Requirements on a differential refractometer for its use in sizing colloidal particles

Augusto García-Valenzuela, Celia Sánchez Pérez

Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Apartado Postal 70-186, 04510 México Distrito Federal, México
E-mail: aaugusto.garcia@ccadet.unam.mx, bcelia.sanchez@ccadet.unam.mx

Abstract

Most colloidal samples have a non-negligible imaginary component of the effective refractive index due to scattering and absorption losses. In this paper we analyze the requirements on a differential refractometer so that it can be used to measure the real part of the effective refractive index increment in colloids for particle size analysis.

Keywords: Differential refractometer, particle sizing, turbid media

1. Introduction

Many techniques have been developed over the years for sizing particles with diameters in the range of a few microns to a few nanometers. Most purely optical techniques may be classified either as spectroturbidimetry [1] or as static light scattering techniques [2]. All these techniques require to know apriori the refractive index of the particles. However, in many cases it is not known and this is an important source of errors. We have recently proposed a technique to retrieve the average size and the refractive index of particles in a colloidal suspension. This technique requires measuring differences in the effective refractive index ($n_{\text{eff}}$) of a suspension of particles and the particles volume concentration ($f$). In a colloid $n_{\text{eff}}$ is usually a complex quantity due to scattering losses, even in the absence of optical absorption. The matrix in which the particles are suspended is assumed to have a real refractive index. The simplest and safest way of measuring the effective refractive index in colloids, with some precaution, is by refraction. In particular, one must be careful in any experiment to ensure that the diffuse field does not interfere with the measurement of the coherent intensity.

The so called differential refractometers [3, 4] measure the refractive index difference between two liquids by refraction of a collimated beam and usually offer a very high resolution in the case of homogeneous transparent liquids (i.e., with a real refractive index). The question arises whether one can use differential refractometers to measure increments of the effective refractive in colloids with particles volume concentration. However, when there is attenuation in the sample, either from absorption or scattering, the differential refractometer may incur in large errors. In this work we study these errors and seek ways to minimize them for accurately characterizing colloids.

2. Sizing colloidal particles from the effective refractive index

Recently, the correct theoretical foundations of the effective refractive index of colloids were clarified [5], ending with the confusion about its existence and limited use. The effective refractive index of a particle suspension, $n_{\text{eff}}(\omega)$, comes from the solution to a non-local dispersion equation for transverse modes for the average wave also referred to as the “coherent wave”. The non-locality of the effective electromagnetic response has important consequences. For instance, we can not use in general the well known Fresnel reflection coefficients with the effective refractive index, and this means that $n_{\text{eff}}(\omega)$ can not always be measured with techniques relying on the measurement of the reflection coefficients; such as with Abbe type refractometers, widely used in the industry today.
In a good approximation the effective refractive index for a dilute colloid is given by the so called van de Hulst formula,

\[ n_{\text{eff}}(\omega) \approx n_m(\omega) \left[ 1 + i \frac{3}{2} \frac{f}{x_m^3} S(0) \right], \tag{1} \]

where \( x_m = k_m a \) is the size parameter in the matrix, \( k_m = n_m(2\pi/\lambda), \lambda \) is the wavelength in vacuum of the light and \( S(0) \) is the forward scattering amplitude of the particles (given by Mie theory for spherical particles). Notice that the effective refractive index is a complex number, regardless of the dielectric properties of the particle. \( n_{\text{eff}} \) may be used safely in the usual way to calculate the refraction, phase delay and attenuation of the coherent wave inside the colloid.

In [6] a methodology to obtain the size and refractive index of colloidal particles with a narrow size distribution from measurements of the effective refractive index of the colloid was proposed and analyzed on theoretical grounds. This methodology requires measuring the volume concentration of the colloidal particles \( f \), the real and the imaginary parts of the refractive index difference between the colloid \( (n_{\text{eff}}) \) and the pure matrix liquid \( (n_m) \). From \( \text{Re}(n_{\text{eff}} - n_m)f \) and \( \text{Im}(n_{\text{eff}} - n_m)f \) it is possible to retrieve the radius \( (a) \) and refractive index of the particles \( (n_p) \) uniquely as long as the particles are not too large. For instance, for \( n_m = 1.36 \) and \( n_p = 2.0 \) at a wavelength of 635 nm (in vacuum) the maximum measurable particle size is about 180 nm, but for \( n_p = 1.4 \) and the same value of \( n_m \), the maximum particle size is about 4 \( \mu \)m [6].

Measuring the imaginary part of the effective refractive index of a colloid can be done by standard techniques relying on Beer-Lambert’s law. Differential refractometers are, in principle, an attractive possibility for measuring \( \text{Re}(n_{\text{eff}} - n_m) \). However, we need first to understand the special requirements of these refractometers for their use with colloidal samples.

3. Modeling differential refractometers

We will first consider the case of a differential refractometer with a lossless sample. A differential refractometer consists of a rectangular cell made of glass slabs and divided into two prismatic compartments by an additional glass slab as shown in Fig. 1. Suppose both compartments of the cell are filled with the same liquid of refractive index \( n_m \) and kept at the same temperature. Then, clearly, a light beam traversing the cell is not deflected. A lateral displacement of the beam, \( \delta x \), occurs as the beam traverses at an oblique angle the dividing glass slab. This lateral displacement can be ignored since it is constant.

Now, let us suppose that a small amount of a different substance, which we will refer to as the sample, is diluted homogenously in the second compartment of the cell, causing the refractive index to change by an amount \( \delta n_m \). In this case, the output beam will deflect by an angle, \( \Delta \theta \equiv \delta n_m \tan(\chi) \), where \( \chi \) is the cell’s division angle indicated in Fig. 1. Clearly, by measuring \( \Delta \theta \) we obtain the difference in refractive index of the liquids filling both compartments of the cell.

Commercial differential refractometers measure the deflection angle from the displacement, \( \Delta x \), of the beam’s spot at some distance, \( l+L \), from the center of the cell. For small deflection angles, the displacement is given by,

\[ \Delta x = \delta n_m \tan(\chi) \left[ \frac{l}{n_m} + L \right] \approx \delta n_m L \tan(\chi). \tag{2} \]

Typically, \( \Delta x \) is measured using a position sensitive detector. Commonly a split detector also referred to as a two quadrant, or bi-cell detector is used.
Now, if the sample has a complex refractive index, then the increment in refractive index, \( \delta n_m \), in the second compartment of the refractometer will be complex. In this case, the above analysis may not be enough. We must take into account the finite width and diffraction of the optical beam. We may not consider it as a ray. Consider the coordinate system shown in Fig. 2. The origin is placed at the center of the entrance plate of the refractometer’s cell. For simplicity here we will assume that a Gaussian beam is incident to the refractometer’s cell. Let us suppose that the electric field at the entrance slab of the refractometer (this is at \( z = 0 \)) is given by, \( \vec{E}(x, y, 0) = E_0 \exp\left[\left(\frac{x^2 + y^2}{w^2}\right)\right] \hat{\epsilon} \), where \( \hat{\epsilon} \) is the polarization vector, and \( w \) is the beam’s radius at \( z = 0 \).

One can picture what happens when the sample has a complex refractive index with the schematic illustration shown in Fig. 2. The upper portions of the light beam travel a shorter distance than the lower portions through the sample. Therefore the lower portions of the beam attenuate more than the upper ones. The maximum of the light intensity is displaced upwards due to the non-uniform attenuation through the beam’s cross section. This displacement depends on the imaginary part of the refractive index and not on the real part. The upward shift of the maximum should be added to the displacement of the beam’s spot at the detector’s plane, and is not taken into account in Eq. (2). Therefore, one will incur in an error when obtaining the real part of the refractive index from the displacement of the beam at the detector’s plane. The relative magnitude of the error will depend on the distance to the detector. It will be smaller the farther away we place the detector. In practical designs of differential refractometers it is not possible to place the detector very far away. Nevertheless,
this error may be eliminated in principle by using an angle-sensitive detector instead of a position sensitive detector (see for example Ref. [7]).

However, when the sample has a complex refractive index it also happens that the angle of refraction will depend to some extent on the imaginary part of the refractive index; and this error can not be eliminated by using an angle-sensitive detector and we must quantify this error.

We have performed a mathematical analysis of the propagation of a monochromatic Gaussian beam through the refractometer’s cell in order to quantify the errors due to the imaginary part of δn_m. Here we will give a brief description of the analysis. A detail description and a more general analysis will be published elsewhere. We used standard 2D-Fourier transform techniques (see for example [8]) but incorporating losses in the second half of the cell. First it was propagated to the division slab of the cell and then to the exit plane of the cell at z = 2l. In each step the coordinate axis was rotated as required by the Fourier technique. The electric field at the exit plane was calculated and the maximum was found to be displaced from its position in the lossless case by,

$$\tau = \pi \frac{w^2}{\lambda} \text{Im}(\delta n_m) \tan \chi.$$  \hspace{1cm} (3)

Then, we propagated the transmitted field to the far-field away from the refractometer cell and evaluated the resulting Fourier transform integral with the stationary phase method [8]. Assuming |δn_m| << 1 and a well collimated Gaussian beam, that is, w >> λ. The obtained intensity distribution in the far field is,

$$I(r, \theta, \phi) = I_0 \exp(-\beta k_2^2) \exp \left[ -\beta \left( k_1 - k_0 \text{Re}(\delta n_m) \tan(\chi) - \frac{\alpha}{2\beta} \right)^2 \right].$$  \hspace{1cm} (4)

Where r, θ and φ are spherical coordinates with the origin at the center of the exit slab of the cell and with the polar and azimuthal axes parallel to the z and x axes respectively, 

$$k_1 = k_0 \sin \theta \cos \phi, \quad k_2 = k_0 \sin \theta \sin \phi, \quad \alpha = -6l \left[ \text{Im}(\delta n_m)/n_m \right] \tan(\chi), \quad \beta = w^2/2 \quad \text{and} \quad I_0 = \left| t_1 t_2 t_3 \right|^2 4\pi k_0^2 \cos^2 \theta \left( w^2 E_0/4r^2 \right) \exp[2k_0 \text{Im}(\delta n_m)l],$$

where t_1, t_2 and t_3 are the transmission coefficients of the entrance, middle and exit slabs, respectively. The angle of refraction of the transmitted field in the plane of refraction is found where the argument of the second exponential is zero, that is, where $k_1 - k_0 \text{Re}(\delta n_m) \tan(\chi) - \alpha/2\beta = 0$. On the plane of refraction (φ=0) we find the maximum intensity when $\theta_{max} = \text{Re}(\delta n_m) \tan(\chi) - \alpha/2\beta k_0$. If the angle of refraction is small, we get,

$$\theta_{max} = \text{Re}(\delta n_m) \tan(\chi) - \frac{6l}{k_0 w^2} \frac{\text{Im}(\delta n_m)}{n_m} \tan(\chi).$$  \hspace{1cm} (5)

The maximum of intensity without a sample diluted, that is with δn_m = 0, is at θ = 0. The change in the angle of refraction due to a difference in refractive index is $\Delta \theta = \theta_{max}$. The first term on the right hand side (RHS) of Eq. (5) is the same as in the lossless case, and the second term is a correction due only to the losses, that is, to the imaginary part of δn_m.

4. Errors and possible improvements to differential refractometers

First let us consider the lateral displacement due to the losses given in Eq. (3). In order for this displacement to be small compared to that due to refraction at the detectors plane we must have $\tau << \Delta x$. The relative error is given by $\tau/\Delta x$. Using Eq. (3) and approximating $\Delta x \approx \text{Re}(\delta n_m)L \tan(\chi)$, the latter condition gives,
Let us suppose we can tolerate at most an error of $E_d$, that is, $\tau/\Delta x \leq E_d$. Then we should ensure that $L$ is large enough to reduce the relative error increase below this limit. In this case, Eq. (6) gives, $L \geq \pi w^2 \text{Im}(\delta n_m)/E_d \lambda \text{Re}(\delta n_m)$. Let us suppose a well collimated Gaussian beam with $w = 600 \lambda$ (this corresponds to a typical low-power gas-laser beam). If we can tolerate a maximum error of $E_d \leq 0.005$, we have, $L \geq (2.26 \times 10^8) \lambda \text{Im}(\delta n_m)/\text{Re}(\delta n_m)$. If we suppose $\text{Im}(\delta n_m)$ is of the same order of magnitude than $\text{Re}(\delta n_m)$ and the wavelength is about 0.5 microns, we have that $L$ must be larger than about one meter. If $\text{Im}(\delta n_m)$ is larger than $\text{Re}(\delta n_m)$, then the distance $L$ must be even larger. Clearly this would be too large for a practical bench top instrument. Therefore it is indeed necessary to change the position sensitive detector to an angle sensitive detector. There are few ways to do this (see for example Ref [7] and references therein).

Now, let us consider the error on the change in angle of travel due to the imaginary part of the difference in refractive index. Let us denote the first and second terms on the RHS of Eq. (5) as $\Delta \theta_{NL}$ and $\Delta \theta_e$ respectively. $\Delta \theta_{NL}$ is the change in angle due to the real part of $\delta n_m$ whereas $\Delta \theta_e$ is due to $\text{Im}(\delta n_m)$. Then the relative error due to losses is,

$$\frac{\Delta \theta_e}{\Delta \theta_{NL}} = \frac{3\lambda}{\pi w^2} \frac{\text{Im}(\delta n_m)}{n_m \text{Re}(\delta n_m)}.$$  (7)

This equation actually give us a limit to the size of the refractometer’s cell (2l). Let us suppose for example that the maximum relative error we may tolerate on measuring $\text{Re}(\delta n_m)$ is $E_\theta$. Then we need the RHS of Eq. (7) to be smaller than $E_\theta$. This gives $\text{Im}(\delta n_m)/\text{Re}(\delta n_m) \leq E_\theta \pi n_m w^2/3\lambda$. For instance, if we again suppose $w = 600 \lambda$, and $E_\theta \leq 0.005$, and in addition suppose $n_m = 1.33$ (water) and $\lambda = 0.5 \mu m$, we get $l \leq 5 \times 10^3 \mu m [\text{Re}(\delta n_m)/\text{Im}(\delta n_m)]$. If we want to measure the real part of the refractive index of samples with an imaginary part of its refractive index at most twice the real part, we get $l \leq 2500 \mu m$. This is about 4 times the radius, $w$, of the incident Gaussian beam. This is in principle possible but it is a strong restriction that commercial refractometers do not generally meet.

5. Conclusion

We provided formulas to design a differential refractometer that may handle lossy samples to some extent. It was shown that to handle samples with a refractive index with an imaginary part comparable to its real part it is necessary to replace the position-sensitive detector with an angle-sensitive detector. We also found that there is a limit to the maximum size of the refractometers cell, which should be in the order of a few times the radius of the incident beam.

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References


