Experimental evidence of an effective medium seen by diffuse light in turbid colloids

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Abstract. The propagation of diffuse light in turbid media is usually modeled with radiative transfer theory. When diffuse light travelling in a turbid colloid is reflected and transmitted at a flat interface where there is a refractive index mismatch, it is not clear whether one should assume the incident diffuse-light is travelling in a medium with a refractive index equal to that of the background medium (usually referred to as the matrix) or if one should assume it travels in an effective medium. Most authors simply avoid this issue and most often use the refractive index of the matrix. While this might be a good approximation for dilute turbid media one may suspect that for highly scattering materials it may not be the case. In this work we investigate experimentally this issue. Our experimental results provide clear evidence that diffuse light inside the turbid colloid travels in an effective medium and not in the matrix.

1. Introduction
The problem of propagation and scattering of light in turbid media has attracted the attention of many researchers since many years ago. Many of them have focused on trying to give an explanation to visual phenomena that occur in nature as the colour of the sky, air turbulence, etc… Colloids are of particular interest in many applications. We refer here to a random ensemble of particles embedded in an otherwise homogeneous substance as colloid. Some common examples of turbid colloids are milk, blood and paint.

When light is transmitted through colloidal media it gets multiply scattered at the randomly located particles. After being scattered, light can be split into an average and a fluctuating component. The average component is usually called the coherent component of light and the fluctuating one is referred to as the diffuse component of light. If the size of particles is very small compared to the wavelength of the incident radiation, the diffuse component carry a small amount of power and the whole description of light propagation can be given only in term of the coherent component. However, if the size of the particles is not very small compared to the wavelength of the incident radiation, the power carried by the diffuse component becomes important, giving rise to a turbid appearance of the system.

Different theories have been developed to model the behavior of coherent component of light in dilute turbid colloids such as extended effective-medium theories and coherent wave-scattering theory (e.g. see Ref. [1] and references therein). Recently, the non-local nature of the effective electromagnetic response of turbid colloids has been established, clarifying the origin of some of the inconsistencies and restrictions previously noted in extended effective medium theories [2].
The propagation of the diffuse component of light within an inhomogeneous medium is usually modeled with radiative-transfer theory. Radiative transfer theory relies on an energy balance equation for the specific intensity (or radiance) obtained from the incoherent addition of the incident and the scattered light [3]. The reflection and transmission of diffuse light at the interfaces of an inhomogeneous medium is commonly treated using Fresnel’s relationships assuming the refractive index of the inhomogeneous media is that of the matrix [e.g., see Refs. [4-7]]. The question arises whether one should consider an effective refractive index of refraction when calculating the reflectance of the coherent components of the diffuse light instead of the refractive index of the matrix alone. Also, one may question the validity of the Fresnel relationships in this case. The present paper is motivated in part by the need to provide experimental evidence on this matter. To this end we use as simple experimental setup, previously proposed in [8], where we can observe clearly whether diffuse light exiting a turbid colloid comes from a medium with the refractive index of the matrix or not. In this paper, we report measurements of light intensity profiles of diffuse light refracted at a plane interface showing the dependence of the light’s refraction on the concentration of colloidal particles; such dependence indicates that the transmission of the diffuse light from a turbid medium depends on the presence of the colloidal particles and not on the optical properties of the matrix alone. Our measurements may be used to test possible models of refraction of diffuse light exiting a turbid inhomogeneous medium through a plane interface.

2. Experimental Device

When diffuse light travelling in a transparent medium is transmitted to a transparent medium of higher refractive index, it is confined to a cone around the normal to the interface. The aperture angle of the diffuse-light cone is equal to the critical angle for that interface. If diffuse light comes from a turbid medium and is transmitted to a transparent glass prism, a diffuse-light cone may be observed. The intensity angular-profile defining the borders of the light cone will depend on the refractive index “seen” by the diffuse light within the turbid colloid.

To measure the intensity angular-profile of the refracted diffuse light refracted out of the turbid medium into a glass of higher refractive index we assembled the experimental device shown in Fig 1. We clamped a cylindrical container at the base of a Dove prism made of BK7 (refractive index of 1.51 at $\lambda = 635$ nm). The prism and container were placed on top of a goniometer to allow adjusting the angle of incidence. A laser beam ($\lambda = 635$ nm) is incident on the prism base at an angle several degrees lower than the critical angle between the prism and distilled water. When the container is filled with a turbid suspension of particles in water, part of the laser beam is transmitted into the turbid colloid and part of it is reflected specularly back into the prism. The light transmitted into the cell is multiply scattered between the colloidal particles giving rise to a diffuse radiation traveling in all directions. A large portion of the diffuse light is reflected back into the prism. The directions of propagation of the reflected diffuse light in the prism are confined in a cone. A lens was placed on the exit face of the prism and thus the angular distribution of the light is mapped at the focal plane to a spatial distribution of light intensity. A CCD camera in the focal plane allows us obtain directly pictures of the angular distribution of the diffuse light reflected back into the prism for different concentration of particles. The linear scale on the CCD picture may be converted to an angular scale of the directions of travel of the diffuse light inside the prism using standard optics. The coherent reflected beam is easily blocked out from the light reaching the CCD as depicted in Figure 1.

The idea of the experiment is to observe the border of the propagation cone formed by diffuse light coming out from a colloidal medium and see whether it depends on the concentration of particles. The performed experiments consisted of filling the container with a turbid colloid composed of tridistilled water (matrix medium) and a known volume concentration of highly scattering particles at different concentrations. We used TiO$_2$ (rutile) particles of mean diameter of about 220 nm with a refractive index of about 2.7 and Latex particles of mean diameter of about 450 nm with a refractive index of 1.48. Both types of particles were dispersed in distilled water. A similar experiment was actually performed by G. H. Meeten and collaborators many years ago [9]. However in their configuration light
was incident to the colloidal cell from the side opposite to the prism interface. The configuration we are using here ensures that only diffuse light is refracted into the prism and allows measuring samples with much higher turbidity. The CCD camera allows us to obtain a snap photo of the intensity angular-profile defining the borders of the light cone.

![Experimental setup](image)

**Figure 1.** Experimental setup used to visualize and measure the borders of the propagation cone formed by the diffuse light refracting out from the turbid medium.

A CCD image consists of a matrix of 640 columns and 480 rows of intensity levels (8 bits). Two examples of images of the transition zone defining the border of the angular cone of light are shown in Figures 2a and 2b. To obtain a profile of the angular-intensity distribution around the transition zone, we sum the values of all pixels in a given column (480 pixels) and plot the resulting values versus the number of the column. Figures 2a and 2c correspond to a diluted colloid of about 2% (Latex $f \approx 2\%$). We can appreciate a well defined border of the light cone. Figures 2b and 2d correspond to a denser colloid (Latex $f \approx 10\%$) and we can appreciate a smoother transition at the border of the light distribution.

![Snap photos and intensity profiles](image)

**Figure 2.** Above, snap photos obtained by the CCD camera from the edge of the cone of diffuse light for a volume concentration of particles of a) $\sim 2\%$ and b) $\sim 10\%$. Down, intensity angular-profile obtained by processing snap photos, c) and d) were obtained from a) and b) respectively.
In order to use quantitatively the measured intensity angular-profiles we must transform the horizontal scale in the photographs to an angle-of-travel scale of the light inside the prism, and verify the linearity of the CCD intensity scale.

2.1. Verification of linear response to the light intensity of the CCD
To ensure that measurements made in our experiments are reliable we needed to verify that the response of the CCD camera to the intensity variations is linear. To this end we performed the following test. A laser beam was passed through two linear polarizers with their polarization axes identified. The polarization axis of the second polarizer (the analyzer) was initially aligned with that of the first polarizer. Then, rotating by an angle $\alpha$ the analyzer reduced the intensity of the transmitted beam according to Malus’ law: $I = I_0 \cos^2 \alpha$.

![Figure 3. Scheme of the experimental setup to observe the linearity of the CCD camera.](image)

The output laser beam was projected to a white diffusing surface that scattered light in all directions. The CCD camera was placed in front of the surface in a fixed position, collecting a portion of the reflected diffuse light. A snap photo was taken initially and then successively after the analyzer was rotated at steps of 10°. If the response of the CCD to variations of the intensity is linear, then the registered value at any pixel of the CCD should follow the function $I = I_0 \cos^2 \alpha$ upon rotating the analyzer. We added the pixel values of several columns across the CCD and plotted the resulting value versus the angle of the analyzer $\alpha$. In all cases the graph followed closely Malus’ law. In Figure 4 we show two examples which correspond to columns near the borders of the CCD.

![Figure 4. Plots of the column-integrated intensity levels at the CCD in the experiment depicted in figure 3. The right side shows the plot obtained for a column of pixels near one of the borders of the CCD. The plot on the left side corresponds to a column of pixels at the other border of the CCD.](image)
2.2. Angular scale
Once an intensity profile about the transition zone is registered on the CCD we must establish the relation between the lateral position along the CCD with the angle of travel of light within the prism with respect to the normal to the base of the prism. First we establish a reference value on the scale. This is done by locating the corresponding position on the CCD of the critical angle for distilled water (at this wavelength and for our prism this angle is $\theta = 61.7^\circ$). To locate this angle we fill the container in the experimental device with distilled water and place a white diffusing bottom in the cell to reflect some light back into the prism. In this case we see a sharp border of the light cone on the CCD which permits us to locate clearly the reference angle on the CCD lateral scale. Then, from the focal distance of the lens used in the set up we obtain the relation between a displacement at the focal plane and a change in the angle of travel of the light before it enters the lens. Finally, using Snell’s law and simple geometry, we relate the change in the angle of travel of light outside the prism to the change in the angle of travel inside the prism.

2.3. Materials
Dispersions in distilled water of TiO$_2$ (220 nm in diameter) and latex (450 nm in diameter) particles were prepared to see whether the angular distribution of the diffuse light scattered around the border of the light cone depends on the concentration of particles. The prepared dispersions were vigorously shaken followed by ultrasonication for 5 min to break up aggregates prior to use.

Latex particles dispersions were prepared at the following volume concentrations: ~2, 5, 8, 10, and 12%, and those of TiO$_2$ particles at about 0.3, 0.6, 1.2, 1.7, 2.1 and 2.5% in volume. Latex particles were very stable and TiO$_2$ particles had sedimentation after a few hours; enough time to make the measurements presented in this paper.

![Figure 5](image.png)

**Figure 5.** Intensity angular-profiles for a concentration of Latex and other of TiO$_2$ particles. In both plots shows the profiles measured every minute during a period of 20 minutes for the same concentration.

To test the stability of the colloidal suspensions during the experiments, we the measured intensity profiles around the transition zone for two samples, one of latex particles and the other for TiO$_2$ particles. In Fig. 5 we plot the measured intensity profiles in both experiments at different times over a period of 20 minutes. One can appreciate that during the 20 minutes period the profiles were not altered. Therefore, we conclude that that the particles did not settle while measurements were performed.
3. Experimental results

In Fig 6 we show the intensity angular-profile obtained by the CCD camera around the border of the cone of diffuse light reflected back into the prism for different volume concentrations of latex and TiO₂ particles immersed in tridistilled water. The left-most curves in both figures were obtained with pure water and a light diffusing screen at the bottom of the sample container. One can clearly see a sharp transition in the intensity angular profile. As the particle concentration increases, it is clear that the transition becomes smoother. In the case of the suspensions of latex particles, whose refractive index is closer to that of the water, it is clear that there is displacement to the right of the intensity angular-profile. In the case of TiO₂ particles whose refractive index is much higher than the index of refraction of the water, it is apparent that upon increasing the concentration of particles, the maximum slope in the intensity profile is drastically reduced.

![Intensity angular-profile at the plane focal of the lens of a portion of the edge of the cone of diffuse light for different volume concentrations of TiO₂ and Latex particles.](image)

The refraction laws between transparent homogeneous media of travelling waves predict that the intensity profile, \( I(\theta) \), should be zero for angle larger than the critical angle. The measured profiles shown in Fig. 6 clearly show that this is not the case for the turbid particle suspensions. Therefore we conclude that the diffuse light cannot be assumed to be travelling waves in the matrix (water in this case). We repeated some of the experiments changing the angle of incidence of laser beam at the prism-sample interface to illuminate the container. The position and shape of the profiles obtained were basically unaltered.

4. Conclusions

This experiment shows that the diffuse light transmission at a plane interface depends on the concentration of colloidal particles and not only of the matrix in which they are embedded. From a macroscopic point of view, the fact that light is transmitted outside the cone defined by the critical angle of the water-prism interface can be interpreted as a change in an effective refractive index ‘seen’ by diffuse light which depends on the type and concentration of the colloidal particles. One may argue that diffuse light can be considered as a superposition of many coherent waves which are incoherent among themselves. By coherent wave we mean the average wave over all permitted configurations of the system [1]. On the other hand, it is well known that a coherent wave travelling on a colloidal medium has an effective wave vector and one may define an effective refractive index [1, 8]. Such effective refractive index is in general a complex quantity, even in the absence of optical absorption. (The imaginary part of the effective refractive index in turbid colloids comes also from the scattering and not only from absorption.) Therefore, it appears likely that diffuse light also ‘sees’ an effective refractive index while travelling within a turbid medium. In summary, our experiments provide clear evidence that description of the refraction and propagation properties of diffuse light should consider...
an effective medium. Extensions of the usual radiative transfer models that incorporate such an effective medium should be explored.

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