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Note: Refractive index sensing of turbid media by differentiation of the reflectance profile: Does error-correction work?

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A widely used method for determining refractive index postulates that the derivative of the angular profile for light reflected from the sample is maximum at the critical angle for total internal reflection (TIR). It is well-known that in turbid media this "differentiation method" yields errors in refractive index. Unexplained anomalies in previous error-calculations are eliminated if one uses a recent model of TIR which departs from traditional Fresnel theory. However we find that, in practical situations, the refractive index obtained by differentiation *even after error-correction* is significantly different from the best estimate for the refractive index obtained by curve-fitting the reflectance data. Thus the differentiation method lacks scientific validity in turbid media. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4746810]

Refractive index sensing of turbid media has received considerable attention over the past few decades (Refs. 1 and 2, and references therein). The most widely used method for refractive index measurement comprises detection of the light reflected from the sample surface at different angles of incidence, with the goal of determining the critical angle for total internal reflection (TIR). The critical angle is straightforwardly related to the refractive index for transparent samples. In the case of a transparent sample if the reflected intensity is plotted as a function of incidence angle, the critical angle manifests as a sharp transition between the regions where TIR occurs and where the light merely refracts through. A technique commonly used by researchers,[2–6] and by commercial TIR-based refractometers,[7] is to locate this transition by taking the derivative with respect to incident angle of the reflected intensity profile and associating the point of maximum slope (which, for transparent samples, coincides with the point at which the slope of the reflectance profile is discontinuous) with an "effective" critical angle. The *differentiation method* is popular because of its perceived "simplicity and technical maturity."[4]

However, for turbid media the TIR transition is not as sharp, and the concept of "critical angle" not as straightforward,[1,2] as for transparent media. A turbid medium is one in which the particle size is comparable to the optical wavelength of the incident light and the particle density is sufficient to generate significant multiple scattering. The differentiation method yields erroneous values for the refractive index in turbid media[2] – this method is valid only for transparent media. Despite the lack of scientific validity it is unfortunately a widespread practice to persist with the differentiation method for turbid media, for two reasons. First, some workers argue that if the error for a certain range of turbidities is less than a pre-defined "acceptable" value, the method of differentiation may be deemed "safe" in this turbidity range.[2–4] Second, there is the perception that the error from the differentiation method may be calculated[2,4] so that, as argued recently,[4] the "error's contribution to a practically measured value may, if necessary, be eliminated."

In this Note we analyze the error in the differentiation method and offer three new insights which have not been emphasized before in the literature. Our work shows that the two reasons cited in the previous paragraph as justification for the use of the differentiation method are invalid. First, we draw the reader's attention to the inexplicable behavior exhibited by the error as calculated from Fresnel theory in Refs. 2 and 4 – the error initially increases with turbidity, then *decreases over a significant range of turbidities, approaching nearly zero,* before again increasing. This is in stark contrast to the logical expectation that, since the error in refractive index measurement by differentiation arises from the presence of turbidity, the error should always increase with turbidity. The inexplicable behavior of the error in Refs. 2 and 4 arises because it is well-known that Fresnel theory does not apply in the case of turbid media.[1] Second, we show that if the error in refractive index measurement by differentiation is instead evaluated using a recent model of TIR in turbid media, which departs from Fresnel theory by introducing an angle dependence in the imaginary part of the refractive index,[1] the error increases everywhere with turbidity thus eliminating the puzzling behavior shown by the error calculated from traditional Fresnel theory. Third and most important, we show that it is simply not feasible for an experimentalist to use the calculated error curves from *either* model to accurately measure the refractive index by the differentiation method. We find that *even after correcting for the error* the refractive index value found by differentiation is *significantly* different from the true value. Note that in practical situations there exists no reliable reference data for the "true" refractive index for highly turbid media – the best estimate is obtained by curve-fitting the reflectance data.[1]

To evaluate the error in measurement of refractive index by the differentiation method, we examine the basic principle of TIR-based refractive index measurement, as outlined in Fig. 1(a).[1,8] A turbid sample of refractive index n_{sample}

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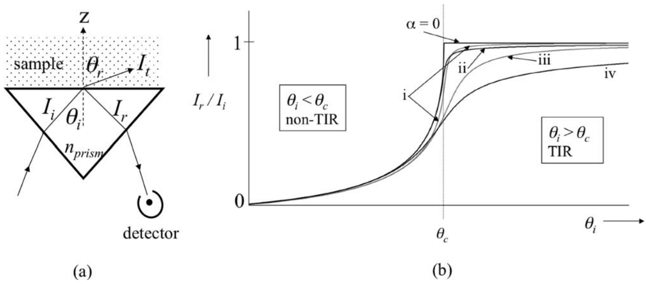

FIG. 1. (Reproduced from Ref. 1) (a) Measurement of the reflectance profile $I_r/I_i(\theta_i)$. (b) Reflectance profiles for a transparent sample ($\alpha = 0$) and two turbid samples $\alpha = 125$ cm^{-1} (curves i and ii) and $\alpha = 1200$ cm^{-1} (curves iii and iv). Curves ii and iv are from traditional Fresnel theory (Eq. (1)), i and iii are from our new model of TIR (Eqs. (1) and (2)). For all curves, n_r is chosen as 1.34.

is placed on top of a glass substrate, typically a prism of known refractive index n_{prism}. For turbid media n_{sample} is complex: $n_{sample} = n_r + in_i$ where the real part n_r arises from the bending of light at the interface as it refracts through, and the imaginary part n_i is directly related to the turbidity. Quantitatively, turbidity is described by the attenuation coefficient α which measures the loss of directed radiation per unit length through the sample owing to scattering and/or absorption, i.e., the intensity $I(z)$ of a light beam propagating in the z-direction through the medium can be written as $I(z) = I_0 \exp(-\alpha z)$, where I_0 is the intensity at $z = 0$. Note that α is the sum of the scattering and absorption coefficients, and is equal to $2n_i\,\omega/c$, where ω is the laser frequency and c is the speed of light in vacuum.[1]

The plot marked "$\alpha = 0$" in Fig. 1(b) shows the theoretical reflectance profile I_r/I_i as a function of the incidence angle θ_i for a transparent sample which follows from the usual Fresnel relation, $I_r/I_i(\theta_i) = [\tan^2(\theta_i - \theta_r)]/[\tan^2(\theta_i + \theta_r)]$ where we assume the incident beam to be p-polarized. For transparent samples the vertical dashed line in Fig. 1(b) marks the sharp transition between the TIR and non-TIR regions, thus locating the critical angle θ_c (this is also the angle at which the gradient of the I_r/I_i-curve is maximum) and hence n_{sample} through Snell's Law: $n_{sample} = n_{prism} \sin\theta_c$. On the other hand, for turbid media the transition between the TIR and non-TIR regions of the reflectance profile exhibits no discontinuity in slope: This is depicted in Fig. 1(b) by curves (i, iii) and curves (ii, iv) which correspond to two different turbidities "$\alpha = 125$ cm^{-1}" and "$\alpha = 1200$ cm^{-1}", respectively. Curves ii and iv are plotted using the traditional Fresnel approach to turbid media – simply allow n_{sample} to be complex in the Fresnel equation above for $I_r/I_i(\theta_i)$, yielding[2]

$$\frac{I_r}{I_i} = \frac{M + P^2\cos^2\theta_i - \sqrt{2}\cos\theta_i(M + \sin^2\theta_i)\sqrt{M+L}}{M + P^2\cos^2\theta_i + \sqrt{2}\cos\theta_i(M + \sin^2\theta_i)\sqrt{M+L}}, \tag{1}$$

where we have used for convenience $P = (n_r^2 + n_i^2)/n_{prism}^2$, $L = [(n_r^2 - n_i^2)/n_{prism}^2] - \sin^2\theta_i$, and $M = \sqrt{P^2 - 2L\sin^2\theta_i - \sin^4\theta_i}$.

For curves ii and iv in Fig. 1(b) we substituted in Eq. (1) two different (but *constant*) values for n_i, and the *same* n_r as for $\alpha = 0$. If we define an effective critical angle as the angle at which the slope of $I_r/I_i(\theta_i)$ is maximum, and substitute this critical angle in Snell's Law above, we obtain an "effective" n_r-value (denoted as $n_{\mathcal{F}}$, where $\mathcal{F}$ stands for "traditional Fresnel theory") for the turbid medium, which is different from the true n_r-value. We define the error as $\mathcal{E}_{\mathcal{F}} \equiv n_{\mathcal{F}} - n_r$.[2,4] We have previously shown that curves ii and iv are never able to accurately fit the data no matter what values may be ascribed to n_r and n_i unless several poorly justified fitting parameters are introduced.[1]

Curves i and iii in Fig. 1(b) are again plots of Eq. (1), but this time with a crucial departure from traditional Fresnel theory: n_i is taken to be an angle-dependent quantity according to a new model of TIR in turbid media[1] that incorporates into Fresnel theory angle-dependent penetration of the incident beam into the turbid medium. The reason for this angle-dependence is that the incident light actually penetrates the medium before undergoing TIR back out. The penetration, and therefore the loss in intensity owing to scattering and/or absorption, depends on θ_i making n_i in Eq. (1) an angle-dependent quantity $n_i(\theta)$, which in terms of the original n_i at normal incidence is:[1]

$$n_i(\theta) = n_i\left(4\pi n_{prism}\sqrt{(M-L)/2}\right)^{-1}. \tag{2}$$

Note that Eq. (2) is derived from standard Fresnel theory for refraction of light into an attenuating medium,[1] and Eq. (1) was derived using standard Fresnel theory for reflection, but their *ad hoc* combination represents a departure from traditional Fresnel theory. Combining Eqs. (1) and (2) enables us, for the first time, to accurately describe reflectance data in actual experiments with a model that has only two fitting parameters - n_r and n_i - which are the unknown parameters of interest.[1] We obtain reflectance-curves i and iii for the two turbidities "$\alpha = 125$ cm^{-1}" and "$\alpha = 1200$ cm^{-1}", respectively, which are substantially different from the curves ii and iv from traditional Fresnel theory (see Fig. 1). We may now employ the method of differentiation on curves i and iii to find an effective refractive index (denoted $n_{\mathcal{AM}}$, where $\mathcal{AM}$ stands for "angle-dependent model"). We define the error $\mathcal{E}_{\mathcal{AM}} \equiv n_{\mathcal{AM}} - n_r$.

In Fig. 2 we plot the absolute values of the errors $\mathcal{E}_{\mathcal{F}}$ and $\mathcal{E}_{\mathcal{AM}}$ as a function of turbidity for (a) p- and (b) s-polarized light, for $n_r = 1.3600$.

The $\mathcal{E}_{\mathcal{F}}$-curves are identical to those shown earlier by other workers.[2,4] Note the inexplicable decrease of $\mathcal{E}_{\mathcal{F}}$ with increasing n_i that we alluded to earlier, for either polarization,

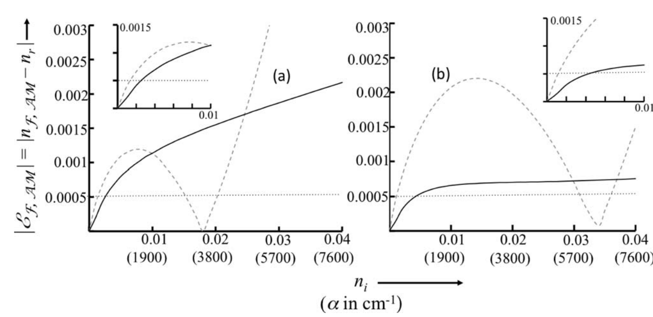

FIG. 2. Theoretical error in refractive index determination by the method of differentiation, from traditional Fresnel theory (dashed line) and from our model of TIR in a turbid medium (solid line), for (a) p- and (b) s-polarized light. Here n_r is taken to be 1.36.

once n_i exceeds 0.01 (as is the case for various printer dyes where $n_i \sim 0.05$ (Ref. 9)). By contrast, the $\mathcal{E}_{\mathcal{AM}}$-curves in Fig. 2 appear reasonable, predicting an error that always increases with increasing n_i. Even within the regime $n_i \lesssim 0.01$, where $\mathcal{E}_{\mathcal{F}}$ appears reasonable as well, there exists a substantial discrepancy between $\mathcal{E}_{\mathcal{F}}$ and $\mathcal{E}_{\mathcal{AM}}$ (see insets, Fig. 2). Therefore, in the following discussion, we choose to ignore the $\mathcal{E}_{\mathcal{F}}$-curves and focus on the $\mathcal{E}_{\mathcal{AM}}$-curves.

One may imagine a potential use for the $\mathcal{E}_{\mathcal{AM}}$-curves in the regime $n_i \leq 0.01$ as follows (however, read concluding paragraphs below). Typical refractometers offer a resolution of 5×10^{-4},[10] which for some applications may be deemed an "acceptable" error (horizontal lines, Fig. 2). The $\mathcal{E}_{\mathcal{F},\mathcal{AM}}$ curves in Fig. 2 suggest that for $n_r \sim 1.36$ the typical device may be used "safely" up to $n_i \leq 0.004$ for *s*-, and ≤ 0.002 for *p*-polarization. To find "safe" turbidity limits at other n_r-values, $\mathcal{E}_{\mathcal{AM}}$-curves as in Fig. 2 may be drawn for several different n_r-values. In order to choose which $\mathcal{E}_{\mathcal{AM}}$-curve to use, it suffices to make a crude n_r-measurement from the typical device – we have verified that a change in n_r-value of up to 0.001 changes $\mathcal{E}_{\mathcal{F},\mathcal{AM}}$ negligibly in the regime $n_i \leq 0.01$.

We now discuss the most important finding of this work. To summarize so far: We plotted theoretical error-curves in Fig. 2 and argued that the $\mathcal{E}_{\mathcal{F}}$-curves should be ignored, proceeding instead with the $\mathcal{E}_{\mathcal{AM}}$-curves in which the error increases everywhere with turbidity. However, *are these theoretical error-curves of any use in practical situations* where the true value n_r is not known? More specifically, can the error in refractive index measured by differentiation of I_r/I_i be calculated and eliminated, as asserted[4] by proponents of the differentiation method? We show here the answer is no. In order to validate our assertion we first need to obtain a best estimate for n_r, which as mentioned earlier, is achieved by fitting the I_r/I_i data using the $\mathcal{AM}$ model[1] – let us denote this best estimate to n_r as n_{fit}. Next we examine what an experimenter does when attempting to measure n_r using the differentiation method: The experimenter differentiates the *measured* I_r/I_i-curve to find the refractive index - let us denote this attempt at measuring n_r as n_{data}. Now, to determine the error in n_{data} the experimenter would look up the error-value from the $\mathcal{E}_{\mathcal{AM}}$-error curve corresponding to this particular value of n_{data} (we assume that the value of n_i has already been determined correctly by some method). Finally, by using the definition for $\mathcal{E}_{\mathcal{AM}}$, modified for use in experimental situations: $\mathcal{E}_{\mathcal{AM}} = n_{data} - n_{corrected}$, the experimenter would find an *error-corrected* estimate for n_r, which we have denoted here as $n_{corrected}$. If the error due to differentiation can indeed be eliminated, the value for $n_{corrected}$ must be acceptably close to that of n_{fit}. However, we find experimentally for several turbid solutions (n_r ranging between 1.34 and 1.37) with turbidity ranging from moderate to high, that this procedure yields values for $n_{corrected}$ which have unacceptably large disagreement with n_{fit} – the disagreement is $\sim$0.001 for a solution with $n_i = 0.0005$ ($\alpha = 100$ cm^{-1}), growing to 0.005 for a solution with $n_i = 0.0034$ ($\alpha = 650$ cm^{-1}). This disagreement between n_{data} and n_{fit} is unacceptable for cutting-edge refractive index based research. For example, in Ref. 6 the refractive index values deduced therein by the method of differentiation and reported to an accuracy of 10^{-4} are inaccurate at least at the 10^{-3}-level for almost every sample quoted in that work.

We checked that the disagreement between n_{data} and n_{fit} is worse if the $\mathcal{F}$, instead of $\mathcal{AM}$, model is used. This is not surprising since, as demonstrated previously,[1] the value of n_{fit} found using the $\mathcal{F}$-model, and also $\mathcal{E}_{\mathcal{F}}$, are less accurate than their $\mathcal{AM}$ counterparts.

We conclude that the differentiation method has no scientific validity in turbid media and should be avoided for refractive index measurement of turbid samples.

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