)} - V_{1,\mathbf{q}}^{(m-1)})\exp(-|q|h_m) = 0, \end{aligned} \tag{9a}$$

$$\begin{aligned} &- i(\varepsilon_m - \varepsilon_{m-1})\mathbf{q} \cdot \mathbf{E}_{\mathbf{0},\mathbf{r}}\zeta_{mq} \\ &\quad + |q|(\varepsilon_m U_{1,\mathbf{q}}^{(m)} - \varepsilon_{m-1} U_{1,\mathbf{q}}^{(m-1)})\exp(|q|h_m) \\ &\quad - (\varepsilon_m V_{1,\mathbf{q}}^{(m)} - \varepsilon_{m-1} V_{1,\mathbf{q}}^{(m-1)})\exp(-|q|h_m) = 0. \end{aligned} \tag{9b}$$

Moreover, when media 0 and N are semi-infinite, the components $U_{1,\mathbf{q}}^{(0)}$ and $V_{1,\mathbf{q}}^{(N)}$ vanish,

$$U_{1,\mathbf{q}}^{(0)}=0,\qquad V_{1,\mathbf{q}}^{(N)}=0. \tag{10}$$

II. POTENTIAL, $V_R^{(m)}(P)$ INSIDE THE LAYER m CALCULATED TO FIRST ORDER IN $(\mathbf{q}\zeta_{\mathbf{m},\mathbf{q}})$

The $2N$ equations (9) allow the calculation of the coefficients $U_{1,q}^{(m)}$ and $V_{1,q}^{(m)}$ of the electrostatic potential $V_R^{(m)}(P)$. These $2N$ equations simplify and one obtains these coefficients by solving the following progressions:

$$U_{1,\mathbf{q}}^{(m)}=(A_1^m-v_1^mV_{1,\mathbf{q}}^{(m)})/u^m \quad \text{and } V_{1,\mathbf{q}}^{(m-1)}=(A_2^m-u_2^mU_{1,\mathbf{q}}^{(m)})/v_2^m \tag{11}$$

with $V_{1,\mathbf{q}}^{(N)}=0$.

Starting from $V_{1,\mathbf{q}}^{(N)}=0$, one calculates successively $U_{1,\mathbf{q}}^{(N)}$, $V_{1,\mathbf{q}}^{(N-1)}$, $U_{1,\mathbf{q}}^{(N-1)}$, and so on up to $m=0$. The coefficients u_1^m, u_2^m, v_1^m, v_2^m, A_1^m, A_2^m are obtained by solving the following progressions from $m=1$ to $m=N$, starting from the initial values $u_1^0=1$, $v_1^0=0$, $A_1^0=0$:

$$\begin{aligned}
u_1^m&=u_1^{m-1}+e^{2|q|h_m}\frac{(\varepsilon_{m-1}-\varepsilon_m)}{(\varepsilon_{m-1}+\varepsilon_m)}v_1^{m-1},\\
v_1^m&=v_1^{m-1}+e^{-2|q|h_m}\frac{(\varepsilon_{m-1}-\varepsilon_m)}{(\varepsilon_{m-1}+\varepsilon_m)}u_1^{m-1},\\
u_2^m&=\frac{2\varepsilon_m}{(\varepsilon_{m-1}+\varepsilon_m)}u_1^{m-1},\\
v_2^m&=e^{-2|q|h_m}\frac{(\varepsilon_{m-1}-\varepsilon_m)}{(\varepsilon_{m-1}+\varepsilon_m)}u_1^{m-1}+v_1^{m-1},\\
A_1^m&=\frac{2\varepsilon_m}{(\varepsilon_{m-1}+\varepsilon_m)}A_1^{m-1}-\frac{1}{q\varepsilon_m}\frac{(\varepsilon_{m-1}-\varepsilon_m)}{(\varepsilon_{m-1}+\varepsilon_m)}(e^{-|q|h_m}u_1^{m-1}(q\varepsilon_0E_{0,z}\\
&\quad+iq_x\varepsilon_mE_{0,x})+e^{|q|h_m}v_1^{m-1}(q\varepsilon_0E_{0,z}-iq_x\varepsilon_mE_{0,x}))\zeta_{m,q},\\
A_2^m&=A_1^{m-1}-\frac{e^{|q|h_m}}{q\varepsilon_m}\frac{(\varepsilon_{m-1}-\varepsilon_m)}{(\varepsilon_{m-1}+\varepsilon_m)}u_1^{m-1}(q\varepsilon_0E_{0,z}\\
&\quad+iq_x\varepsilon_{m-1}E_{0,x})\zeta_{m,q}.
\end{aligned} \tag{12}$$

III. REFLECTED FIELD TO SECOND ORDER IN $(\mathbf{q}\zeta_{\mathbf{q}})$

The above calculation and Eq. (6) give the potential $V_R^{(m)}$ to first order in $(q\zeta_{m,q})$. From this potential and Eqs. (4), (5) and (7) one obtains the field radiated by the dipoles of the interface to second order in $q\zeta_q$.

At the Brewster angle the equations simplify by using the following equations:

$$k_{0,x}=\frac{k_0k_N}{\sqrt{k_0^2+k_N^2}},\qquad k_{0,z}=\frac{k_0^2}{\sqrt{k_0^2+k_N^2}},\qquad k_{N,z}=\frac{k_N^2}{\sqrt{k_0^2+k_N^2}}. \tag{13}$$

The real field $\mathbf{E}_R^{(m)}(P)$ in each layer m derives from the potential $V_R^{(m)}(P)$ [Eq. (6)]. It is the sum of a uniform component $\left(\mathbf{E}_{0,\mathbf{r}},\frac{\varepsilon_0}{\varepsilon_m}E_0,z\right)$ which is the order zero in $q\zeta_{m,q}$ and a nonuniform component which is the order one in $q\zeta_{m,q}$. The field radiated by the dipoles induced by the uniform component can easily be calculated using Eq. (4a), taking into account Eqs. (5) and (7). After summation on the volumes, one obtains

$$E_p^{(0)}=i\frac{1}{k_{0,z}}\sum_{m=1}^{N-1}(h_{m+1}-h_m)\left([(\mathbf{W}_p)_x]^2-\frac{\varepsilon_N}{\varepsilon_m}[(\mathbf{W}_p)_z]^2\right)E_0. \tag{14a}$$

At the Brewster angle, taking into account Eqs. (5) and (13) one obtains

$$E_p^{(0)}=i\frac{\pi}{\lambda}\frac{1}{\sqrt{\varepsilon_0+\varepsilon_N}}\sum_{m=1}^{N-1}\frac{(\varepsilon_m-\varepsilon_0)(\varepsilon_m-\varepsilon_N)}{\varepsilon_m}(h_m-h_{m+1})E_0. \tag{14b}$$

The first term due to the roughness which does not vanish is second order in $q\zeta_q$. This term is easier to calculate using Eq. (4b) than Eq. (4a) and is obtained by incorporation of the first order term $V_1^{(m)}(P)$ of the potential $V_R^{(m)}(P)$ in Eq. (4b). Remarking that $V_{1,q}^{(m)}(\mathbf{r},Z(r))=V_{1,q}^{(m)}(\mathbf{r},h_m)+\frac{d}{dz}V_{1,q}^{(m)}(\mathbf{r},h_m)\ \xi_{m,q}$, Eq. (4b) becomes

$$\begin{aligned}
\delta E_p^{(2)}&=\frac{i}{k_{N,z}k_0^2+k_{0,z}k_N^2}\sum_{m=1}^{N}\sum_{|q|>1/\lambda}(k_m^2-k_0^2)\\
&\quad\times\Big\{-iq_xk_{n,z}k_0([U_{1,q}^{(m)}\exp(|q|h_m)+V_{1,q}^{(m)}\exp(-|q|h_m)]\zeta_{m,-q}^*-[U_{1,q}^{(m)}\exp(|q|h_{m+1})+V_{1,q}^{(m)}\exp(-|q|h_{m+1})]\zeta_{m+1,-q}^*)\\
&\quad+|q|\frac{k_{0,x}}{k_0}k_n^2([U_{1,q}^{(m)}\exp(|q|h_m)-V_{1,q}^{(m)}\exp(-|q|h_m)]\zeta_{m,-q}^*-[U_{1,q}^{(m)}\exp(|q|h_{m+1})-V_{1,q}^{(m)}\exp(-|q|h_{m+1})]\zeta_{m+1,-q}^*)\Big\}
\end{aligned} \tag{15}$$

with $\zeta_{n+1,-q}=0$ since the interface $N+1$ is the flat interface of the ideal distribution of matter I. In this equation, terms which contain $\exp(2i\mathbf{q}\cdot\mathbf{r})$ or $\exp(-2i\mathbf{q}\cdot\mathbf{r})$ are eliminated since their summation on the illuminated area vanishes.

The ellipticity at the Brewster angle is given by $\bar{\rho}=\mathrm{Im}(\delta r_p/r_s^F)$ with $r_s^F=(\varepsilon_0-\varepsilon_2)/(\varepsilon_0+\varepsilon_2)$. From the zero-order term of the reflected light, one deduces the zero-order term of the ellipticity,

$$\bar{\rho}^{(0)}=i\frac{\pi}{\lambda}\frac{\sqrt{\varepsilon_0+\varepsilon_N}}{\varepsilon_0-\varepsilon_N}\sum_{m=1}^{N}\frac{(\varepsilon_m-\varepsilon_0)(\varepsilon_m-\varepsilon_N)}{\varepsilon_m}(h_m-h_{m+1}). \tag{16}$$

This last equation is the Drude's equation for thin films (when the roughness vanishes).

IV. ONE ROUGH LAYER

For one rough layer, $N=2$. The mean thickness of the layer is $h=h_1-h_2$. One obtains the second-order term in $q\zeta$ of the ellipticity,

$$\begin{aligned}\bar{\rho}^{(2)}=&-\frac{\pi}{\lambda}\frac{\sqrt{\varepsilon_0+\varepsilon_2}}{(\varepsilon_0-\varepsilon_2)}\frac{1}{\varepsilon_1}\sum_{|\mathbf{q}|>1/\lambda}\frac{1}{q[(\varepsilon_0+\varepsilon_1)(\varepsilon_1+\varepsilon_2)+(\varepsilon_0-\varepsilon_1)(\varepsilon_1-\varepsilon_2)e^{-2|q|h}]}\\&\times\{\zeta_{1,q}\zeta_{1,-q}[(\varepsilon_1+\varepsilon_2)(q^2\varepsilon_2+q_x^2\varepsilon_1)+(\varepsilon_2-\varepsilon_1)(q^2\varepsilon_2-q_x^2\varepsilon_1)e^{-2|q|h}](\varepsilon_1-\varepsilon_0)^2\\&+\zeta_{2,q}\zeta_{2,-q}[(\varepsilon_0+\varepsilon_1)(q^2\varepsilon_0+q_x^2\varepsilon_1)+(\varepsilon_0-\varepsilon_1)(q^2\varepsilon_0-q_x^2\varepsilon_1)e^{-2|q|h}](\varepsilon_1-\varepsilon_2)^2\\&+2(\zeta_{1,q}\zeta_{2,-q}+\zeta_{1,-q}\zeta_{2,q})(\varepsilon_0-\varepsilon_1)(\varepsilon_1-\varepsilon_2)(q_x^2\varepsilon_1^2+q^2\varepsilon_0\varepsilon_2)e^{-|q|h}\}\end{aligned} \tag{17a}$$

which simplifies for an isotropic roughness ($\zeta_{1,q}$ and $\zeta_{2,q}$ are independent of the direction of the vector $\mathbf{q}$ and the mean value of q_x^2 for q=constant is $q^2/2$). The ellipticity becomes

$$\begin{aligned}\bar{\rho}^{(2)}=&-\frac{\pi}{2\lambda}\frac{\sqrt{\varepsilon_0+\varepsilon_2}}{(\varepsilon_0-\varepsilon_2)}\frac{1}{\varepsilon_1}\sum_{|\mathbf{q}|>1/\lambda}\frac{q}{(\varepsilon_0+\varepsilon_1)(\varepsilon_1+\varepsilon_2)+(\varepsilon_0-\varepsilon_1)(\varepsilon_1-\varepsilon_2)e^{-2|q|h}}\\&\times\{\zeta_{1,q}\zeta_{1,-q}[(\varepsilon_1+\varepsilon_2)(2\varepsilon_2+\varepsilon_1)+(\varepsilon_2-\varepsilon_1)(2\varepsilon_2-\varepsilon_1)e^{-2|q|h}](\varepsilon_1-\varepsilon_0)^2\\&+\zeta_{2,q}\zeta_{2,-q}[(\varepsilon_0+\varepsilon_1)(2\varepsilon_0+\varepsilon_1)+(\varepsilon_0-\varepsilon_1)(2\varepsilon_0-\varepsilon_1)e^{-2|q|h}](\varepsilon_1-\varepsilon_2)^2\\&+2(\zeta_{1,q}\zeta_{2,-q}+\zeta_{1,-q}\zeta_{2,q})(\varepsilon_0-\varepsilon_1)(\varepsilon_1-\varepsilon_2)(\varepsilon_1^2+2\varepsilon_0\varepsilon_2)e^{-|q|h}\}.\end{aligned} \tag{17b}$$

In these two last equations, $\zeta_{1,q}\zeta_{1,-q}$ and $\zeta_{1,q}\zeta_{1,-q}$ are the square of the amplitudes of the modes q of the upper and lower faces of the film while the term $(\zeta_{1,q}\zeta_{2,-q}+\zeta_{1,-q}\zeta_{2,q})$ results from the correlations of the roughness of the upper and the lower interface. In practice one must take the mean values of these quantities which fluctuate from one point to the other or with time for fluid interfaces.

In the following, we examine the application of this equation to some particular systems that have been studied by ellipsometry.

V. EXAMPLE OF APPLICATIONS OF THIS MODEL TO PHYSICAL SYSTEMS

A. Interface between two fluids

One supposes that the interfacial layer in which the refractive index is different from ε_0 or ε_2 is much thinner than the amplitude of the thermal fluctuations and consequently its thickness can be neglected [Fig. 2(a)]. For $\varepsilon_1=\varepsilon_0$ or $\varepsilon_1=\varepsilon_2$ or $h=0$ and $\zeta_{2,q}=\zeta_{1,q}=\zeta_q$, Eq. (17b) simplifies and one obtains the ellipticity of a rough interface between the media 0 and 2 for which the refractive index change abruptly from ε_0 to ε_2 [13–16],

$$\langle\bar{\rho}^{(2)}\rangle=-\frac{3}{2}\frac{\pi}{\lambda}\frac{(\varepsilon_0-\varepsilon_2)}{\sqrt{\varepsilon_0+\varepsilon_2}}\left\langle\sum_{|\mathbf{q}|>1/\lambda}q|\zeta_q^2|^2\right\rangle. \tag{18}$$

Moreover, for interfaces between two fluids, the roughness is due to thermal fluctuations, the ellipticity fluctuates and the experiment measures its mean value. The mean square amplitude of a mode $\mathbf{q}$ is $\langle\zeta_q^2\rangle=k_BT/\gamma q^2$ where k_B is the Boltzmann constant, T is the temperature, and γ is the interfacial tension. The density of modes is $qdq/2\pi$,

$$\left\langle\sum_{|\mathbf{q}|>1/\lambda}q\zeta_q^2\right\rangle=\int_0^{q_{\max}}\frac{k_BT}{\gamma q^2}\frac{q^2dq}{2\pi}=\frac{k_BT}{2\pi\gamma}q_{\max}, \tag{19}$$

$q_{\max}$ is a molecular cutoff limit of validity of the continuous model of a fluid [15–17].

B. Interface between two fluids separated by a film of constant thickness

In practice, the dielectric constant does not change abruptly from ε_0 to ε_2 through a liquid interface. There is a layer through which the dielectric constant varies from ε_0 to ε_2. Interfaces having a low surface tension can be modeled

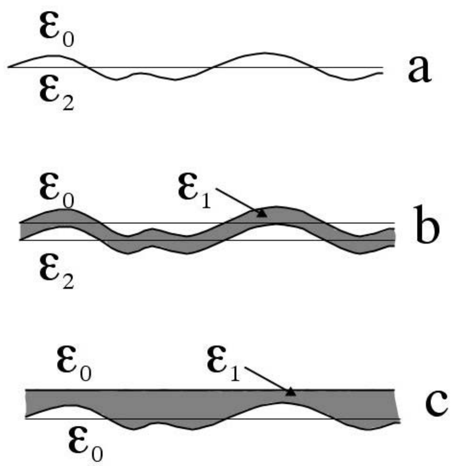

FIG. 2. Three examples of models of rough interfaces employed to explain some experimental results of ellipsometric measurements on liquid-liquid interfaces. (a) A thin but rough interface separating two media of dielectric constant ε_0 and ε_2. (b) A thin and rough layer of constant thickness and dielectric constant ε_1 separating two media of dielectric constant ε_0 and ε_2. (c) A layer of dielectric constant ε_1 with one plane face and one rough face separating two media of dielectric constant ε_0 and ε_2.

by one (or several) rough layer of refractive index different from ε_0 or ε_2. For simplicity, one supposes that this layer has a constant thickness.

A similar model applies when there is a surfactant film with a low surface tension separating two liquid phases (oil and water phases for instance). The interfacial film is supposed to have an isotropic dielectric constant ε_1 and a constant thickness h $\zeta_{2,q}=\zeta_{1,q}=\zeta_q$ [Fig. 2(b)]. Moreover, one supposes $qh \ll 1$. To first order in qh, Eq. (15) becomes

$$\langle \bar{\rho}^{(2)} \rangle = -\frac{3}{2}\frac{\pi}{\lambda}\frac{(\varepsilon_0-\varepsilon_2)}{\sqrt{\varepsilon_0+\varepsilon_2}}\left(\left\langle \sum_{|\mathbf{q}|>1/\lambda} q\zeta_q^2 \right\rangle + 4h\frac{\varepsilon_0\varepsilon_2}{\varepsilon_1}\frac{(\varepsilon_0-\varepsilon_1)(\varepsilon_2-\varepsilon_1)}{(\varepsilon_0-\varepsilon_2)^2(\varepsilon_0+\varepsilon_2)}\left\langle \sum_{|\mathbf{q}|>1/\lambda} (q\zeta_q)^2 \right\rangle\right). \tag{20}$$

The ellipticity is the sum of three terms: the Drude's term $\bar{\rho}^{(0)}$ [Eq. (16)] due to the film thickness and two roughness terms [Eq. (20)], one of them similar to (18) and a second roughness term,

$$4h\frac{\varepsilon_0\varepsilon_2}{\varepsilon_1}\frac{(\varepsilon_0-\varepsilon_1)(\varepsilon_2-\varepsilon_1)}{(\varepsilon_0-\varepsilon_2)^2(\varepsilon_0+\varepsilon_2)}\left\langle \sum_{|\mathbf{q}|>1/\lambda} (q\zeta_q)^2 \right\rangle$$

which does not appear in the Marvin and Toigo calculation [21].

A surfactant film at a liquid-liquid interface is characterized by a surface tension and a bending elasticity K. The mean square amplitude of a thermal mode $\mathbf{q}$ is given by the equation $\langle \zeta_q^2 \rangle = k_BT/(\gamma q^2+Kq^4)$. By integration over the modes, one obtains

$$\left\langle \sum_{|\mathbf{q}|>1/\lambda} q\zeta_q^2 \right\rangle = \int_0^\infty \frac{k_BT}{\gamma q^2+Kq^4}\frac{q^2dq}{2\pi} = \frac{1}{4}\frac{k_BT}{\sqrt{\gamma K}}\frac{2\tan^{-1}\sqrt{K/\gamma}q_{\max}}{\pi}, \tag{21a}$$

$$\left\langle \sum_{|\mathbf{q}|>1/\lambda} q^2\zeta_q^2 \right\rangle = \int_0^{q_{\max}} \frac{k_BT}{\gamma q^2+Kq^4}\frac{q^3dq}{2\pi} = \frac{k_BT}{4\pi K}\ln\left(1+\frac{K}{\gamma}q_{\max}^2\right). \tag{21b}$$

The bending elasticity introduces a natural cutoff in Eq. (21a) when

$$\sqrt{K/\gamma}q_{\max} \gg 1 \left(\frac{2\tan^{-1}\sqrt{K/\gamma}q_{\max}}{\pi} \approx 1\right).$$

One obtains [5]

$$\left\langle \sum_{|\mathbf{q}|>1/\lambda} q\zeta_q^2 \right\rangle = \int_0^\infty \frac{k_BT}{\gamma q^2+Kq^4}\frac{q^2dq}{2\pi} = \frac{1}{4}\frac{k_BT}{\sqrt{\gamma K}}. \tag{21c}$$

The first roughness term is proportional to $\gamma^{-0.5}$, while the second one has a logarithmic dependence over γ. When the roughness is large (γ and K small) a large part of the ellipticity is due to the roughness originating from thermal fluctuations. A plot of the ellipticity as a function of $\gamma^{-0.5}$ is linear and the slope of the straight line allows the determination of the bending elasticity K of the surfactant film [17–19].

Remark. In this model the surfactant film is modeled by a layer of constant thickness of an isotropic medium of refractive index n_1. The model can take into account an optical anisotropy of the monolayer. This is very simple for a uniaxial anisotropy of the interfacial layer with an ordinary dielectric constant ε_{o1}, an extraordinary dielectric constant ε_{e1}, and a symmetry axis normal to the surfactant film in each point or a symmetry axis parallel to the surfactant film. For a symmetry axis normal to the film one obtains [10]

$$\bar{\rho}^{(0)} = \frac{\pi}{\lambda}\frac{\sqrt{\varepsilon_0+\varepsilon_2}}{\varepsilon_0-\varepsilon_2}\left(\frac{(\varepsilon_0-\varepsilon_{e1})(\varepsilon_2-\varepsilon_{e1})}{\varepsilon_{e1}} + \varepsilon_{o1}-\varepsilon_{e1}\right)h \tag{22a}$$

and $\langle \bar{\rho}^{(2)} \rangle$ is obtained by taking ε_{e1} in place of ε_1 since ε_1 in this equation originates from Eq. (8b). For a symmetry axis in the plane of the surfactant layer and with a random orientation [11] one obtains

$$\bar{\rho}^{(0)} = \frac{\pi}{\lambda}\frac{\sqrt{\varepsilon_0+\varepsilon_2}}{\varepsilon_0-\varepsilon_2}\left(\frac{(\varepsilon_0-\varepsilon_{o1})(\varepsilon_2-\varepsilon_{o1})}{\varepsilon_{e1}} + \frac{\varepsilon_{e1}-\varepsilon_{o1}}{2}\right)h \tag{22b}$$

and $\langle \bar{\rho}^{(2)} \rangle$ is obtained by taking ε_{o1} in place of ε_1.

C. A thick fluid layer with very large fluctuations of its thickness

In some experiments, one observes a thick wetting liquid film on a liquid for which the surface tension of the lower interface (liquid-film) is ultralow ($\gamma \approx 10^{-4}$–10^{-7} N/m) while that of the upper interface of the film is large (10^{-2} N/m). Thermal fluctuations of the lower interface are large and can induce an entropic repulsion between the two faces of the wetting film due to the fact that the amplitude of the thermal fluctuations of the lower interface are limited by the presence of the upper interface. On the contrary, the thermal fluctuations of the upper interface are very small and can be neglected since its surface tension is large, $\zeta_{1,q}=\zeta_{1,-q}=0$ [Fig. 2(c)]. This is observed with wetting films close to a critical point [24,25] or for oil films on water when a surfactant film strongly decreases the oil-water interfacial tension [22,23]. The ellipticity can be written

$$\bar{\rho}^{(0)} + \langle \bar{\rho}^{(2)} \rangle = i\frac{\pi}{\lambda}\frac{\sqrt{\varepsilon_0+\varepsilon_2}}{\varepsilon_0-\varepsilon_2}\frac{(\varepsilon_0-\varepsilon_1)(\varepsilon_2-\varepsilon_1)}{\varepsilon_1} \times \left[h + \frac{3}{2}\frac{(\varepsilon_1-\varepsilon_2)}{(\varepsilon_0-\varepsilon_1)}\frac{(2\varepsilon_0+\varepsilon_1)}{(\varepsilon_1+\varepsilon_2)} \times \sum_{|\mathbf{q}|>1/\lambda}\left(1+\frac{(\varepsilon_0-\varepsilon_1)(2\varepsilon_0-\varepsilon_1)}{(\varepsilon_0+\varepsilon_1)(2\varepsilon_0+\varepsilon_1)}e^{-2|q|h}\right) q|\zeta_{2,q}|^2 \right]. \tag{23a}$$

Moreover, the two dielectric constant ε_2 and ε_1 (of the liquid and of the wetting film, respectively) are close and consequently

$$|\varepsilon_1-\varepsilon_2| \ll \varepsilon_0, \varepsilon_1 \text{ or } \varepsilon_2, \quad \frac{(\varepsilon_0-\varepsilon_1)(2\varepsilon_0-\varepsilon_1)}{(\varepsilon_0+\varepsilon_1)(2\varepsilon_0+\varepsilon_1)} \ll 1,$$

and can be neglected. The ellipsometric signal contains a thickness term and a roughness term. For systems in which the amplitude of the high frequency fluctuations of the lower interface are limited by a bending rigidity [22,23], Eq. (23a) becomes

$$\bar{\rho}^{(0)} + \langle \bar{\rho}^{(2)} \rangle = i\frac{\pi}{\lambda}\frac{\sqrt{\varepsilon_0+\varepsilon_2}}{\varepsilon_0-\varepsilon_2}\frac{(\varepsilon_0-\varepsilon_1)(\varepsilon_2-\varepsilon_1)}{\varepsilon_1} \times \left(h + \frac{3}{8}\frac{(\varepsilon_1-\varepsilon_2)}{(\varepsilon_0-\varepsilon_1)}\frac{(2\varepsilon_0+\varepsilon_1)}{(\varepsilon_1+\varepsilon_2)}\frac{k_B T}{\sqrt{\gamma K}} \right). \tag{23b}$$

The ratio of the thickness term and the roughness term depends upon the system.

Remark. Equations (4b) and (11) allow the calculation of the light reflected by a rough interface to first order in h and second order in the amplitude of the roughness $\mathbf{q}\zeta_q$. This means that this calculation is valid only if the term in $(h/\gamma)^2$ which was neglected is much smaller than the roughness terms. This is generally the case in the experiments in Refs. [19,22–25] since the roughness and h have the same order of magnitude.

VI. CONCLUSION

Equations (11) and (12) allow the calculation to second order in $(q\zeta_q)$ of the reflectivity or the ellipticity of any rough interface whose roughness has a small slope ($|\nabla\zeta| \ll 1$). In practice, the most interesting case is probably the case of one homogenous rough layer.

We have solved these equations in the case of one rough layer and for an incidence equal to the Brewster angle since this is the angle of incidence used in ellipsometry. At this angle the equations simplify. We have specially studied the case of liquid films whose roughness originates from thermal fluctuations and is a function of a small number of parameters.

Since Drude, it is well known that ellipsometry is able to give information on the interfacial thickness of interfaces much thinner than the wavelength of the light. As we have shown in this paper, ellipsometry allows giving more information when the interfacial tension is sufficiently low to induce thermal fluctuations with amplitudes comparable to the intrinsic thickness of the interface. This must be noticed since ellipsometry is a technique that has the advantage on x-ray reflectivity or neutron reflectivity to be much cheaper and simpler to use. Moreover it allows studying interfaces between two fluids as oil-water interfaces which cannot be studied—or are very difficult to study—using x-ray reflectivity or neutron reflectivity. The model presented in this paper allows the determination of what parameter can be extracted from ellipsometry as a function of the optical characteristics of the interface.

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