Absolute values of transport mean free path of light in non-absorbing media using transmission and reflectance measurements

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We derived a relation between the transport mean free path of light, and transmittance and the reflectance in non-absorbing turbid media. This allowed us to develop an experimental procedure to obtain absolute values for the transport mean free path of light just by measuring in an integrating sphere both the transmittance and the reflectance in this kind of system. We determined how accurate our method was by comparing our transport mean free path measurements with calculations made for colloidal suspensions of particles using Mie scattering theory and with measurements made in colloidal suspensions of polystyrene microspheres using diffusive wave spectroscopy. The agreement is excellent.

Keywords: Transport mean free path of light; DWS.

En este trabajo se deriva una relación entre el camino libre medio de trasporte de la luz y la transmitancia y la reflectancia de un medio turbio no absorbente. Esto nos permitió desarrollar un procedimiento experimental para obtener valores absolutos de los caminos libes medio de transporte de la luz con sólo medir, en una esfera integradora, la trasnmitancia y la reflectancia en esta clase de sistemas. Hemos determinado cuán preciso es nuestro método comparando nuestras medidas de camino libre medio de transporte con cálculos efectuados para suspensiones coloidales utilizando la teoría de dispersión de Mie y con medidas hechas en suspensiones coloidales de microesferas utilizando espectroscopia de onda difusa. El acuerdo es excelente.

Descriptores: Camino libre medio de trasporte de luz; DWS.

1. Introduction

Light scattering techniques had been widely used in several fields to extract dynamical and structural information in complex fluids. Initially, these techniques were limited to transparent samples, where single scattering is a good approximation. However, in the past fifteen years, new developments made it possible to take into account multiple scattering, leading to diffusive wave spectroscopy (DWS) [1]. This technique extends the single scattering experiment to multiple scattering assuming that light transport in the sample can be treated as a diffusive process. Using DWS, it is possible to measure the mean square displacement, $\langle \Delta r^2(t) \rangle$, of embedded colloidal particles in a fluid, which makes it possible to obtain the response of viscoelastic materials to shear excitations through the complex shear modulus, $G^*(\omega)$. This modulus determines the stress induced on a material upon application of an oscillatory shear strain at a frequency ω. Normally, $G^*(\omega)$ is determined using mechanical rheometers, where viscoelastic properties are measured by application of strain, while measuring stress or vice versa. This bulk mechanical susceptibility $G^*(\omega)$ also determines the response of colloidal particles embedded in a fluid. These probe particles, excited by thermal stochastic forces, move in Brownian motion along the fluid. [2, 3] $\langle \Delta r^2(t) \rangle$ can be related to $G^*(w)$ by describing the motion of particles with a generalized Langevin equation incorporating a memory function to take into account the viscoelasticity of the fluid where the particles are embedded. In this way, the particle fluctuation spectrum can be used to measure the relaxation spectrum of the fluid. With DWS, there is no strain applied to the material during the measurement. This is a useful characteristic for complex fluids where even small imposed strains can cause structural reorganization of the material and can change its viscoelastic properties.

In a DWS experiment, a laser beam strikes a slab formed by a turbid suspension made of the liquid under study and probe colloidal particles that scatter light. The temporal autocorrelation function of a small fraction of the light that passes through the slab is measured. The transport of light through the slab is treated as a diffusive process and photons are treated as random walkers, with a random walk step length equal to the transport mean free path l^* and a resultant diffusion coefficient $D = vl^*/3$, where v is the speed of light in the suspension. The diffusion approximation is valid for calculating transport of light only over distances much longer than l^* [1]. When scattering is not isotropic, which is the case for particle sizes close to and larger than the photon wavelength, the random walk step length is longer than the photon mean free path length l. These lengths are connected by $l^*/l = 2k_o^2/\langle q^2 \rangle$, where $k_o = 2\pi n/\lambda$ is the photon wave vector in the solvent, λ is the laser wavelength in a vacuum, n is the effective index of refraction in the sample, and $\langle q^2 \rangle$ represents the average angle for the squared scattering vector for a typical scattering event experienced by the photon in the medium.

l^* is a key parameter that enters into the DWS analysis and has to be determined independently. It is usually mea-

sured by comparing the system transmittance with that of calibrated suspensions of latex spheres in water where l^* is known [1,4,5]. There are just a few experimental procedures to determine l^* without using a reference sample. Mitani *et al.* [6] used coherent backscattering, Weitz and Pine [1] used pulsed DWS where l^* is estimated by measuring the delay time of a signal due to the multiple scattering. Garcia *et al.* [7] developed a procedure where microwave radiation power is measured in the forward scattering geometry, using boundary conditions so that reflected waves from an integrating cavity can be neglected.

In this paper, we present a procedure to obtain absolute values of the transport mean free path of light in non-absorbing media made of a colloidal suspension of polystyrene microspheres. In this procedure, the basic issue is to measure the transmission and the reflectance of the colloidal suspension under study using an integrating sphere. We determined how accurate our method was by comparing our results with calculations made for colloidal suspensions of particles using Mie scattering theory and with experimental measurements made in colloidal suspensions using diffusive wave spectroscopy. The agreement is excellent.

1.1. Transport mean free path

In this section, we present the basic equations to obtain l^* from transmittance and reflectance measurements carried out in turbid non-absorbing samples made of colloidal particles dispersed in a fluid, using an integrating sphere as shown in Fig. 1. The system is contained in a rectangular cell with parallel windows. Here, a collimated light of power P^0 is sent to an integrating sphere with an internal Lambertian surface. Light is collected by a detector placed on the wall of the integrating sphere, in the following conditions: one with no sample at entrance and reflectance ports (beam striking directly on the sphere wall), one in transmission geometry (sample at entrance port, shown in Fig. 1) and one in reflection geometry (sample at reflection port). As we shall show from these measurements, by taking into account the transmission and reflectance of the cell walls, it is possible to obtain reliable values of l^*.
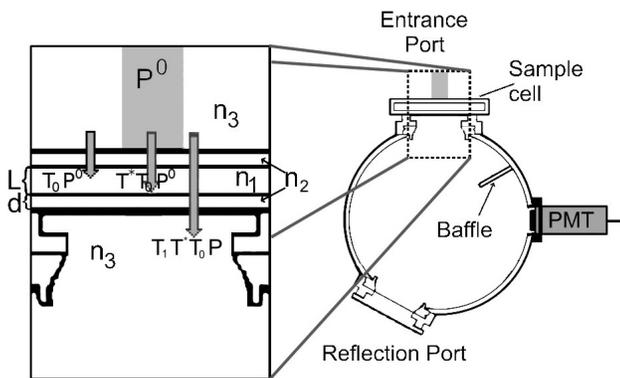

FIGURE 1. Schematic diagram of the integrating sphere with an amplification showing the light transmittances along the cell walls and sample, from outside to the integrating sphere.

1.1.1. Transmittance and reflectance of a fluid sample obtained using an integrating sphere

To obtain the transmittance T^* of a turbid colloidal suspension, we need to analyze the transmission and reflection of light when the suspension is placed in two different configurations: at the entrance port and at the reflection port of an integrating sphere. The transmitted or the reflected light from the sample is multiply reflected by the surface of the integrating sphere before reaching the detector. The collected light is a function of the incident power and of the geometric and reflection parameters of the sphere. Pickering *et al.* [8, 9] studied just this problem, so we shall use their derivation to obtain some of our working equations. For transmittance, the collected power at the detector, P_d^T, is given by:

$$P_d^T = \frac{\delta}{A}\left[\frac{mA_{eff}T_{cd}}{1 - [r\frac{\delta}{A} + mA_{eff} + R_d(s''/A)]}\right]P^{0T}. \quad (1)$$

When the sample is in reflection geometry, light first strikes the integrating sphere, thus, diffuse light irradiates the sample. The collected power, P_d^R, at the detector can be expressed as:

$$P_d^R = \frac{\delta}{A}\left[\frac{m}{1 - [r\frac{\delta}{A} + mA_{eff} + R_d(s'/A)]}\right]P^{0R}. \quad (2)$$

In these equations, P^{0T} and P^{0R} are the incident powers, δ is the area of the detector, m is the reflection factor of the sphere wall, R_d is the diffuse reflection factor of the sample for diffuse incident light, s'' and s' are the areas of the transmission and reflection ports, respectively. A is the total area of the sphere, T_{cd} is the diffusive transmission factor of the sample for collimated incident light (sample including the cell walls), $A_{eff} = 1 - (\delta/A + d/A + h/A)$ is the area fraction of the sphere wall relative to the total sphere area, h is the area of the sphere open holes, and d is s'' or s' depending on the measurement type. A baffle between the entrance port and the detector was considered and the term $r\delta/A$ was not neglected as it was in Pickering *et al.* [8]. Equations 1 and 2 can be rewritten in the following manner:

$$P_d^T = b\frac{A_{eff}T_{cd}}{1 - cR_d}P^{0T}, \quad (3)$$

and

$$P_d^R = b\frac{1}{1 - cR_d(s'/s'')}P^{0R}, \quad (4)$$

where

$$b = \frac{\delta}{A}\left[\frac{m}{1 - [r\frac{\delta}{A} + mA_{eff}]}\right]$$

and

$$c = \frac{s''}{A}\left[\frac{1}{1 - (r\frac{\delta}{A} + mA_{eff})}\right].$$

Solving for T_{cd} in Eq. 3 and substituting R_d using Eq. 4, we obtain the following equation:

$$T_{cd} = \frac{1}{bA_{eff}} \left[1 - \frac{s''}{s'} \left(1 - b\frac{P^{0R}}{P_d^R} \right) \right] \frac{P_d^T}{P^{0T}}. \quad (5)$$

If collimated light, P^0, is allowed to enter the sphere directly, striking the sphere wall, in a geometry where there is no sample in any port ($R_d = 0$), we find using Eq. 4, that $P_d^0 = bP^0$ and

$$T_{cd} = \frac{1}{A_{eff}} \left[1 - \frac{s''}{s'} \left(1 - \frac{P_d^0}{P_d^R} \right) \right] \frac{P_d^T}{P_d^0}. \quad (6)$$

Therefore, if the same incident light is used in all cases, $P^0 = P^{0R} = P^{0T}$, Eq. 6 allows us to obtain, T_{cd} in just one experiment by measuring P_d^0, P_d^T and P_d^R, *i.e.*, the power as measured with the detector at the sphere wall when there is no sample, in transmission geometry and in reflection geometry, respectively.

Some final considerations need to be mentioned, because T_{cd} is the total transmittance through the sample and also through the cell walls. We need the transmittance through just the colloidal suspension alone. Therefore, a correction has to be made. Observing Fig. 1, transmittances along the optical path in the sample are related as $T_{cd} = T_1 T^* T_0$, where T_0 is the transmittance of the first cell wall in the path followed by the light beam. It can be obtained from Fresnel coefficients at normal incidence, producing

$$T_0 = \frac{16m_{13}}{(m_{12} + 1)^2 (m_{23} + 1)^2} \approx 0.95,$$

where $m_{ij} = n_i/n_j$ and n_i are the refractive indices for air (1), cell wall (2), and sample (3). T_1 is the transmittance for diffusive light coming from the sample through the exit cell wall to the sphere. T_1 can be approximated by considering multiple reflections for an infinite non-absorbing slab with a transmittance given by $T_\infty = 1 - R_\infty$. Now, we shall consider an approximation where the ratio of the finite size transverse window reflectance to the infinite slab reflectance is an expression equal to the ratio used for the transmittance, *i.e.*, $T_0/T_\infty \approx R/R_\infty$, since the index of refraction for microemulsions and cell wall are very close. Then, $T_0 \approx (R/R_\infty)(1 - R_\infty)$. An expression for calculating R will be given below in Eq. 16. Finally, using this correction T^*, the actual transmittance just through the colloidal suspension can be calculated and related to l^* as shown in the following paragraph.

1.1.2. *Equations relating T^* with l^**

In this section, a derivation to obtain a relation between T^* and l^* is presented. The suspension sample is considered a slab of infinite transverse extent and thickness L, placed in a static transmission geometry at the front port of an integrating sphere as shown in Fig. 1. Here, laser light is coming into the sample from $z < 0$ direction and some diffuse light passes through the sample. Some light is transmitted to the integrating sphere and some diffuse light is reflected back to the sample. In this configuration, the static transmission coefficient can be calculated within the photon diffusion approximation, modifying the procedure used by Pine *et al.* [3] and by Kaplan *et al.* [10].

The transmission coefficient for the sample can be calculated using the diffusion approximation by dividing the transmitted flux by the total flux:

$$T^* = \frac{|J_+(L)|}{|J_+(L)| + |J_-(0)|}, \quad (7)$$

where $J_\pm$ are the fluxes for the diffusing photons in the $+z$ and $-z$ directions. In the absence of absorption, the photon transport is described by the photon energy density U. Solving the steady-state one-dimensional diffusion equation for the photon energy density $U(z)$, we obtain

$$U(z) = \begin{cases} A_l + B_l z, & z < z_o \\ A_r + B_r z, & z \geq z_o \end{cases}, \quad (8)$$

where $z_o = \alpha^* l^*$, and $\alpha^* \approx 1$. The solution $U(z)$ must be continuous at z_o [10]; therefore,

$$A_l + B_l z_o = A_r + B_r z_o. \quad (9)$$

To define the boundary conditions for the one-dimensional diffusion equation, the net flux on the sample must be considered. At $z = 0$, $J_+(0) = -RJ_-(0)$. Nevertheless, at $z = L$, it is necessary to take into account the diffused light transmitted from the sample to the integrating sphere and reflected back to the sample. Actually, this is the difference between our derivation and Eq. A8 given in Ref.10. We consider two contributions for the $J_-(L)$ calculation: the light reflected at the cell wall, $RJ_+(L)$, and the fraction of light reflected back from the integrating sphere. The last term comprises the light going from the sample through the cell wall, $T_{wo}J_+$, then reflected back from the integrating sphere, $R_{sp}(T_{wo}J_+)$, and re-entering the sample through the cell wall with a transmission coefficient $T_{wb}(R_{sp}(T_{wo}J_+))$. Then, the net calculation produces the actual reflection coefficient:

$$R_{ef} = R + T_{wo}R_{sp}T_{wb}. \quad (10)$$

The boundary condition for the sample at $z = L$ is:

$$J_-(L) = R_{ef}J_+(L) = (R + T_{wo}R_{sp}T_{wb}) J_+(L).$$

The explicit expressions for

$$J_- = \frac{v}{2} \left[\frac{U(0)}{2} + \frac{l^*}{3} \frac{\partial U}{\partial z}(0) \right]$$

and

$$J_+ = -\frac{v}{2} \left[\frac{U(0)}{2} - \frac{l^*}{3} \frac{\partial U}{\partial z}(0) \right]$$

can be used with the boundary conditions at $z = 0$ and $z = L$, to obtain [10]:

$$U(0) - C_0 \frac{\partial U}{\partial z}(0) = 0$$

and

$$U(L) + C_L \frac{\partial U}{\partial z}(L) = 0, \tag{11}$$

where

$$C_0 = \frac{2}{3}\frac{(1+R)}{(1-R)} \quad \text{and} \quad C_L = \frac{2}{3}\frac{(1+R_{ef})}{(1-R_{ef})}.$$

Now, using Eqs. 8, 9, and $J_\pm$ expressions, we obtain the following expressions for the fluxes:

$$J_-(0) = \frac{v}{2}\frac{A_l}{C_0 l^*}\left[\frac{C_0 l^*}{2} + \frac{l^*}{3}\right] = \frac{vA_l}{12C_0}(3C_0 + 2), \tag{12}$$

$$J_+(L) = -\frac{vA_l l^*}{12C_0}\frac{(C_0 + \alpha^*)(3C_L + 2)}{(L + C_L l^* - z_o)}, \tag{13}$$

and

$$J_T = |J_-(0)| + |J_+(L)| = \frac{vA_l}{12C_0}$$
$$\times \left[\frac{(3C_0+2)(y+C_L-\alpha^*)+(C_0+\alpha^*)(3C_L+2)}{(y+C_L-\alpha^*)}\right], \tag{14}$$

where $y = L/l^*$. Finally, the static transmission coefficient is given by:

$$T^* = \frac{(C_0+\alpha^*)(3C_L+2)}{(3C_0+2)(y+C_L-\alpha^*)+(C_0+\alpha^*)(3C_L+2)}. \tag{15}$$

This final expression for T^* depends on α^*, L, and l^* as well as on R and on R_{ef} through C_0 and C_L. As we shall show below, all variables involved in this equation can be measured to obtain l^*. α^* can be obtained through a backscattering experiment, as described in Appendix C, while R is calculated with the procedure given by Kaplan *et al.* [10], using:

$$R = \frac{3C_2 + 2C_1}{3C_2 - 2C_1 + 2}. \tag{16}$$

where

$$C_1 = \int_0^{\pi/2} R(\theta)\cos\theta\sin\theta d\theta$$

and

$$C_2 = \int_0^{\pi/2} R(\theta)\cos^2\theta\sin\theta d\theta.$$

R_{ef} can be calculated using the procedure presented in Appendix A, where the following formula is obtained:

$$R_{ef} = \frac{3D_2 - 2D_1}{3D_2 + 2D_1 + 2}, \tag{17}$$

with

$$D_1 = -C_1 + R_{sp}T_{wb}\int_{\pi/2}^{\pi} T_{wo}(\theta)\cos\theta\sin\theta d\theta,$$

and

$$D_2 = C_2 + R_{sp}T_{wb}\int_{\pi/2}^{\pi} T_{wo}(\theta)\cos^2\theta\sin\theta d\theta.$$

Finally, solving for l^* in Eq. 15 and taking into account the transmittance along the wall cells, we obtain:

$$l^* = \frac{(3C_0+2)T_{cd}L}{(C_0+\alpha^*)(3C_L+2)(T_1T_0-T_{cd})+(C_L-\alpha^*)(3C_0+2)T_{cd}}. \tag{18}$$

This expression is our basic working equation to obtain l^* from experimental data.

2. Experimental section

Materials. Polystyrene microspheres (Bangs Labs Inc, USA) of different diameters were used to prepare the water suspensions and also functioned as microsphere tracers in the DWS experiments to measure l^* . Glass cells were supplied by Hellma GmbH (Germany) and by Starna Cells Inc (USA) with different optical paths (2 mm to 4 mm) and different cross sections (3.0×4.2 mm and 2.8×3.7 mm). Water was milli-Q water (Nanopure-UV, USA; $18.3M\Omega$). Microspheres were added to water while stirring. Water suspensions were usually prepared with volume fractions < 0.04.

Integrating sphere throughput. An integrating sphere (Oriel Newport, USA) was used to obtain l^* in the colloidal suspensions. Here, light detection was carried out by a photo multiplier tube (Hamamatsu Ltd, Japan) attached at the wall sphere. We obtained the integrating sphere throughput by measuring the incident power, P^0, at the front entrance port of the integrating sphere, and then maintaining the laser light power; constant the light power at the detection port of the integrating sphere, P_d^0, was measured. The throughput is $b = P_d^0/P^0$. The integrating sphere is part of the instrument described below.

Transport mean free path, l^*. We measured transmittance and reflectance for the suspensions under study with an integrating sphere as shown in Figs. 1 and 2, where a laser beam ($\lambda = 514.5$ nm) expanded and collimated with a 2 mm pinhole was sent at normal incidence into the entrance port of the sphere. To measure l^*, we followed Eq. (18), where the total transmittance T_{cd} for a sample-cell system was measured, as described in Eq. (6), using the light power collected by the sphere detector in three different cases: when the sample is placed at the entrance port (transmission geometry, P_d^T), when it is placed at the reflection port (reflection geometry, P_d^R), and when there is no sample on any port, P_d^0.
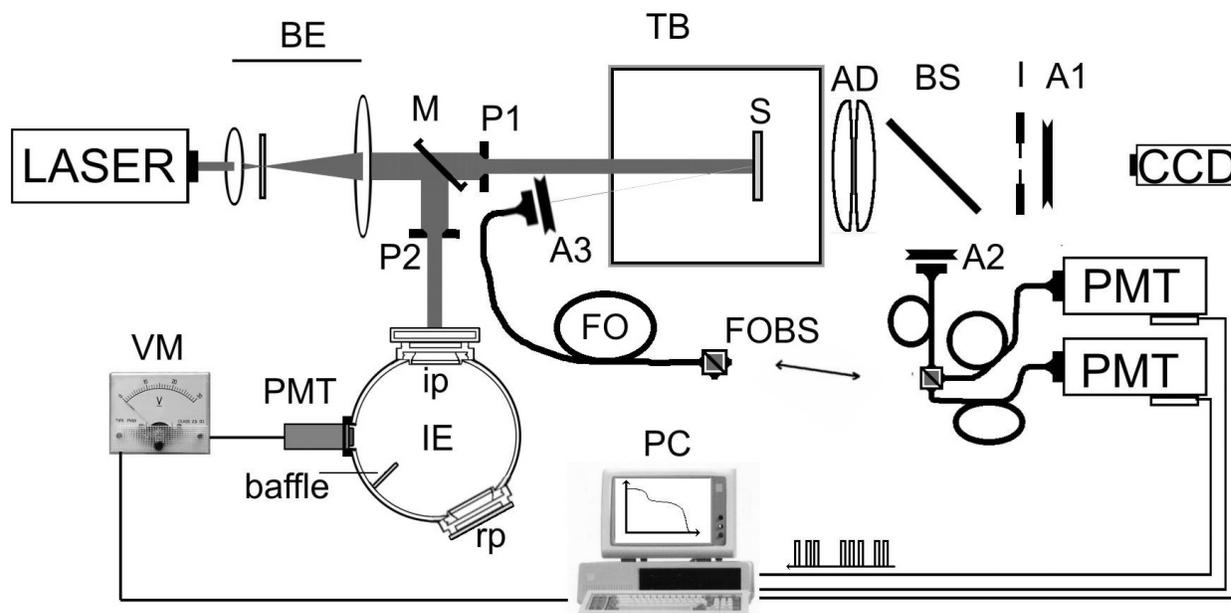
FIGURE 2. Schematic diagram of the DWS instrument. A laser beam is sent through a filter and a beam expander (BE). The beam is deviated by a mirror (M) depending on the experiment. In the case of l^* measurements, the beam is sent into the sample and the scattered light is collected by an integrating sphere. In the case of DWS measurements, the beam is sent into the sample (S) that is in a temperature controlled bath (TB). The scattered light is collected, with the aid of an achromatic doublet (AD) and a beam splitter (BS), by a couple of photomultipliers in cross correlation and by a CCD camera to make multispeckle DWS.

Instrument. The integrating sphere is included in a home-made instrument shown schematically in Fig. 2, which is mainly used to make DWS measurements. A laser beam (Coherent Innova 300, Coherent Inc, USA) is filtered and subsequently expanded to avoid sample heating and to ensure the plane wave approximation. The beam is sent at normal incidence onto a square cell where the colloidal suspensions made with microspheres that multiply scatter light are placed. The scattered light is collected by photomultiplier tubes (Thorn EMI, England) through polarizing maintaining optical fibers from OZoptics Inc (USA). Signals are converted into TTL pulses using ALV preamplifiers (ALV GmbH, Germany) and processed by an ALV/5000E multi-tau correlator (ALV GmbH, Germany) to obtain the intensity ACFs; most of our work was done in transmission geometry.

3. Results and Discussion

We determined l^* for different colloidal water suspensions with the method described in the experimental section. We also determined how accurate our method is for obtaining l^*, comparing our results with other, both theoretical and experimental ones ways to obtain l^*.

In Fig. 3, we present the results of our l^* measurements for water suspensions of latex microspheres at different concentrations using the integrating sphere method that employs Eq. (18); the sizes of the dispersed microspheres were also varied. As may be observed, l^* decreases as $1/\phi$ for the explored concentration range, where ϕ is the volume fraction. From Eq. (B.1) in Appendix B, a necessary consequence

of this concentration dependence is that the structure factor $S(q) \sim 1$ indicates that the interaction among microsphere particles is negligible. The dependence of l^* on particle diameter between 250 and 800 nm is not simple, as previously shown by [4].

To assess the quality of our l^* measurements for colloidal suspensions with microspheres with different sizes, we calculated l^* using Mie scattering theory following the procedures developed by several authors [5, 11, 12] and described in Appendix B. Also, we measured l^* using DWS in transmission geometry for suspensions where the properties of the particles are known. Here, the field autocorrelation function $g_1(\tau)$, was obtained for water suspensions made of particles with a known diameter and refractive index ($n_{mic} = 1.59$ at 514.5 nm), at different particle concentration. $g_1(\tau)$ is related to the $\langle \Delta r^2(\tau) \rangle$ of the particles through the fundamental working equation in DWS [1]:

$$g_1(\tau) = \frac{\frac{L/l^*+4/3}{\alpha^*+2/3} \left[\sinh\left[\alpha^* x\right] + \frac{2}{3}x \cosh\left[\alpha^* x\right] \right]}{\left(1 + \frac{4}{9}x^2\right) \sinh\left[\frac{L}{l^*}x\right] + \frac{4}{3}x \cosh\left[\frac{L}{l^*}x\right]} \quad (19)$$

This equation is valid for the transmission of a plane wave through a slab of thickness $L \gg l^*$ and infinite transverse extent, made of the scattering particles immersed in the liquid. $x = [k_o^2 \langle \Delta r^2(\tau) \rangle]^{1/2}$ and $\alpha^* = z_o/l^*$; z_o is the distance into the sample from the incident surface to the place where the diffuse source is located. Therefore, measuring the intensity correlation function $g_2(\tau)$ allows us to obtain $g_1(\tau)$ through the Siegert relation:

$$g_{(2)}(\tau)_t = 1 + \beta \left| g_{(1)}(\tau)_t \right|^2,$$

where β is an instrumental factor determined by collection optics. However, for microspheres moving in Brownian motion, $\langle\Delta r^2(\tau)\rangle$ can also be evaluated using the Einstein equation for hard-spheres corrected for concentration [13], *i.e.*,

$$D = (k_B T/6\pi\eta_w a)\left(1 - 1.83\phi + 0.88\phi^2\right) = \langle\Delta r^2(\tau)\rangle/6t,$$

where η_w is the water viscosity, a is the microsphere radius, T is the temperature and k_B is the Boltzmann constant. Then, using this $\langle\Delta r^2(\tau)\rangle$ in Eq. 19 and the known values for a and L, we were able to calculate l^* as a free parameter fitting the experimental $g_1(\tau)$ given in Eq. 19 for a DWS experiment.

In Fig. 3, we included the l^* values obtained by using the integrating sphere method, the Mie scattering theory, and the DWS measurements. The agreement between the measured l^* using the integrating sphere and l^* calculated with Mie scattering theory is excellent. There is just a 3.8% mean deviation between theory and experiment, except for the case of the colloidal suspension made with microspheres with a diameter of 620 nm. This is because at this volume fraction the requirement that $L \gg l^*$ is not followed ($L/l^* \sim 8$); in this particular case, the deviation was close to 12% . The mean deviation between the measured l^* using the integrating sphere and DWS was less than 2.5%. From these experiments, it is clear that we have developed a reliable method to obtain l^*.

4.　Conclusion

We have developed a procedure to obtain absolute values of l^* measuring the static transmittance and reflectance of a colloidal suspension using an integrating sphere, and the agreement with values coming from theory or from experiments is excellent.
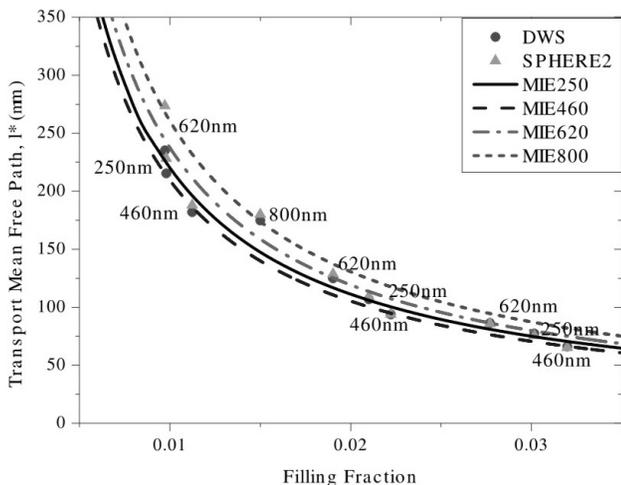

FIGURE 3. l^* for suspensions of polystyrene microspheres in water vs volume fraction. Microspheres of different diameters were used. Circles correspond to DWS measurements (see text), and triangles to measurements obtained using an integrating sphere. Lines were obtained from calculations using Mie scattering theory for spheres embedded in water.

Appendix A. R_{ef} and calculation of $R(\theta)$ and $T(\theta)$

Estimation of R_{ef}

Our derivation starts with expression 3.2 given in Ref. 14:

$$J(\theta) = \frac{v}{2}\left[U(0) + l^* \cos\theta \frac{\partial U}{\partial z}(0)\right]\cos\theta\sin\theta. \quad (A.1)$$

At $z = L$, the only diffusive flux in the $-z$ direction comes from the effective reflected light given by a reflective coefficient R_{ef}. Integrating along all θ for the $+z$ semi-space, we obtain:

$$J_-(L) = -\int_{\pi/2}^{\pi} R_{ef}(\theta)J(\theta)d\theta, \quad (A.2)$$

where

$$R_{ef}(\theta) = R(\theta) + R_{sp}T_{wb}T_{wo}(\theta). \quad (A.3)$$

As shown below, R_{sp} and T_{wb}, do not depend on θ, so they can be treated as constants. Continuity conditions for the energy density allow us to write, at the boundary:

$$\frac{v}{2}\left[\frac{U_0}{2} + \frac{l^*}{3}\frac{\partial U_0}{\partial z}\right] = -\int_{\pi/2}^{\pi} R_{ef}(\theta)J(\theta)d\theta, \quad (A.4)$$

Here, the LHS is the J_- flux in the bulk. Substituting $J(\theta)$ from Eq. A.1 in Eq. A.4, we obtain at $z = L$,

$$U(L) + l^* \frac{\left(\frac{1}{3} + D_2\right)}{\left(\frac{1}{2} + D_1\right)}\frac{\partial U}{\partial z}(L) = 0, \quad (A.5)$$

with

$$D_1 = \int_{\pi/2}^{\pi} R_{ef}(\theta)\cos\theta\sin\theta d\theta$$

and

$$D_2 = \int_{\pi/2}^{\pi} R_{ef}(\theta)\cos^2\theta\sin\theta d\theta.$$

Equation (A.5) is the same as Eq. (11) at $z = L$. Using both expressions we finally arrive at the following expression:

$$R_{ef} = \frac{3D_2 - 2D_1}{3D_2 + 2D_1 + 2}.$$

Calculation of $R(\theta)$ and $T(\theta)$

In Eq. A.3, $R_{ef}(\theta)$ is given in terms of $R(\theta)$ and $T_{wo}(\theta)$. Both terms are estimated considering multiple internal reflections at the cell wall [10] as shown in Fig. 4. Each reflectance

and transmittance is calculated using Fresnel's law [10, 14]. The total reflectance due to the cell wall is given by:

$$R(\theta_1) = R_{12}(\theta_1)$$
$$+ T_{12}(\theta_1)R_{23}(\theta_2)T_{21}(\theta_2)$$
$$\times \frac{1 - (R_{21}(\theta_2)R_{23}(\theta_2))^{N+1}}{1 - R_{21}(\theta_2)R_{23}(\theta_2)} \quad \text{(A.6)}$$

and the total transmittance through the cell wall is given by:

$$T_{13}(\theta_1) = T_{12}(\theta_1)T_{23}(\theta_2)$$
$$\times \frac{1 - (R_{21}(\theta_2)R_{23}(\theta_2))^{N+1}}{1 - R_{21}(\theta_2)R_{23}(\theta_2)}, \quad \text{(A.7)}$$

where $R_{12}(\theta_1)$, $T_{12}(\theta_1)$, $R_{23}(\theta_2)$ and $T_{21}(\theta_2)$ are the reflectances and transmittances at the sample-wall(12) and wall-air (23) interfaces, and

$$N = \left[\frac{D/2}{h}\right] = \left[\frac{D}{4d\tan\theta_2}\right],$$

with D the height and d the thickness of the cell walls. N is included as a cutoff due to the finiteness of the cell transversal extension.

T_{wb}

Now, the transmittance through the cell wall, from the integrating sphere back to the sample, can be obtained using
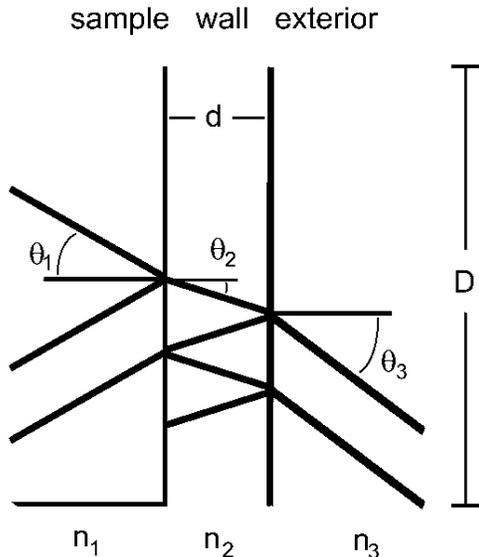

sample wall exterior

FIGURE 4. Diagram showing reflection and transmission emerging beams form the sample at the cell wall. θ_1, θ_2, and θ_3 are the incident angle, transmitted in the cell, and angle transmitted out of the cell, respectively. n_1, n_2, and n_3 are the refraction indices for the water, cell wall and air, respectively. d is the cell wall thickness and D is the sample cell height; beyond this distance multiple reflections are not taken into account.

Eq.(A.7) but now with θ_3 as the incident angle and considering the transmittance from media 3 through media 1.

$$T_{wb}(\theta_3) = T_{32}(\theta_3)T_{21}(\theta_2)\frac{1 - (R_{21}(\theta_2)R_{23}(\theta_2))^{N+1}}{1 - R_{21}(\theta_2)R_{23}(\theta_2)}.$$

If no preferred direction of incidence is assumed, the total transmittance is calculated by integrating over all angles with a constant probability distribution. Therefore:

$$T_{wb} = \frac{1}{2\pi}\int_0^{2\pi}\int_{\pi/2}^{\pi} T_{wb}(\theta)\cos(\theta)\sin(\theta)d\theta d\phi, \quad \text{(A.8)}$$

which does not depend on the angular distribution of $J_\pm$.

R_{sp}

R_{sp} is the fraction of light that enters the integrating sphere and returns to the cell wall. This can be estimated in the same way as in Pickering *et al.* [8]. Light entering the integrating sphere from the sample is reflected many times onto the integrating sphere, detector and sample; also some of the light escapes through the empty ports. Taking this into consideration, the total fraction of light incident on the cell wall is

$$R_{sp} = \frac{s''}{\delta}b\frac{P_d^T}{P_d^{0T}}, \quad \text{(A.9)}$$

where b is a constant for the sphere in the geometry used.

Appendix B. l^* from Mie and Percus-Yevick

Transport mean free path, l^*, is related to the mean free path by [1]:

$$l^* \equiv \frac{l}{\langle 1 - \cos\theta \rangle} = \frac{1}{\rho \langle 1 - \cos\theta \rangle \sigma_{sca}},$$

where θ is the scattering angle, $\langle \rangle$ is the average over all scattering angles, $\rho = \phi/(4\pi a^3/3)$ the number density and

$$\sigma_{sca} = \frac{2\pi}{k_o^4}\int_0^{2k_o} P(q)S(q)q\,dq$$

is the scattering cross section [15] for multiple scattering in the far field. Here, $P(q) = k_0^2(d\sigma_{sca}/d\Omega)$ [11, 12] is the Mie scattering function for a single sphere, $S(q)$ is the static structure function, and $q = 2k_0\sin(\theta/2)$ is the scattering vector magnitude. We can write l^* as

$$l^* = \frac{k_o^6}{\pi\rho\int_0^{2k_o} P(q)S(q)q^3 dq}, \quad \text{(B.1)}$$

where we have used

$$2k_0^2\langle 1 - \cos\theta \rangle = \langle q^2 \rangle = \frac{\int_0^{2k_o} P(q)S(q)q^3 dq}{\int_0^{2k_o} P(q)S(q)q\,dq}.$$

If $P(q)$ and $S(q)$ are known, l^* can be determined using Eq. (B.1). To give an estimate, we calculated $P(q)$ with Mie theory for a *non-absorbing* spherical particle immersed in a non-absorbing medium using:

$$P(\theta) = k_o^2 \sigma_{diff}(\theta) = \pi \left[|S_1(\theta)|^2 + |S_2(\theta)|^2 \right],$$

with

$$S_1(\theta) = \sum_{n=1}^{\infty} \frac{(2n+1)}{n(n+1)}$$
$$\times \left[a_n \pi_n(\cos\theta) + b_n \tau_n(\cos\theta) \right], \qquad (B.2)$$

$$S_2(\theta) = \sum_{n=1}^{\infty} \frac{(2n+1)}{n(n+1)}$$
$$\times \left[a_n \tau_n(\cos\theta) + b_n \pi_n(\cos\theta) \right]. \qquad (B.3)$$

Here, $\tau_n(\cos\theta) = (d/d\theta) P_n^1(\cos\theta)$ and

$$\pi_n(\cos\theta) = \frac{P_n^1(\cos\theta)}{\sin\theta},$$

with $P_n^1(\cos\theta)$ the Legendre polynomials, and a_n and b_n coefficients determined by the boundary conditions.

$S(q)$ can be calculated for a system of hard spheres using Percus-Yevick closure [16], which gives:

$$\frac{1}{S(q)} = 1 + \frac{p_1}{q^3} \sin(2q) - 2q\cos(2q)$$
$$- \frac{p_2}{q^3} \left(\left(\frac{1}{q^2} - 2 \right) q\cos(2q) + 2\sin(2q) - \frac{1}{q} \right)$$
$$+ \frac{\phi p_1}{2q^3} \left[\frac{3}{q^3} + 4 \left(1 - \frac{3}{2q^2} \right) \sin(2q) \right]$$
$$- \frac{\phi p_1}{2q^3} \left[2 \left(1 - \frac{3}{q^2} + \frac{3}{2q^4} \right) q\cos(2q) \right], \qquad (B.4)$$

where $p_1 = \frac{3\phi(1+2\phi)^2}{(1-\phi)^4}$ and $p_2 = \frac{(3\phi)^2}{2} \frac{(2+\phi)^2}{(1-\phi)^4}$.

Appendix C. Estimation of α^*

$\alpha^* = z_o/l^*$ can be estimated using a DWS experiment by fitting the intensity autocorrelation function for the back scattered light from a colloidal suspension made of particles of the same size as those to be used in the fluid to be investigated [4], using the expression:

$$(g_2(t) - 1)_{pol} = \beta \exp\left[-2\gamma_{pol}\sqrt{\frac{6t}{\tau}} \right]. \qquad (C.1)$$

Here, the subscript pol is used to indicate the polarization detection used in the experiment, VV for parallel and VH for cross polarization. Here, $\tau = \left(k_o^2 D \right)^{-1}$ is the relaxation time and D is the diffusion coefficient, and $\gamma_{pol} = \alpha_{pol}^* + 2/3$. As D is known, $\alpha^* \equiv \langle \alpha^* \rangle = (\alpha_{VV}^* + \alpha_{VH}^*)/2$ can be determined from a fitting.

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