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Rotational diffusion of hard spheres: forward depolarized light-scattering measurements and comparison to theory and simulation

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Abstract. By studying the time-dependence of the depolarized field scattered in the forward direction (zero angle), we have measured the rotational diffusion coefficient of hard-sphere colloidal particles. The results are compared to those we previously obtained by using depolarized dynamic light scattering at finite scattering angle. The experimental concentration-dependence of the rotational diffusion constant is discussed in relation to existing theoretical results and numerical simulations.

1. Introduction

In recent years dynamic light scattering has been used widely for the investigation of the Brownian motion of interacting colloidal particles [1]. Some years ago, the concentration-dependence of the rotational diffusion coefficient D_S^r for spherical particles was calculated to first order in the particle volume fraction Φ [2] and was then measured by our group [3] by using depolarized dynamic light scattering (DDLS) from spherical colloids which present an intrinsic optical anisotropy due to a partially crystalline internal structure [4]. Experimental measurements and theoretical results concerning the Φ -dependence of D_S^r for hard-sphere suspensions have recently been extended to a wide range of volume fractions up to the colloidal crystal region [5].

In this paper we present new experimental results obtained by a totally different approach, based on the heterodyne detection of the fluctuating depolarized component in the transmitted beam (forward depolarized light scattering, FDLS) [6]. The new set of data agrees extremely well with the results obtained by DDLS, showing that FDLS is a promising technique, in particular due to its sensitivity and speed. Moreover, we compare our DDLS and FDLS experimental data to theoretical and numerical simulation results.

2. DDLS from anisotropic particles

We recall that the field scattered by anisotropic spherical particles, when the incident field is linearly polarized in the vertical direction, is the superposition of two terms: the first is a vertically polarized component with amplitude proportional to the optical mismatch between particle and solvent; the second is a depolarized component with amplitude proportional to the particles optical anisotropy, which gives rise to the horizontally polarized scattered field

E_{VH} [4]. The effect of the optical anisotropy on the statistics of the scattered field is that both the phase and the amplitude of the field scattered by each particle become fluctuating quantities, summing up to a zero-mean Gaussian scattered field.

A DDLS experiment performed at a scattering angle θ gives the modulus $|G_{VH}(t)|$ of the normalized correlation function of E_{VH} which, assuming that the orientations of the optical axis of different particles are uncorrelated and that the particle orientation and translation are de-coupled, can be written as

$$|G_{VH}(t)| = F_r(t)F_s(k, t) \quad (1)$$

where $F_s(k, t)$ is the translational self-correlation function (self-dynamic structure factor), \mathbf{k} is the scattering vector with modulus $k = (4\pi n_s/\lambda) \sin(\theta/2)$ and $F_r(t)$ is the rotational self-correlation function, which is the time average of the second Legendre polynomial of the quantity $\mathbf{n}(0)\mathbf{n}(t)$, $\mathbf{n}(t)$ being a unit vector parallel to the particle optical axis. In the case of hard spheres, the de-coupling hypothesis is rigorously true at short times and is expected to be approximately satisfied at all times [5]. Notice that, for scattering angles tending to 0, $|G_{VH}(t)|$ becomes proportional to $F_r(t)$.

In the case of spherical non-interacting particles, the functions $F_r(t)$ and $F_s(k, t)$ are exponential, and

$$|G_{VH}(t)| = \exp[-(k^2 D_0^t + 6D_0^r)t] \quad (2)$$

where D_0^t and D_0^r are, respectively, the translational and rotational diffusion coefficients of a single particle at infinite dilution, so that both the self-translational and the rotational diffusion constant can be determined by measuring $|G_{VH}(t)|$ as a function of k^2 . Although both $F_s(k, t)$ and $F_r(t)$ are in general non-exponential for concentrated suspensions, the first cumulant of the depolarized field correlation function still yields the particle's short-time translational and rotational self-diffusion coefficients [4].

3. Forward depolarized dynamic light scattering

In the last few decades several attempts have been made to analyse the rotational dynamics of suspended particles from the time-dependence of the depolarized light scattered in the forward direction, that is at zero-degree scattering angle (see, for instance, [7–9]).

We have shown recently [6] that careful design of the optical set-up is essential in such an experiment. The transmitted beam can be found by adding to the unscattered field all the contributions in the forward direction from the individual scatterers [10]. A peculiar result of this re-construction procedure is that the forward scattered field is out of phase by $\pi/2$ with respect to the unscattered beam. If the particles are optically anisotropic, an additional fluctuating depolarized contribution to the forward propagating field, again in quadrature with the unscattered beam, is present. Particle orientation fluctuations due to rotational diffusion can then be measured by analysing the time-dependence of the polarization fluctuations of the transmitted beam.

The basic arrangement of such an experiment consists of sending through the sample an incident light beam with a very high degree of linear polarization and isolating the orthogonally polarized scattered intensity by using a crossed polarizer (analyser). A more convenient approach is that of heterodyning the scattered and transmitted beams [6]. If the analyser is set slightly off the crossed position, a small portion of the incident beam reaches the photodetector surface together with the depolarized scattered beam. However, because the phase of the scattered field is shifted by $\pi/2$ with respect to the incident field, no interference can occur between the two fields, unless a quarter-wave plate is inserted

between the scattering cell and the analyser. The role of the quarter-wave plate is to introduce a further $\pi/2$ phase shift between the transmitted and the depolarized scattered fields, so that a heterodyne signal can indeed be generated [6]. Partial mixing can also be obtained even in the absence of the quarter-wave plate due to the non-ideality of the used optical components, such as residual stress birefringence. However, in such a case no control of the reference signal is possible and the amount of heterodyning can fluctuate because of thermal or mechanical instabilities of the set-up. It should be noticed that the introduction of a quarter-wave plate has the additional benefit of allowing one to reduce these parasitic effects greatly [11]. Heterodyne FDLS measurements do not suffer from most of the classical problems of heterodyne optical set-ups: good superposition of reference and signal beams is indeed ensured, mechanical stability is less critical and the level of the reference signal can be carefully controlled. A situation in which heterodyne detection can clearly be preferred to homodyning is when the depolarized scattering signal is very weak. A less obvious advantage is singled out when one is interested in detecting the long-time behaviour of the correlation function. Extracting $|G_{VH}(t)|$ from the intensity correlation function measured by a homodyne measurement means indeed taking a square root, which is a noise-amplifying procedure. On the contrary, the heterodyne intensity correlation function directly yields $|G_{VH}(t)|$. Experimentally, a gain in signal-to-noise ratio seems to be present whenever photon noise is not the dominant noise source, provided that intensity fluctuations of the incident beam are limited. A peculiar feature of the forward scattered field is the following: in the forward direction all contributions to the total scattered field have the same phase, so that the scattered field becomes a random variable with constant phase and Gaussian amplitude. The statistics of the intensity scattered in the forward direction is then no longer exponential, and the usual Siegert relation between the intensity and field correlation functions is modified as follows [6]:

$$\langle I_{VH}(0)I_{VH}(t) \rangle = 1 + 2|G_{VH}(t)|^2. \quad (3)$$

This result is strictly valid only if the incident field is a plane wave. For a more realistic Gaussian beam, a general relation has been found by Ricka [12]. In principle it could be possible to detect this effect by measuring the homodyne correlation function of the scattered field, but in practice the residual transmitted beam in full extinction is always too large to avoid partial heterodyning.

4. Experimental details

We have studied aqueous dispersions of spherical colloidal particles made of a tetrafluoroethylene copolymer (MFA), prepared and kindly donated to us by Ausimont, Milan, Italy. Details on the particle structure have been given in [4]. By using the procedure described in [5], solvent exchange was made in order to prepare the samples under conditions as close as possible to suspensions of hard-spheres, and to match the particle and solvent refractive indices.

The depolarized intensity correlation function was measured for each sample at seven angles ranging from 15° to 135° as in [5]. FDLS measurements were performed by using an optical set-up composed of a low-power He–Ne laser, a Glan–Thompson polarizer and an analyser having an extinction ratio better than 10^{-7} , a mica quarter-wave plate and a scattering cell with very low residual stress birefringence. Despite the very high rejection of the incident polarization, the incident beam power had still to be attenuated down to about $100 \mu\text{W}$ to avoid excessive count rates. For the same reason and to allow for large count rates, detection was made by using a fast H5783P Hamamatsu photomultiplier and a

high-speed discriminator. The analyser was offset from extinction by a small angle, which was trimmed, depending on the amount of depolarized scattering from each sample, to give a signal-to-reference ratio in the range 10^{-2} – 10^{-3} .

The depolarized field correlation functions $|G_{VH}(t)|$ obtained for two samples at similar particle volume fraction by FDLS and by DDLS (at scattering angle $\theta = 15^\circ$, for which the translational contribution to the decay of $|G_{VH}(t)|$ is negligible) are compared in figure 1. The data suggests that it is possible to follow the decay of $|G_{VH}(t)|$ for about half a decade more by FDLS than by DDLS, even if the accumulation time used for FDLS (300 s) is about one third of that used in the DDLS measurement. FDLS shows moreover a greater sensitivity, allowing one to perform measurements with short accumulation times on very diluted samples which gave a very low count rate with DDLS. However, it should be noticed that FDLS measurements, despite their better sensitivity and statistics, suffer sometimes from slow fluctuations of the reference signal which could be due to changes in the laser output, convection in the cell or weak thermal effects on the polarization optics. Other serious effects are due to dust, which is a relevant problem for measurements in the forward direction. Finally, due to the fact that the scattered intensity is only a very small fraction of the total detected intensity, short-time-scale distortions of the correlation function due to photomultiplier after-pulses could be another drawback of heterodyne measurements.

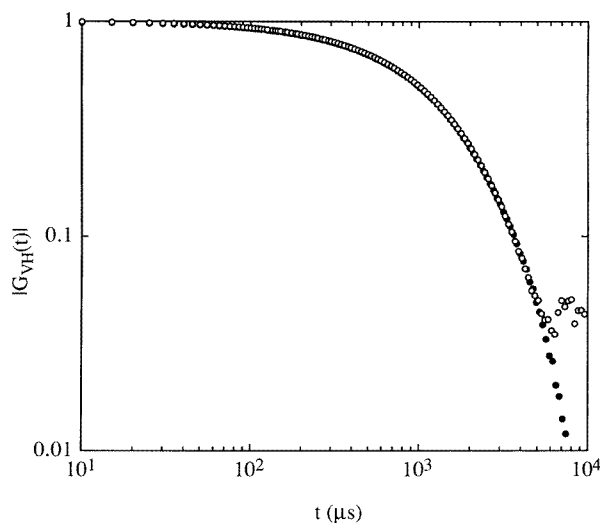


Figure 1. The normalized time-dependent part of the FDLS (full dots) heterodyne correlation function, compared to the normalized field-correlation function extracted from a DDLS measurement at a scattering angle $\theta = 15^\circ$ (open dots). Both measurements refer to MFA suspensions at a particle volume fraction $\Phi \approx 0.1$.

5. Comparison with theory and simulations

The rotational self-diffusion coefficient D_S^r measured by FDLS as a function of particle concentration is compared in figure 2 to the results obtained by DDLS. It can be seen that the two methods yield very similar results, although, presumably for the reasons presented above, FDLS data present a larger statistical uncertainty. Notice, however, that, because of the reduced number of measurements and the reduced need for data analysis, FDLS results

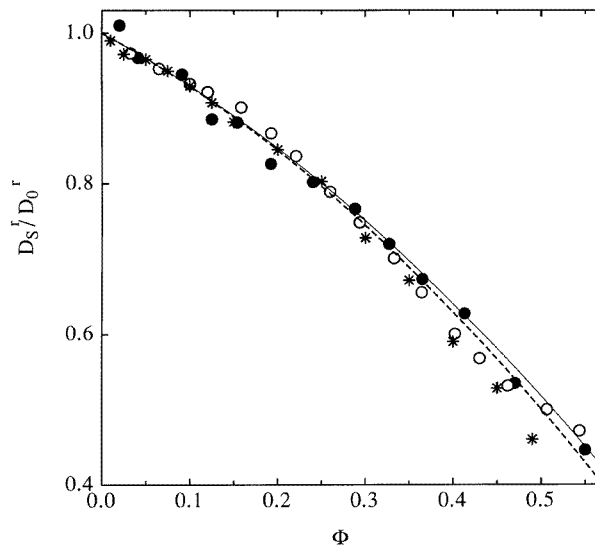


Figure 2. The Φ -dependence of the short-time rotational self-diffusion coefficient D_S^r , normalized with respect to its dilute limit D_0^r . Full dots and open dots are the results of FDLS and DDLs measurements respectively. The full line and the broken line are the theoretical results of [5] and [13] respectively. Stars show the numerical simulation results of [14].

were obtained in a much shorter time than were DDLs data. The concentration-dependence of the rotational diffusion constant has been calculated up to order Φ^2 by Clerx and Schram [13] and, starting from the generalized Smoluchowski equation, in [5]. The two approaches yield very similar expressions for the coefficients of the virial expansion of D_S^r , giving

$$D_S^r = D_0^r(1 - 0.63\Phi + H_2^r\Phi^2) \quad (4)$$

where $H_2^r = -0.74$ in [13] and $H_2^r = -0.67$ in [5].

Without recalling here all the calculation steps in [5], we only try to single out some physically meaningful aspects of the theory. At variance with that which is found for translational diffusion, for which the Φ^2 term is only a small correction to a large negative Φ term, the Φ^2 coefficient in the virial expansion for D_S^r is large and negative. This is because, in the case of translation, a large negative two-body contribution to the Φ^2 term is more or less compensated by a large positive three-body contribution. Rotations, however, are mainly affected by hydrodynamic interactions near contact, so that three-body effects play a much lesser role.

Figure 2 shows that the experimental data conform to a reasonable degree to the results of [5, 13], although the more accurate DDLs data seem to imply that D_S^r decreases more than predicted at large Φ , in particular if we notice that comparison should be limited only to $\Phi < 0.5$, that is in the colloidal fluid phase. In figure 2 we also compare the experimental data to numerical simulation results by Phillips *et al* [14], which were obtained by a Stokesian dynamics approach. This method allows for far-field many-body interactions, while short-range lubrication forces are treated using a pairwise additivity approximation. In spite of the fact that the validity of this approach has been questioned by some authors, figure 2 shows that the agreement between the results in [14] and DDLs data is very good. We also found a similarly good agreement for the translational self-diffusion coefficient.

6. Conclusions

We have shown that forward depolarized light scattering can be profitably used to study the rotational dynamics of optically anisotropic particles in solution. In particular, compared with DDLS, the full concentration-dependence of D_S^r can be obtained in a much shorter time with only a slightly reduced accuracy. The accuracy of FDLS data can presumably be increased by using a better stabilized source, improved thermal control of the optical set-up and, in order to allow for a higher incident intensity, a fast real-time analogue correlator. Both FDLS and DDLS results compare reasonably well with the theoretical predictions, and an extremely good agreement is found between DDLS data and the existing numerical simulation results.

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