Multispeckle diffusing wave spectroscopy of colloidal particles suspended in a random packing of glass spheres

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Received 14 November 2008 and Received in final form 6 February 2009
Published online: 12 June 2009 – © EDP Sciences / Società Italiana di Fisica / Springer-Verlag 2009

Abstract. We use a multispeckle diffusing wave spectroscopy (MSDWS) method to study the ensemble-averaged dynamics of the fluctuating speckle pattern when illuminating colloidal particles suspended in a static and opaque porous medium with a coherent light source. Experiments were performed with Brownian latex particles in a random packing of glass spheres. The mixing of the light scattered by the moving colloidal particles and the porous matrix gives rise to a plateau value of the intensity autocorrelation function in the long-waiting-time limit. From the plateau in the correlation function, we can determine the fraction of light scattered from moving particles and estimate the photon mean free path in the colloidal solution. The method opens up promising possibilities to probe the static fraction in semisolid materials.

PACS. 42.25.Dd Wave propagation in random media – 78.35.+c Brillouin and Rayleigh scattering; other light scattering – 83.80.Hj Suspensions, dispersions, pastes, slurries, colloids

1 Introduction

The property of colloidal matter to scatter light is at the basis of many different ways to study and to characterize colloidal dispersions. Static light scattering (SLS) is a well-established method for determining size, shape and structure of colloidal particles by measuring the intensity as a function of the scattering wave vector \cite{1,2}. The information about the number density of colloidal scatterers can be obtained from the measurement of the transmitted or scattered light flux through a turbid sample with respect to the intensity scattered from a suspension with known optical properties \cite{2}. However, the interpretation of comparative measurements remains particularly challenging as the illumination volume closely depends on sample turbidity. When the colloidal matter is illuminated with coherent enough light, interference effects arise. The analysis of the fluctuating interference pattern is at the basis of Dynamic Light Scattering (DLS) methods with a single point-like detector to probe the motion of colloidal scatterers in optically thin samples \cite{3,4}. Diffusing wave spectroscopy (DWS) extends traditional DLS to the multiple scattering regime by treating the transport of light as a diffusion process \cite{5}. In the case of opaque suspensions and backscattering geometry, the number density of colloidal scatterers weakly influences the dynamics of speckle fluctuations \cite{5}.

We propose in this work a convenient DWS method to measure the fraction of light scattered from moving particles in a static and highly turbid porous medium. The effect on scattered waves of the presence of Brownian particles localized in a opaque medium has been investigated by Heckmeier \textit{et al.} \cite{6,7}. They show that the coherence of the scattered wave is a function of the fraction of photons crossing Brownian particles. In the present work, the Brownian particles are dispersed homogeneously in the porous solid. As the light scattering sample is non-ergodic, different speckles are sampled in parallel by using a Charge Coupled Device (CCD) camera \cite{8–11}. In the present method, the mixing of both scattered and unscattered waves from colloidal particles leads to a non-zero value of the intensity autocorrelation function in the long-waiting-time limit. The fraction of light scattered from moving particles is directly obtained from measurement of the plateau value in the correlation function. So, apart from the characterization of the time scales of the dynamics, multispeckle DWS can also be used to obtain the dynamic fraction of the system and estimate the number density of colloidal particles in a static porous medium. The article is organized in the following way. The next sect. 2 concerns the principle of the method and the
We have represented, in fig. 1b, the scattered field in the complex plane as the summation of the elementary scattered fields. We note $E_f$ (respectively, $E_m$) the partial summation of fixed phasors (respectively, mobile phasors), and $I_f = |E_f|^2$ (respectively, $I_m = |E_m|^2$) the corresponding intensity. The values of the intensities vary with the point at which the detection is considered. Let $(I_f)$ and $(I_m)$ the values of intensities averaged on many different speckle spots. Equation (1) only concerns a single polarization of the scattered light. The extension to an unpolarized scattered light, as observed in the following experiments, is straightforward [14].

We consider now the scattering system at two times separated by a delay $\tau$. The ensemble-averaged intensity autocorrelation function can be written in terms of the electric field correlation function as [3]

$$\langle I(0) \cdot I(\tau) \rangle = \langle I \rangle^2 + \beta \langle |E(0) \cdot E^*(\tau)|^2 \rangle,$$

(2)

where $\langle I \rangle = \langle I_f \rangle + \langle I_m \rangle$ is the ensemble-averaged intensity and $\beta$ is a coherence factor that depends upon the illumination source and the detection optics. As the phases of the constant and fluctuating vectors are uncorrelated, the normalized intensity autocorrelation function $g_2(\tau) = \langle I(0) \cdot I(\tau) \rangle / \langle I \rangle^2$ takes the form [15]

$$g_2(\tau) = 1 + \beta \left( \frac{\langle I_f \rangle + \langle E_m(0) \cdot E^*_m(\tau) \rangle}{\langle I_f \rangle + \langle I_m \rangle} \right)^2.$$

(3)

We introduce the time scale $\tau_m$ such that the colloids move enough that the phases $\phi_m$ of partial waves that encounter a colloid vary $\sim 2\pi$. The time scale $\tau_m$ of such fluctuation is $\tau_m \sim (4DK^2)^{-1}$ [5,12], where $k = 2\pi n / \lambda$ with $\lambda$ the wavelength of light in the medium of refractive index $n$, and $D$ the diffusion constant of particles. For particles of diameter $0.5\mu m$ dispersed in water and light from a 633 nm laser, we obtain a characteristic diffusion time $\tau_m \sim 5$ ms.

After a delay time $\tau$ large compared to the characteristic time $\tau_m$, but small enough that we may indeed consider as fixed a path that do not collide with a colloid particle, the autocorrelation function $\langle E_m(0) \cdot E^*_m(\tau) \rangle$ of the fluctuating electrical field decays to zero. From (3), the normalized ensemble-averaged intensity autocorrelation function then takes a non-zero plateau value in the long-waiting-time limit:

$$g_2(\tau \gg \tau_m) = 1 + \beta F^2,$$

(4)

where $F = \langle I_f \rangle / (\langle I_f \rangle + \langle I_m \rangle)$ represents the ratio of the intensity of light unscattered from colloidal particles over the total scattered light intensity. We see from (4) that the long-time correlation of the scattered light can be interpreted as a measure of the static fraction of the system. Therefore, starting from a porous medium filled with an unscattering solvent and increasing the concentration of the colloidal scatterers, the plateau value $g_2(\tau \gg \tau_m)$ in the correlation is expected to decrease from 1 + $\beta$ to 1. So the measure of the plateau correlation should be related to the concentration $\phi_c$ of colloidal scatterers. We report the discussion of the relationship $F(\phi_c)$ in sect. 4, and detail now the multispeckle DWS experiments.

2 Principle of the experiment

We consider a colloidal solution dispersed into a porous material as represented in fig. 1a. The opaque material is illuminated with a coherent beam and the multiply scattered light is observed in backscattering geometry. The light penetrates into the porous medium, and then follows a succession of scattering events from both the porous matrix and the colloids. A porous medium has been already considered for studying the dynamics of Brownian particles within the pore spaces of the material [5,12,13]. The light scattered from the material may be viewed as the superposition of a large number of fixed (f) and mobile (m) phasors.

relation between the coherence of the scattered wave and the dynamic fraction of the system. In sect. 3, we present multispeckle DWS experiments for a random packing of non Brownian glass spheres filled with a suspension of latex colloidal particles. In sect. 4, we analyze the dependence of the fraction of light scattered from moving particles upon the scattering properties of the porous medium and the concentration of the colloidal suspension. We further compare the results from multispeckle DWS experiments with the theory. Finally, we discuss the utility of the method in sect. 5 and different applications to monitor the ageing of soft complex dispersions.
3 Experimental part

The scattering sample consists of glass microspheres (soda-lime “A” glass with refractive index 1.51, Potters Ballotini) sieved to diameters between 63 μm up to 71 μm (fig. 2) and extensively washed in water. Glass spheres are added in a salt-free solution of monodispersed latex microspheres (Polysciences Europe GmGh) with mean diameter d_c = 0.202 μm or d_c = 1.025 μm (standard deviation 0.01 μm). After settling of glass spheres and removal of the supernatant colloidal solution, the suspension with a solid content of about 0.59 is mixed and poured into a 2 cm square quartz cell of height 4 cm. The cell is placed into a massive metal sample holder with a large heat capacity and thermostated by two side peltier elements at 25 °C with a temperature stability of ±0.05 °C.

A He-Ne linearly polarized laser beam with low power 1mW for preventing heat-induced convection in the sample is directed almost normal to the center of the cell with a Gaussian spot size of 2 mm. A CCD array (Webcam Phillips SPC900NC) with a VGA sensor (640 × 480 pixels) and a maximum frame rate of 60 Hz captures images of the speckle pattern in the backscattering direction. A hole acting as a diaphragm and an interference filter block the parasitic ambient light. The sample-to-camera distance of about 20 cm is adjusted so that the speckle size determined from the spatial intensity correlation function is about 4 to 5 pixels. The scattered light is found experimentally non-polarized, and no polarizing device are present in the detection. The USB Webcam is controlled with the image processing package ImageJ [16] and video frames are analyzed in real time using a custom java plug-in.

The change in the speckle pattern is quantified by computing the ensemble-averaged intensity correlation between frames taken at time t and t + τ for various lag times:

\[ g_2(t, \tau) = \frac{\langle I_p(t) \cdot I_p(t + \tau) \rangle}{\langle I_p(t) \rangle \langle I_p(t + \tau) \rangle} \]

(5)

The exponential distribution function \( P(I_p) \) of pixels intensity is further tuned to distribute the brightness levels over the whole gray level histogram and get a correlation \( g_2(\tau = 0) = 1 + \beta \approx 2 \) between identical frames. One further introduces the normalized intensity correla-

![Fig. 2. Glass microspheres examined under a Hitachi TM-1000 tabletop scanning electron microscope. Note the weak surface roughness of glass spheres on the right higher resolution image.](image)

![Fig. 3. Time evolution of \( g^*(t, \tau) \) for a random packing of glass spheres in pure water and lag times \( \tau = 1 \) s (gray curve) or \( \tau = 10 \) s (black curve). The inset shows the probability density function of \( \delta g^* = g^*(\tau) - \langle g^*(\tau) \rangle \) and the solid line is a Gaussian fit to the data with a variance \( \text{var}(\delta g^*) = 2 \cdot 10^{-6} \).](image)

From (4), the simple expression \( g^*(\tau \gg \tau_m) = F^2 \) is obtained for the plateau correlation in the long waiting time.

After the granular suspension is placed in the cell, the thermalization and the consolidation of the non-equilibrium loose packing of glass spheres in water (mean packing fraction of about 0.59) requires a delay of about 1 hour defined as the initialization time \( t = 0 \). For a wet sediment no longer subjected to significant residual stress, the degree of correlation \( g^*(t, \tau) \) between pairs of speckle images separated by a lag time \( \tau \) takes a constant value close to unity (fig. 3) as expected for static scatterers. The observed dynamics further show no evidence of rearrangement events during a few hours, except small Gaussian fluctuations (see inset in fig. 3) due to the CCD noise and the limited number of pixels. Note that the loose packing of spheres remains static for smooth enough glass spheres (fig. 2) while a temporally heterogeneous dynamics can be observed at long time for rough glass microspheres in water [17].

We have further determined the optical characteristics of light propagation through the packing of glass spheres in pure water. The transport of light through a random porous medium is known [18,19] to obey a diffusion equation [20]. The transport mean free path \( l^* \) inside the multiple-scattering material is determined by measuring the light diffuse transmission though the beads packing as a function of the sample thickness. For this purpose, the beads are placed in a dihedral cell of thickness varying from \( L = 2 \) mm up to \( L = 10 \) mm. The diffuse transmissions are normalized with the diffuse intensity transmitted through a reference polyball sample constituted of monodisperse polystyrene spheres. Figure 4 shows the evolution of the diffuse transmission as a function of the
Fig. 4. Normalized diffuse transmission $T$ through the loose packing of glass spheres in pure water as a function of the sample thickness $L$. Line is the fit from eq. (7).

cell thickness. Data are fitted according to [18,21]

$$T(L) = \frac{l^* (\rho + \gamma)}{L_a} \frac{1}{1 + 2dl^* / L_a} \exp(-L / L_a),$$  (7)

where $L_a$ is the diffusive absorption length, $\gamma$, taken as unity, is the distance expressed in $l^*$ from the boundary at which the diffusion approximation is valid, and $\rho = (2/3)(1 + R)/(1 - R)$ is the reflection coefficient of the diffusing wave, with $R$ the reflection coefficient of the air/glass/water interface. Best fit of experimental data leads to $L_a = 2.68 \pm 0.04$ mm and $l^* = 523 \pm 26 \mu$m.

We are now concerned with the dynamics of the highly turbid packing of glass spheres in a colloidal solution of latex particles. After a delay time of 1 hour, the Gaussian distribution of $g^*(\tau)$ indicates a temporally homogeneous dynamics without any intermittent behavior resulting from weakened contacts between glass spheres in the colloidal solution (fig. 5).

As expected, light scattering from Brownian particles in the static sediment induces a partial decorrelation between pairs of speckle images. In the limit $\tau \gg \tau_m$ of long delay times (i.e. $\tau > 0.1$ s for $d_c = 0.202 \mu$m and $\tau > 1$ s for $d_c = 1.025 \mu$m), the scattering experiments indeed show a stationary plateau in the correlation function (fig. 6). At times $\tau > 100$ s optical stability of the setup and small reorganization of the porous matrix can damage the stability of the plateau. The mean value of $g^*(\tau \gg \tau_m)$ decreases as the latex volume fraction $\phi_c$ increases (fig. 6). The width of the Gaussian distribution of $g^*$ values increases with the loss of correlation between pairs of speckle images. Contrary to [22–24], the width of the distribution depends only on the mean of value of $g^*$, but not explicitly on the delay time $\tau$ (fig. 7). This is because in our experiment the decorrelation occurs mainly at delay times smaller than $\tau = 0.1$, and does not evolve significantly for delay times larger than 0.1 s.

4 Discussion

Experiments clearly show a variation of the mean plateau correlation $g^*(\tau \gg \tau_m)$ in the long-waiting-time limit with

Fig. 5. Time evolution of $g^*(t, \tau)$ for a random packing of glass spheres in a latex solution of volume fraction $\phi_c$. (a) $d_c = 0.202 \mu$m, (b) $d_c = 1.025 \mu$m. Lag times $\tau = 1$ s (grey curves) or $\tau = 10$ s (black curves).

Fig. 6. Mean of $g^*(\tau)$ as a function of the lag time $\tau$ for a random packing of glass spheres in a latex solution of volume fraction $\phi_c = 2 \cdot 10^{-5}$ (circles), $\phi_c = 8 \cdot 10^{-4}$ (squares) and $\phi_c = 2 \cdot 10^{-3}$ (triangles). Latex sphere diameter $d_c = 0.202 \mu$m (open symbols) or $d_c = 1.025 \mu$m (filled symbols). Continuous lines are guidelines to the eye.
is a guideline to the eye.

The path length distribution depends both on the setup geometry and on the scattering properties of the diffusive material. The path length distribution of photons in the scattering material.

The scattering cross-section \( \sigma \) is computed from the Mie theory [25], with a latex refractive index \( n_l = 1.59 \) and a water refractive index \( n_w = 1.33 \). Although this last hypothesis seems reasonable, there is no evidence that the scattering properties of colloidal spheres depend only on the solvent optical properties, and not on the glass spheres optical properties. This assumption will be discussed below.

The determination of the static fraction \( F(l_s) \) from \( P(s) \) already computed for different usual geometries [4,5] under the assumption that the transport of light obeys a diffusion approximation [20]. Extensive calculation may further be avoided by noticing that the integrals in (8) involve the Laplace transform of the path length distribution \( P(s) \)

\[
f(\kappa) = \int_s P(s)e^{-\kappa s}ds,
\]

where \( \kappa \) has the dimension of the inverse of a length. Equation (8) then becomes

\[
F = \frac{\int (\alpha_{l_s} + \kappa_a) \kappa_a}{f(\kappa_a)},
\]

with \( \kappa_c = 1/l_c \) and \( \kappa_a = 1/l_a \).

Fig. 7. Variance of \( g^*(\tau) \) as a function of the mean of \( g^*(\tau) \) for a random packing of glass spheres in a latex solution. Latex sphere diameters are \( d_c = 0.202 \mu m \) (open symbols) and \( d_c = 1.025 \mu m \) (closed symbols). Delay times are \( \tau = 0.1s \) (circles), \( \tau = 1s \) (squares) and \( \tau = 10s \) (triangles). The continuous line is a guideline to the eye.

Fig. 8. Mean of \( g^*(\tau) \) as a function of the volume fraction \( \phi_c \) of latex particles for \( d_c = 0.202 \mu m \) (open circles) and \( d_c = 1.025 \mu m \) (filled squares). Dashed lines are guidelines.
is obtained with metrical optic model. However, we may see on fig. 9 that on the determination of the transport mean free path $l^*$, the Mie scattering theory with a surrounding medium of refractive index $n_w = 1.33$. However, latex spheres are not dispersed in water. For example, the scattering cross-section of a latex sphere touching a glass sphere should be intermediate between the value for a latex sphere in water and the one for a latex sphere in glass. Quantitative evaluation of such effects are clearly outside the scope of this paper. We simply compare the experimental data with the scattering of latex spheres in a homogeneous effective medium of refractive index $n_{eff}$. For an effective refractive index $n_{eff} \approx 1.39$, we have found that scattering lengths $l_c$ of our latex spheres are multiplied by a factor $\approx 1.62$ compared to spheres dispersed in water. For this value, the experimental data are well reproduced using (8-11).

5 Conclusion

A multispeckle DWS method was used to measure the long-time decorrelation of the scattered intensity from moving particles in a porous medium and determine the photon mean free path in the colloidal solution. In the case of a highly scattering porous medium, scattering events from moving particles produce small changes in the distribution of photon path lengths and result in a long-time plateau correlation of the multispeckle pattern. MSDWSS experiments in highly turbid porous media offer the possibility of extending the use of dynamic scattering methods for analyzing either the absorption kinetics of moving particles or changes in the structure of the static medium. A low-sensitivity webcam with a VGA sensor can detect a loss of correlation for a maximum scattering mean free path $l_c \approx 10l^*$ corresponding to a very dilute solution. For less diluted solutions, pairs of speckle images remain partially correlated for a minimum scattering mean free path $l_c \approx 2l^*$.

The use of this method for quantitative measurements needs some information about the light propagation through the porous material. Those information may be obtained, as proposed here, from model of light propagation. Limitations of model may eventually be tackled by experimental characterizations of the porous matrices. Gitting et al. [26] have proposed to characterize the fraction of residence of a photon in the liquid phase of a foam with a monitoring of the absorption of the liquid phase. A calibration of the porous matrix with colloidal solutions of known solid fraction is also possible.

The method opens up promising possibilities to probe the static fraction in semisolid materials and to study the adsorption kinetics of small particles at the surface of a porous material or the drying processes of complex dispersions (paints, varnishes, ...) in a nondestructive way. The growth of a static diffusive interface during paint drying or film formation can also be monitored through the
time evolution of the long-time decorrelation of the multi-speckle pattern in the backscattering geometry.

This work has been supported by ANR grants NT05-4_2012 “MICMAC” and 05-BLAN-0105-01 “SLLOCDYN”.

References