On the retrieval of particle size from the effective optical properties of colloids

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1. Introduction

Since many years ago, it has been acknowledged that when an electromagnetic wave is incident on a turbid colloidal medium, an average or “coherent” wave travels through the colloid with an effective wave vector [1]. From this effective wave vector, an effective refractive index, neff of the colloid may be defined. Clearly, the effective refractive index will depend on the physical properties of the colloidal particles, and therefore, its correct measurement could be used to characterize the colloidal particles. This is one of the practical interests on the understanding and use of the effective refractive index of turbid colloids.

Particle sizing is an old problem with a large variety of important applications and has been addressed by many authors over the years [2]. Several techniques have been developed and many commercial apparatus are in the market today. However, all techniques used today are still limited in one way or another and several challenges remain [2]. In particular, turbidimetry techniques are attractive from a practical point of view because the instrumentation and experimental methodology are less complicated than other techniques and they can be used for less diluted colloids [3]. The main limitation of the inversion of turbidimetry techniques is that one needs to know with good precision on the refractive index of the particles in order to estimate correctly the particle size, and is particularly critical when particles are small compared to the wavelength. It is not difficult to show that in turbidimetry techniques one measures the imaginary part of the effective refractive index but not its real part. Measuring the real part of neff in addition to its imaginary part compliments turbidimetric measurements and permits retrieving the size of medium and small particles (with respect to the wavelength of radiation). However, the physical nature of the effective refractive index of colloids remained rather obscure until recently. In Ref. [3] it is shown that the effective electromagnetic response of a colloidal medium is actually non-local and spatially dispersive. The range of non-locality in a colloid is given by the diameter of the particles. It was also shown in Ref. [3] that the non-local dispersion equation for transverse modes in a dilute colloid has a fundamental solution given to a good approximation by the so called van de Hulst formula. This formula was used in the past by several authors, however its non-local origin was not understood at the time, causing in many cases errors or confusion when using it. For instance, when the particle size in the colloid is not very small compared to the wavelength of radiation, the effective refractive index can not be used safely in Fresnel formulas to calculate the coherent reflection coefficients. Therefore, measurements of the effective refractive index of colloids using techniques relying on the measurements of the reflectance of light may incur in large errors.

However, with a few precautions neff may be measured safely by refraction of the coherent wave [4]. Also in Ref. [4], it was shown that it is possible to retrieve the radius and refractive index of colloidal particles from the measurement of the real and imaginary parts of neff per unit of the volume fraction at a single frequency when the particles are moderately sized with respect to the wavelength and the imaginary part of np is smaller than about 10−3 (weakly absorbing particles). In this paper, we extend the methodology proposed in Ref. [4] to highly absorbing particles. Additionally, we analyze the main sources of uncertainty.
2. Sizing dielectric particles from the effective refractive index of colloids

The van de Hulst formula for the effective refractive index at a frequency \( \omega \) of a dilute colloid made of particles of radius \( a \) and refractive index \( n_0(\omega) \), may be written as, 
\[
n_{\text{eff}}(\omega) \approx n_m(\omega) \left( 1 + \frac{2\pi}{k_m} \rho_1 S_0(0) \right),
\]
where \( n_m(\omega) \) is the refractive index of the matrix where the particles are suspended which we assume to be a real quantity, \( k_m = n_m k_0 \) where \( k_0 \) is the wave number in vacuum, \( \rho_1 \) is the number density of particles, and \( S_0(0) \) is the forward scattering amplitude of particles or radius \( a \) at the frequency \( \omega \). In the laboratory, one can measure and control the volume fraction occupied by the particles, \( f \), and not the total number density of particles \( \rho \). These are related by \( f = \rho r V_p \) where \( V_p = 4\pi a^3/3 \) is the volume of one particle. The contribution of the colloidal particles to the refractive index may be written in terms of the volume fraction occupied by the particles as
\[
\Delta n_{\text{eff}} \approx \frac{3}{2} n_m \frac{S_0(0)}{k_m^2} \frac{x^2}{x_m},
\]
where \( x_m = k_m n_m \) is the so-called size parameter of the particles. The effective refractive index increment in Eq. (2) is in general a complex quantity, \( \Delta n_{\text{eff}} \approx \Delta n_{\text{eff}}'^{\prime} + i\Delta n_{\text{eff}}'^{\prime\prime} \). The imaginary part of the effective refractive index of a colloid, \( \Delta n_{\text{eff}}'^{\prime\prime} \), takes into account attenuation of the coherent wave due to scattering and absorption. The scattering losses convert the coherent radiation into diffuse radiation whereas absorption losses convert the coherent radiation into heat.

Let us suppose we have a dilute colloid made of particles of radius \( a \) and real refractive index \( n_0 \), embedded in a homogeneous substance (the matrix) with a real refractive index \( n_m \). Let us define the effective colloid parameters,
\[
x_1 \equiv \frac{\Delta n_{\text{eff}}'^{\prime} + \Delta n_{\text{eff}}'^{\prime\prime}}{f}
\]
and
\[
x_2 \equiv \frac{\Delta n_{\text{eff}}'^{\prime\prime}}{f}.
\]
To see whether we may retrieve \( a \) and \( n_0 \) from the measurement of the effective properties vector, \( \mathbf{x} = (x_1, x_2) \), we can plot curves of \( x_1 \) versus \( x_2 \) for constant \( n_0 \) and different values of \( a \). If these curves are well separated in the \( (x_1, x_2) \)-space, then the inversion of \( n_0 \) and \( a \) is unique and well conditioned. We obtain \( n_0 \) simply by recognizing to which curve the experimental point \( \mathbf{x} \) belongs and \( a \) from its position along the curve. An example is illustrated here in Fig. 1. We plot two curves of \( x_2 \) vs. \( x_1 \) for \( n_0 = 1.7 \) and \( n_0 = 1.8 \) and varying \( a \) at steps of \( \Delta a = 10 \text{nm} \) from \( a = 0 \) to 500 nm, assuming a wavelength of \( \lambda = 635 \text{nm} \). For larger particle radius, both curves tend to the origin and cross each other and the inversion of \( a \) and \( n_0 \) is no longer possible [4].

When the particles absorb light their refractive index is a complex quantity, \( n_p = n_p^\prime + i n_p^\prime\prime \). At a specific wavelength we may view \( n_p^\prime \) and \( n_p^\prime\prime \) as independent variables. In Fig. 1b we compare the curves of Fig. 1a with the same two curves but for particles with an imaginary part of their refractive index of \( n_p^\prime = 0.1 \). Clearly one may not retrieve the value of \( a \) or \( n_0 \) if one does not know that \( n_p^\prime = 0.1 \). In Ref. [4] it was shown that if \( n_p^\prime < 10^{-3} \) we can ignore it and retrieve correctly \( a \) and \( n_0 \) from the measurement of the effective properties, \( \mathbf{x} = (x_1, x_2) \). When \( n_p^\prime \) is larger we cannot ignore it and we have three unknowns in the inverse problem. Therefore, we need at least three effective optical properties of the colloid to solve for the three particle’s parameters.

3. Extended methodology for highly absorbing particles

The imaginary part of the effective refractive index of a colloid, in the dilute regime, is proportional to the so-called extinction cross section of the particles \( C_{\text{ext}} \). We have, \( \Delta n_{\text{eff}}' = f C_{\text{ext}}/2k_0 V_p \) [5]. It is well known that the extinction cross section can be divided as the sum of a scattering and an absorption cross section, that is, \( C_{\text{ext}} = C_{\text{sca}} + C_{\text{abs}} \) [5]. Then, we can split the imaginary part of the effective refractive index in two components, one due to scattering and one due to absorption. That is
\[
\Delta n_{\text{eff}}'^{\prime\prime} = (\Delta n_{\text{eff}}'^{\prime\prime})_{\text{sca}} + (\Delta n_{\text{eff}}'^{\prime\prime})_{\text{abs}}
\]
where \( (\Delta n_{\text{eff}}'^{\prime\prime})_{\text{sca}} = f C_{\text{sca}}/2k_0 V_p \) and \( (\Delta n_{\text{eff}}'^{\prime\prime})_{\text{abs}} = f C_{\text{abs}}/2k_0 V_p \). As already said, the measurement of the coherent transmittance of a collimated beam readily gives \( \Delta n_{\text{eff}}'^{\prime\prime} \), whether it has contributions from scattering or absorption or both.

However, it is also possible to measure the optical absorption by the particles independently of the scattering of the particles. Such measurements are in principle possible by either photothermal techniques [6] or by integrating-cavity techniques [7]. In either case one could determine experimentally what fraction of the coherent beam was absorbed and therefore can determine \( (\Delta n_{\text{eff}}'^{\prime\prime})_{\text{abs}} \). Then, let us define the third effective optical property

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needed in the case of highly absorbing particles as

$$x_3 \equiv \frac{(\Delta n)_{abs}}{f}$$

To see whether the three measurements \(x = (x_1, x_2, x_3)\) are sufficient to determine \(a, n_p, n_i\) in the case of highly absorbing particles, we may plot, using Eq. (2), curves of constant \(n_p\) and \(n_i\) for different values of \(a\) in the \((x_1, x_2, x_3)\) space. If these curves are well separated from each other, it means that the values of \(a, n_p,\) and \(n_i\) may be inverted from experimental measurements. In Fig. 2 we plot the same curves of Fig. 1b but in the three dimensional space \((x_1, x_2, x_3)\). We can appreciate that the four curves are well separated from each other and thus the inversion of the particles’ parameters is unique and well conditioned.

Another example is considered in Fig. 3 for metallic particles. We plot curves of constant \(n_p\) and \(n_i\) varying \(a\) from 0 to 100 nm at steps of 5 nm at a wavelength of \(\lambda = 635\) nm. The values of \(n_p\) and \(n_i\) for each curve are close to those for gold particles at this wavelength.

We can appreciate in Fig. 3 that, again, all the curves are separated from each other, and thus, the inversion of the particle’s parameters is well conditioned and unique in this example. In the next section we point out some aspects on the measurement of \(\Delta n_{eff}\) that need special care.

4. Necessary precautions for the measurements of \(n_{eff}\)

The experimental determination of the effective refractive index of a turbid colloid requires several precautions. First, one must determine \(n_{eff}\) from measurements of the coherent intensity only. Therefore, one must subtract any contribution of diffuse light that may be superimposed to the coherent power collected by the detector. Second, one must bear in mind the non-local origin of the effective refractive index, and this rules out the unrestricted use of common techniques based on reflectance measurements [4]. The imaginary part may be obtained from the measurement of the attenuation of the coherent intensity as it travels through the bulk of the colloid and the real part may be obtained from the measurement of the refractive angle of the coherent component of light at a colloidal interface.

For the determination of the imaginary part of \(n_{eff}\) one must ensure that the transmission coefficients of the coherent light entering and leaving the colloid does not affect the measurement. This is so because we do not have a general and safe way to calculate these transmission coefficients. On the other hand, these transmission coefficients depend also on the real part of \(n_{eff}\) which are to be determined as well. Experimentally, this can be accomplished by measuring the transmittance factor of the coherent beam, as illustrated in Fig. 4a, for two cells of different widths but otherwise identical. The ratio of these two measurements will depend only on the attenuation of the coherent beam on the difference in cell’s widths, and will be independent of the transmission coefficients at the cell’s interfaces.

In an experiment to determine the real part of \(n_{eff}\), one can use the refraction of a well defined optical beam at the interfaces of a colloid. For instance, one may use a prismatic cell filled with the colloid and measure the deflection angle of a beam transmitted trough it. The so called differential refractometer, illustrated here in Fig. 4b, may be particularly convenient for measuring \(\Delta n_{eff}\). The deflection angle will be obtained from the shift in position of the intensity maximum or the intensity “centroid” of the light spot of the coherent beam at some detection plane. For a given optical beam and colloidal prism, one must carefully calculate the lateral displacement and deflection angle of the coherent beam.
transmitted through the colloidal prism, which in general depend on both, the real and imaginary parts of the effective refractive index. For very well collimated beams which start to diffract at distances large compared with the dimensions of the colloidal cell it can be shown that the angle of deflection depends only on the real part of \( n_{\text{eff}} \) [8]. However, one must be careful on subtracting the lateral shift of the beam that occurs as it traverses the prismatic cell with the colloid [8]. If the beam is not so well collimated, as it could be with non-laser beams, the deflection angle may depend also on the imaginary part of \( n_{\text{eff}} \). The latter effect may be thought as being due to uneven attenuation of the coherent beam due to diffraction.

We have already applied the proposed methodology in our laboratory to sizing small glass and polystyrene particles in water. The radii of the particles were in the range between 20 nm and 60 nm. To obtain \( f \) in the colloidal samples we first withdraw a know volume, \( v_0 \), of the colloid with a precision syringe and weight it. Then we let the water evaporate and weight the remaining solids. Knowing the density of water we calculated the volume of evaporated water, \( v_{\text{water}} \), and obtained the volume fraction occupied by the particles in the colloid as \( f = (v_f - v_{\text{water}})/v_0 \). We measured \( \Delta n_{\text{eff}} \) and \( \Delta n_{\text{eff}} \) using a prismatic cell and a rectangular one respectively. We performed the measurements at \( \lambda = 475 \text{ nm} \) using a solid state laser. First we made measurements with pure water and then added the colloidal particles and obtained \( \Delta n_{\text{eff}} \) and \( \Delta n_{\text{eff}} \). We found good agreement between the retrieved particle radii with the proposed methodology and those measured by a commercial apparatus based on dynamic light scattering and with TEM micro-photographs of the colloidal particles. Details of these and other measurements will be published elsewhere. In our measurements the largest experimental relative error was on the determination of the volume fraction occupied by the particles. In the next section we analyze the uncertainty on the retrieval of \( a \) and \( n_p \) arising from the uncertainty on \( f \).

5. Uncertainty on particle sizing due to errors in determining \( f \)

Let us suppose the relative error on the measurements of the real and imaginary parts of the effective refractive index are small compared to the relative error on measuring \( f \). If the three parameters \( x_1 \), \( x_2 \) and \( x_3 \) were obtained for the same colloidal sample, the error in \( f \) is the same for the three measurements and their uncertainties are correlated. The uncertainty on the value of \( x_j \) is given by \( \delta x_j \approx x_j (f/\delta f) \) for \( j = 1, 2 \) and 3. Then we can write, \( \delta x = x (df/df) \), where \( x = (x_1, x_2, x_3) \). Now, when surfaces of constant \( a \) are separated from each other in the \((x_1, x_2, x_3)\)-space, there is a well defined inverse function \( a(x) \). Then, if for a given colloid, we determine experimentally \( x = x \pm \delta x \), the uncertainty in retrieving \( a \) is given by, \( \delta a = Va \cdot \delta x \). In the \( x \)-space, \( Va \) is a vector perpendicular to the surfaces of constant \( a \). Its direction may be found from the cross product of two vectors on that surface, say, \( N = \delta x/\delta n_{\text{eff}} \) and \( M = \delta x/\delta n_{\text{eff}} \). Then we may write, \( \delta a = |Va| \cdot \delta x \). The magnitude of the gradient of \( a \) at \( x \) may be calculated as \( |Va| = da/ds \) where \( ds \) is the distance in \( x \)-space between the surface for particles of radius \( a + da \) and that for particles of radius \( a \) at point \( x \). Now, consider the differential vector in \( x \)-space, \( dx = (\delta x/\delta a) da \). If we project this vector along the direction \( \hat{n}_a \) we get the corresponding value of \( ds \) for a given value of \( da \), that is, \( ds = dx \cdot \hat{n}_a \). Thus, we get, \( da = |(\delta x/\delta a) \cdot \hat{n}_a|^{-1} ds \), and therefore, \( |Va| = 1/|(\delta x/\delta a) \cdot \hat{n}_a| \). Using the formulas just given we may write, the relative uncertainty on the retrieved value of the particle radius due to the uncertainty in the particle’s volume fraction as \( \delta a /a = F (df/df) \), where the factor \( F \) is given by \( x \cdot \hat{n}_a /|\delta a/(\delta x/\delta a) \cdot \hat{n}_a| \). Similar formulas may be obtained for the relative uncertainty on retrieving \( n_{\text{eff}} \) and \( n_{\text{eff}} \). For instance, \( \delta n_{\text{eff}} /n_{\text{eff}} = G (df/df) \) where the \( G \) factor is given by \( G = x \cdot \hat{n}_a /|n_{\text{eff}}/(\delta x/\delta a) \cdot \hat{n}_a| \) and where \( \hat{n}_a \) is the corresponding unit vector of \( n_a = (\delta x/\delta a) \times (\delta x/\delta n_{\text{eff}}) \).

We illustrate in Fig. 5a the normal vector \( \hat{n}_a \) and the tangent vector \( N \) in the 2D-space \((x_1, x_2)\) for the case of dielectric particles. Numerical evaluation of the factors \( F \) and \( G \) in the case of dielectric particles smaller than one wavelength and with low refractive index contrast with the matrix show that these are less than one. In other cases these factors may be smaller or larger than one. In Fig. 5b we plot some values of the \( F \) and \( G \) factors calculated for an example of metallic particles. In this particular example, the magnitude of the factor \( F \) is always less than 0.5, but that of the \( G \) factor is larger than one, meaning that the relative error in retrieving the particle radius will be smaller than that on retrieving the real part of the refractive index of the particles.

Another important source of uncertainty will come in the case of colloids that have a wide size distribution. In the next section we briefly analyze the effect of the size distribution when estimating the size of colloidal particles with the proposed methodology.

6. Polydisperse colloids

The methodology described above assumes a monodisperse colloid, that is, it is assumed that the colloidal particles have a narrow size distribution. We may consider a colloid to be monodisperse when the most probable particle radius, the average particles’ radius, and the radius of a particle with the average volume, are close to each other in terms of the required precision for the size determination. If the size distribution is not narrow, we refer to the colloid as being polydisperse. In this case we will need to perform additional measurements to obtain information on the particle’s size distribution. When particles are not too small it may be enough to perform the same measurements but at other wavelengths.
If the colloid is polydisperse, the effective refractive index may be written as,

\[ n_{\text{eff}}(\omega) \approx n_m(\omega) \left( 1 + \frac{2\pi}{\lambda m} \int_0^\infty \rho(a) n_p(a) da \right), \] (6)

where \( \rho(a) da \) is the number density of particles with radius between \( a \) and \( a+da \). We may write \( \rho(a) = \rho_T n(a) \) where \( \rho_T \) is the number density of all particles regardless of their radius and \( n(a) \) is the size distribution function. In this case the volume fraction occupied by the particles is given by \( f = \rho_T \langle V_p \rangle \) where \( \langle V_p \rangle = 4\pi \langle a^3 \rangle / 3 \) is the average volume of one particle. The average in this case is taken over the size distribution function \( n(a) \), that is, \( \langle \cdot \rangle = \int \langle \cdot \rangle n(a) da \). The refractive index increment in the case of a polydisperse colloid may be written in terms of the volume fraction occupied by the particle, \( f \), as,

\[ \Delta n_{\text{eff}} \approx \frac{3}{2} n_m \langle S_0(0) \rangle \left( \frac{k_0^2}{\langle a^3 \rangle} \right) \] (7)

Therefore, with polydisperse colloids we will actually obtain an equivalent particle radius \( a_e \) and refractive index \( n_{pe} \) that solves the real and imaginary parts of the equation \( S_0(0)/a_e^2 = \langle S_0(0) \rangle / \langle a^2 \rangle \). In general, \( a_e \) will coincide with neither the most probable radius, nor the average radius, nor the radius of the average volume. For instance, for very small particles, it is not difficult to show that we will retrieve an equivalent particle radius that is larger than the average radius and the radius of the average volume. For very small particles we may approximate [5],

\[ S_0(0) = -i/(k_0^2 a^3 + \frac{1}{2} i^2 k_0^2 a^6 + \ldots) \] where \( \beta = (m^2-1)/(m^2+2) \) and \( m \) is the relative refractive index \( n_p/n_m \). Corrections to the imaginary and real parts of the later expansion of \( S_0(0) \) are of order \( O(k_0^2 a^3) \) and \( O(k_0^2 a^7) \), and higher, respectively. For instance, let us suppose a log-normal particle size distribution,

\[ n(a) = \frac{1}{a \sqrt{2\pi \ln \sigma}} \exp \left( \frac{-\ln^2(a/a_0)}{2 \ln^2 \sigma} \right) \] (8)

where \( \sigma \) and \( a_0 \) are the width and particle radius parameters respectively. \( a_0 \) is close but somewhat larger than the most probable radius. Using (8) to calculate \( \langle S_0(0) \rangle / \langle a^3 \rangle \) yields,

\[ \text{Re}(\Delta n_{\text{eff}}) = \frac{3}{2} n_m \beta \] and

\[ \text{Im}(\Delta n_{\text{eff}}) = n_m \beta^2 k_0^2 a_0^3 \exp(2\ln^2 \sigma) \] (9)

Therefore, in this case, the retrieved value of the particles’ refractive index is actually \( n_p \) but the retrieved value of the particles’ radius is \( a_e = a_0 \exp(\ln^2 \sigma) \). We may compare the retrieved equivalent radius with the radius of the average volume: \( a_v = a_0 \exp(\ln^2 \sigma) \). We can see that the equivalent radius

**Fig. 5.** (a) Schematic illustration of constant \( a \) and constant \( n_p \) curves in the \( (x_1, x_2) \) space. The normal and tangent vectors \( \mathbf{n}_a \) and \( \mathbf{N} \) are indicated. (b) Numerical evaluation of the factors \( F \) and \( G \) for metallic particles with \( n_p=0.17+3.1 i \) in water for various values of \( a \).

**Fig. 6.** Log-normal size distribution for \( f=0.02 \), \( a_0=80 \text{ nm} \), and (a) \( \sigma=1.1 \), (b) \( \sigma=1.4 \). The average radius and the radius of the average volume are indicated. Also the equivalent radius retrieved for a colloid of particles with \( n_p=1.6 \) in water \( (n_m=1.33) \) is indicated.
is \( \exp(3\ln^2 \sigma) \) times larger than \( a_v \). Thus, for \( \sigma = 1.1, 1.2, 1.3 \) and 1.4 the retrieved radius is 2.8\%, 10\%, 23\% and 40\% larger than the radius of the average particle volume. Of course, for other size distribution functions the relation between \( a_e \) and \( a_v \) will be different, but in any case, the value of \( a_v \) will be well within the interval of particle sizes, but towards the region of larger particles. For larger particles we can expect \( a_e \) to be closer to \( a_v \) and eventually it could be smaller. As an example, in Fig. 6a and b we show a log-normal size distribution for \( f = 0.02 \) and \( a_0 = 80 \text{nm} \), with \( \sigma = 1.1 \) and 1.4, respectively. We indicate in the figures the average radius, the radius of the average volume, and the equivalent particles' radius retrieved for particles of refractive index \( n_p = 1.6 \) in water.

7. Summary and conclusions

It is possible to retrieve the radius and refractive index of small and moderately sized, weakly absorbing particles, from the measurement of the real and imaginary parts of the effective refractive-index increment \( \Delta n_{\text{eff}} \) per unit volume fraction occupied by the particles. If one also measures the contribution from optical absorption to the imaginary part of \( \Delta n_{\text{eff}} \) it is possible to retrieve the size and complex refractive index of highly absorbing particles. We analyzed the uncertainty on the retrieved parameters due to the uncertainty on determining the volume fraction of the particles and discussed the case when the colloidal particles have a wide size distribution.

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References