

Measurement of the short-time self-diffusion coefficient in dilute and concentrated suspensions: Influence of direct particle interactions

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(Received 28 April 1987; accepted 2 July 1987)

The short-time self-diffusion coefficient of two types of monodisperse colloidal particles differing only in interparticle interactions were measured by dynamic light scattering both in dilute as well as in concentrated dispersions. The results indicate that the short-time self-diffusion is remarkably insensitive to direct particle interactions. The dependence on concentration is in good agreement with the theoretical predictions.

I. INTRODUCTION

By means of dynamic light scattering (DLS) various aspects of the diffusive motions of colloidal particles can be probed. These motions, which arise from the Brownian impacts of the solvent molecules, are influenced both by direct and hydrodynamic interparticle interactions. This makes the calculation of the diffusion coefficients of colloidal particles a challenging many-body problem of considerable complexity in statistical mechanics and hydrodynamics which has received ample attention in recent years (for a review see Ref. 1).

In this paper we report DLS measurements of the short-time self-diffusion both for dilute as well as concentrated dispersions (volume fractions up to 0.45). In order to measure the short-time self-diffusion, which involves the motion of a single colloidal particle over distances small compared to the particle radius a , DLS measurements have to be made at values of the scattering vector q larger than those at which significant oscillations occur in the static structure factor. This means $qa \gg 12$ thus necessitating the use of relatively large particles ($a \gg 0.4 \mu\text{m}$). Concentrated dispersions of such large particles tend to be very turbid and so light scattering measurements are complicated by multiple scattering. By closely matching the refractive index of the solvent to that of the particles highly concentrated dispersions that are relatively transparent, can be prepared. However, this matching of the refractive index—that is required for high volume fractions, makes it difficult to perform DLS measurements on dilute systems, especially since we are operating at values of qa where the single particle form factor is small.

One of the principal difficulties in comparing experimental data with theoretical predictions is the determination of the “hard sphere” volume fractions. In earlier work on short-time self-diffusion where polymer colloids were used this was indeed a major concern.²⁻⁴ In this work we used silica particles, which, unlike most latex particles, do not swell and therefore we were able to determine the volume fraction rather accurately.

In order to assess the effect of particle interactions on the short-time self-diffusion coefficient we used two types of silica particles, differing only in stabilizing coating. One type is uncharged and may be assumed to behave as nearly hard spheres, whereas the other type of particle carries a residual

charge giving rise to a long-range soft repulsion. Surprisingly, we found that the difference in particle interactions hardly affected the short-time self-diffusion coefficient.

In the next section we briefly review the connection between the various diffusion properties of colloidal particles and DLS measurements. In Sec. III we describe the sample preparation and DLS procedure followed to obtain data both for dilute as well as concentrated systems. The results are presented in Sec. IV and a general discussion is given in the final section.

II. THEORETICAL BACKGROUND

A. Brownian diffusion properties of colloidal particles

The Brownian diffusion of colloidal particles is the consequence of irregular motions to which these particles are subjected and which find their origin in the thermal motion of the molecules of the medium in which the particles are dispersed.^{1,5} A quantitative measure of diffusion is the mean square displacement $\langle \Delta r^2(t) \rangle$ of the particles as a function of time. For independent colloidal particles the mean-square displacement is linear in time for times larger than the relaxation time of the Brownian fluctuations in their velocities. For spherical particles this time scale is of the order $\tau_B = m/6\pi\eta a$, where a is the particle radius, m its mass, and η the shear viscosity of the solvent. For times larger than τ_B the mean square displacement of an independently diffusing particle is given by the well-known result⁶

$$\langle \Delta r^2(t) \rangle = 6D_0 t, \quad t > \tau_B. \quad (1)$$

Here D_0 is the single particle diffusion coefficient

$$D_0 = k_B T / 6\pi\eta a, \quad (2)$$

where k_B is Boltzmann's constant and T is the absolute temperature.

However, when the dispersion is not dilute both the direct interactions as well as the hydrodynamic interactions between the particles will influence the mean square displacement. These interactions depend on the particle configuration. Therefore, the diffusion characteristics change with the particle configuration. This changing of the particle configuration will be felt on a time scale where a particle diffuses over its interaction length. For hard sphere particles this time scale is $\tau_I = a^2/D$; here D is of the order of D_0 .

The mean-square displacement is now linear both for

“short” times $\tau_B \ll t \ll \tau_I$ and for “long” times $t \gg \tau_I$, however with different proportionality constants, i.e., different diffusion coefficients. Denoting the short- and long-time self-diffusion coefficients by D_s^{short} and D_s^{long} we can write

$$\langle \Delta r^2(t) \rangle = 6D_s^{\text{short}}t \quad \tau_B \ll t \ll \tau_I, \quad (3)$$

$$\langle \Delta r^2(t) \rangle = 6D_s^{\text{long}}t \quad t \gg \tau_I. \quad (4)$$

In general $D_s^{\text{long}} < D_s^{\text{short}}$ indicating that the changes in the particle configuration on average give rise to a hindering of the motion of the diffusing particles.

In the case of a system with macroscopic gradients in the concentration of the colloidal particles the irregular Brownian movements to which the particles are subjected bring about a gradual transfer of particles from regions of high concentration to regions of low concentration. This process can be described by the diffusion equation

$$\frac{\partial \rho}{\partial t} = D_c \nabla^2 \rho, \quad (5)$$

where ρ is the (number) density of the colloidal particles and D_c is the collective diffusion coefficient. In the limit of infinite dilution $D_c = D_0$. As in the case of self-diffusion the collective diffusion coefficient in nondilute dispersions is influenced by direct and hydrodynamic interactions.

B. Diffusion and dynamic light scattering

By dynamic light scattering on a monodisperse suspension of colloidal particles one can determine the dynamic structure factor $F(q,t)$ of the colloidal particles:

$$F(q,t) = \frac{1}{N} \left\langle \sum_{j,l=1}^N \exp\{iq \cdot [\mathbf{r}_j(t) - \mathbf{r}_l(0)]\} \right\rangle. \quad (6)$$

From the temporal evolution of this function information about the Brownian diffusion of the colloidal particles can be obtained. Specifically, the time derivative of the dynamic structure factor is closely related to the diffusion coefficient. Indeed one can define an effective diffusion coefficient as follows:

$$D_{\text{eff}}(q) = -\frac{\dot{F}(q,0)}{q^2 F(q,0)} = -\frac{\dot{F}(q,0)}{q^2 S(q)}, \quad (7)$$

where $S(q)$ is the static structure factor.

On the time scale we are considering here, i.e., $t \gg \tau_B$ the dynamics of the colloidal particles can be described by the N -particle Smoluchowski equation⁷

$$\frac{\partial P(\mathbf{r}^N, t)}{\partial t} = \sum_{i,j=1}^N \frac{\partial}{\partial \mathbf{r}_i} \cdot \mathbf{D}_{ij}(\mathbf{r}^N) \times \left[\left(\frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_j} \right) \frac{P(\mathbf{r}^N, t)}{k_B T} + \frac{\partial P(\mathbf{r}^N, t)}{\partial \mathbf{r}_j} \right]. \quad (8)$$

Here $P(\mathbf{r}^N, t)$ is the probability that the N particles in the suspension adopt the configuration $\mathbf{r}^N(\{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$ their Cartesian coordinates) at time t , $U(\mathbf{r}^N)$ is the interparticle potential and $\mathbf{D}_{ij}(\mathbf{r}^N)$ is the generalized diffusion tensor, which is related to the mobility matrix by the generalized Einstein relation

$$\mathbf{D}_{ij} = k_B T \mathbf{b}_{ij}. \quad (9)$$

Using the N -particle Smoluchowski equation the time deriv-

ative appearing in Eq. (7) can be calculated and one obtains

$$D_{\text{eff}}(q) = \frac{1}{NS(q)q^2} \times \sum_{j,l=1}^N \langle \mathbf{q} \cdot \mathbf{D}_{jl} \cdot \mathbf{q} \exp\{iq \cdot [\mathbf{r}_j(0) - \mathbf{r}_l(0)]\} \rangle. \quad (10)$$

In the limit q large, i.e., well beyond the oscillations in the structure factor Eq. (10) simplifies considerably because

$$\lim_{qa \rightarrow \infty} S(q) = 1 \quad (11)$$

and further the terms $j \neq l$ in the summation on the right-hand side of Eq. (10) go to zero leaving only the N (equivalent) terms $j = l$. Thus we obtain

$$\lim_{qa \rightarrow \infty} D_{\text{eff}}(q) = \frac{\langle \mathbf{q} \cdot \mathbf{D}_{11} \cdot \mathbf{q} \rangle}{q^2}. \quad (12)$$

This is precisely the short-time self-diffusion coefficient. Thus

$$D_s^{\text{short}} = \lim_{qa \rightarrow \infty} \left(-\frac{\dot{F}(q,0)}{q^2 F(q,0)} \right) = k_B T \frac{\langle \mathbf{q} \cdot \mathbf{b}_{11} \cdot \mathbf{q} \rangle}{q^2}. \quad (13)$$

In the limit q small, i.e., such that we may replace the static structure factor by its value at $q=0$ and set the term $\exp\{iq \cdot [\mathbf{r}_j(0) - \mathbf{r}_l(0)]\}$ in the right-hand side of Eq. (10) equal to 1 we obtain

$$\lim_{qa \rightarrow \infty} D_{\text{eff}}(q) = \frac{1}{NS(0)q^2} \sum_{j,l=1}^N \langle \mathbf{q} \cdot \mathbf{D}_{jl} \cdot \mathbf{q} \rangle. \quad (14)$$

This corresponds to the collective diffusion coefficient. Thus,

$$D_c = \lim_{qa \rightarrow \infty} \left(-\frac{\dot{F}(q,0)}{q^2 F(q,0)} \right) = \frac{k_B T}{NS(0)q^2} \sum_{j,l=1}^N \langle \mathbf{q} \cdot \mathbf{b}_{jl} \cdot \mathbf{q} \rangle. \quad (15)$$

Finally we note that also the long-time self-diffusion coefficient D_s^{long} can be obtained from DLS measurements.^{8,9} One then has to work with a bidisperse suspension consisting of two kinds of particles that only differ in scattering power. In that case the measured dynamic structure factor $F^M(q,t)$ can be written as

$$F^M(q,t) = (1-x)F(q,t) + xF_s(q,t). \quad (16)$$

Here

$$x = \frac{\bar{f}^2 - \bar{f}^2}{\bar{f}^2}, \quad (17)$$

with \bar{f} the average scattering amplitude and \bar{f}^2 the mean-square scattering amplitude. Further $F_s(q,t)$ is the self-dynamic structure factor, which is defined as

$$F_s(q,t) = \langle \exp\{iq \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)]\} \rangle. \quad (18)$$

Now the long-time self-diffusion coefficient can be obtained from the self-dynamic structure factor in a way similar to the extraction of D_s^{short} and D_c from the dynamic structure factor:

$$D_s^{\text{long}} = \lim_{qa \rightarrow 0} \left(\frac{\dot{F}_s(q,t)}{-q^2 F_s(q,t)} \right) \left(t \gg \frac{a^2}{D} \right). \quad (19)$$

Thus, we see that, whereas D_c and D_s^{short} can, under appropriate conditions, be obtained from DLS measurements on monodisperse suspensions, D_s^{long} can only be obtained by light scattering on a properly prepared bidisperse suspension.

C. Theoretical results for the short-time self-diffusion coefficient

In order to calculate the short-time self-diffusion coefficient from Eq. (13) one has to know the configuration-dependent mobility function $\mathbf{b}_{11}(\mathbf{r}^N)$. This quantity can be considered as a sum of one, two, three, etc. particle contributions

$$\mathbf{b}_{11}(\mathbf{r}^N) = \mathbf{b}_{11}^{(1)} + \sum_{j=2}^N \mathbf{b}_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_j) + \sum_{\substack{j,k=2 \\ j \neq k}}^N \mathbf{b}_{11}^{(3)}(\mathbf{r}_1, \mathbf{r}_j, \mathbf{r}_k) + \dots \quad (20)$$

The one-particle contribution is of course the inverse of the well known Stokes friction factor

$$b_{11}^{(1)} = 1/6\pi\eta a. \quad (21)$$

For the relevant hydrodynamic two sphere mobility functions both analytic expressions as well as numerical results are available. These results have been reviewed by Batchelor¹⁰ and recently Jeffrey and Onishy¹¹ have provided further accurate analytical results on the hydrodynamic interaction between two spheres. Averaging the relevant two particle mobility functions over the two-particle distribution function to lowest order in the density one obtains the first-order correction in the volume fraction ϕ to D_s^{short} . This contribution was first calculated by Batchelor¹⁰ who obtained

$$D_s^{\text{short}} = D_0(1 - 1.83\phi). \quad (22)$$

The correction term in ϕ^2 contains two distinct contributions: (i) the appropriate two-body hydrodynamic mobility function averaged over the second-order density contribution of the two-particle distribution function and (ii) the relevant three-body hydrodynamic mobility function averaged over the lowest-order density contribution of three particle distribution function. This calculation was performed by Beenakker and Mazur¹² using hydrodynamic mobility functions to order $(a/r)^7$ in the interparticle distance r . They obtain

$$D_s^{\text{short}} = D_0(1 - 1.73\phi - 0.93\phi^2 + 1.80\phi^3), \quad (23)$$

where the first of the two terms of order ϕ^2 is due to two-body hydrodynamic interactions, while the second one results from three-body contributions. The difference in the contribution to order ϕ in Eqs. (22) and (23) is due to the fact that in obtaining Eq. (22) accurate numerical values for the two sphere hydrodynamic mobility functions were used whereas Eq. (23) was obtained using analytical results to order $(a/r)^7$. The higher terms in the density expansion are very difficult to calculate. Using a special summation technique Beenakker and Mazur^{13,14} succeeded in taking into account the many-body hydrodynamic interactions between an arbitrary

number of spheres and obtained numerical values for the self-diffusion coefficient up to volume fractions of 0.45.

III. EXPERIMENTAL

A. Sample preparation

Short-time self-diffusion coefficients were measured in two types of dispersions, both containing silica particles of 440 nm radius, differing only in stabilizing coating. First, monodisperse spherical silica particles were synthesized according to the method of Stöber.¹⁵ A new type of coating reaction, recently developed in this laboratory, was applied to these particles. Basically it consists of a reaction between the surface silanol groups and 3-methacryloxypropyltrimethoxysilane (here called TPM).¹⁶

Due to the milder reaction conditions, silica particles coated with TPM are optically much more homogeneous than silica particles coated with stearylalcohol (frequently used in this laboratory as hard sphere model systems¹⁸), which are slightly optically inhomogeneous at the periphery.^{17,18} The reduction of scattered intensity by refractive index matching—necessary to prevent multiple scattering—is severely limited by these kind of inhomogeneities, especially for large particles.

After the reaction with TPM, the particles are dispersible in weakly polar solvents, but they still carry some charge, possibly because not all silanol groups have reacted. In order to remove this charge, we tried to block the remaining silanol groups with a small molecule, in this case trimethylhydroxysilane (TMHS).

Only a part of the dispersion was submitted to this second coating reaction. We thus obtained two systems: a single-coated silica (SC), stabilized by steric repulsions and charge, and a double-coated silica (DC), almost completely stabilized by steric repulsions. The radius of the particles as obtained by electron microscopy was 440 nm with a polydispersity (relative standard deviation in size) of 3%.

To avoid multiple scattering, which would complicate the results of DLS measurements, one has to select a solvent with a refractive index close to that of the particles. Furthermore, the particles have to be stable in this solvent. It appears that tetrahydrofurfuryl alcohol (THFA) satisfies both requirements. The optical matching point was situated between 30 and 35 °C. Moreover, by using a pure solvent instead of a mixture of solvents, we avoided problems like specific adsorption of one of the components, or changing of the composition due to evaporation and its influence on the viscosity and refractive index of the medium. The high boiling point of THFA (178 °C at 760 mm Hg), combined with its low-evaporation rate, guaranteed the constancy of the concentration over periods of weeks.

We could only find one literature value for the viscosity of THFA at 20 °C, namely, $\eta = 6.24$ mPa s.¹⁹ In order to compare diffusion constants at different temperatures we measured the viscosity of THFA at a number of temperatures with a DEER rheometer equipped with a Couette geometry.²⁰ The results at the temperatures used for light scattering measurements are given in Table I.

Qualitative electrophoretic mobility measurements

TABLE I. Viscosity of THFA (measured relative to 20 °C, where $\eta = 6.24$ mPa s is adopted). Values of D_0 given by the intercepts of Fig. 1 (see the text). Calculated hydrodynamic radius a_H from D_0 , EM radius 440 nm; relative standard deviation of size distribution 3% (13 nm).

Temp/°C	η /mPa s	$D_0/10^{-14}$ m ² s ⁻¹	a_H /nm
20	6.24	7.5 ₀	459
25	5.31	8.9 ₅	459
30	4.57	10.4 ₆	464
35	4.01	12.1 ₂	464

were made both with the single- and the double-coated silica. It turned out that in THFA the double-coated silica particles are uncharged, whereas the single-coated silica particles still carry a negative charge, as indicated by their electrophoretic mobility. On the other hand, in ethanol even the double-coated silica showed a very small electrophoretic mobility, though still much less than the electrophoretic mobility of the single-coated silica in ethanol. This indicates that the double-coated system has indeed less charge than the single-coated silica, but—depending on the solvent chosen—some charge may remain. Anyhow, in THFA the double coated silica particles were uncharged.

All light scattering measurements were made with the same cylindrical $\varnothing = 1$ cm cell. The highest particle concentration was obtained by repeatedly centrifuging the particles down in this cell, removing the supernatant and adding stock dispersion. Lower particle concentrations were obtained by diluting with weighed amounts of THFA. From the dilution ratio new weight fractions were calculated.

As a check the weight fractions were also measured by drying weighed samples from the cell. The drying procedure was improved by first diluting the sample with ethanol. Volume fractions were calculated from the densities of silica and THFA, 1.58 and 1.04 g cm⁻³, respectively.

B. Dynamic light scattering procedure

Dynamic light scattering (DLS) measurements were made with an argon ion laser (Spectra Physics model 165) operating at 514.5 nm. The laser beam was focused in the sample cell, which was placed in a cylindrical refractive index matching bath. The temperature of this surrounding bath was controlled within 0.1 °C. Autocorrelation functions were measured with a Malvern Multibit K7025 128 points correlator.

In order to estimate the influence of multiple scattering, measurements with the double coated silica were made at four temperatures (20, 25, 30, and 35 °C), as will be discussed in Secs. III C and IV B. The single-coated silica was only measured at 30 °C.

At each concentration, the sample cell was shaken vigorously and allowed to stand for a few hours. After altering the temperature of the surrounding bath the sample was allowed to stand for at least 1 h to attain equilibrium. After 24 h the effects of gravitational settling could be seen. A thin layer (1 mm) of supernatant appeared at the top of the sample and a dense sediment at the bottom. DLS measurements

were always made in the middle region between these layers (at least 1 cm high). We occasionally checked the influence of gravitational settling by remeasuring the same concentration at the same temperature after four or five days of sedimentation. Both measurements gave the same value of $D_{\text{eff}}(q)$. Nevertheless we decided to shake the cuvette every other day.

Twenty scattering angles θ were chosen in the range $50^\circ < \theta < 130^\circ$. The correlator sample time was chosen so that the observed electric field correlation function spanned about one decay time. Effective diffusion coefficients were obtained from a second order cumulant fit to the first 50 channels (spanning about half a decay time). No difference could be seen when this number of channels was altered to 20 or 80. We have also tried other combinations of correlator sample time and data analysis. The initial decay, or first cumulant Γ , obtained by a linear fit to the very first points, or by a second-order cumulant fit over a somewhat wider span, was essentially the same within a few percent. Changing the correlator sample time gave the same values too, if the number of points taken along in the fit was changed accordingly. Anyhow, the uncertainty in the measurement of Γ due to the data fitting is very systematic and seems to disappear when the ratios of diffusion constants $D_{\text{eff}}(q)/D_0$, obtained from the same analyzing procedure, are calculated.

C. Experimental difficulties

If polydispersity is neglected, the average intensity of the light singly scattered by the dispersion can be written as

$$I(q) \approx \rho S(q) P(q), \quad (24)$$

where $S(q)$ is the structure factor and $P(q)$ is the single particle form factor. For our systems $P(q)$ has approximately the Rayleigh–Gans–Debye form for a homogeneous sphere. Near the optical matching point deviations from this form are only due to particle inhomogeneities. The maximum value of qa reached was about 15.

One of the main difficulties in light scattering studies of large particles is that we want to be able to study both very dilute samples, even at angles where $P(q)$ is nearly zero, and of very concentrated samples, at angles where $\rho S(q) P(q)$ is very high. The lowest intensities scattered from the dilute sample must be sufficiently higher than the scattered intensity of the solvent. Otherwise the autocorrelation function will vanish in the noise. On the other hand, the scattered intensities of the concentrated samples must be sufficiently low, if we do not want multiple scattering to corrupt our data. Roughly, these scattered intensities must be less than 1000 times the scattered intensities of pure solvents, when a 1 cm sample cell is used. It is impossible to meet all requirements, because the ratio of the highest to the lowest concentration is about 100 and $P(q)$ varies by a factor of the order 10^3 to 10^4 . In practice the highest concentrations will suffer from multiple scattering and the lowest concentrations scatter too weak to be properly measured.

Although both our systems are more homogeneous than silica particles coated with stearylalcohol, they nevertheless remain slightly inhomogeneous. This is because TPM and TMHS have a refractive index different from silica. Due to

this inhomogeneity it is impossible to have a complete refractive index match of the particle and the solvent. There is of course still a temperature of minimum turbidity (close to 31 °C); but the dependence of the turbidity on temperature is not symmetrical around this point. The turbidities at 30 and 35 °C were more or less equal. At 25 and 20 °C the turbidities were 50% and 100%, respectively higher than the turbidities close to the "matchpoint." The highest turbidities at 30 and 35 °C were close to 3 cm⁻¹. With such high turbidities, multiple scattering must be considered. We decided to measure at 20, 25, 30, and 35 °C and compare the data obtained at these different levels of multiple scattering.

Nevertheless, even at 20 °C the matching between solvent and particles was so good, that it was hardly possible to measure intensity autocorrelation functions from dilute samples ($\phi < 0.01$). Already at $\phi \sim 0.02$ the effects of close matching appeared. At those angles where $P(q)$ has its minimum, the apparent diffusion coefficient suddenly increased. A few particles of very small radius (dust or other impurities) are probably responsible for this effect.

Like Pusey and van Megen² we also noticed that semilog plots of correlation functions of light scattered from weakly scattering (i.e., dilute) samples occasionally showed downward curvature. This kind of almost unphysical behavior (negative second cumulants) has been observed in our laboratory with many other "perfectly matched" dispersions, concentrated or dilute. The reasons for it are not always completely understood, but are probably different for concentrated or dilute samples. It can be due to particle motions induced by convection or radiation pressure, or slowly settling of dust particles or clusters, or residual swirling motions after the sample cell was shaken. Often this downward curvature disappeared when the cell was allowed to stand for rest for many hours. Sometimes it was due to laser instabilities or using too high laser intensities. By choosing a suitable laser intensity and using grey filters the effect then disappeared.

Another experimental difficulty encountered in the study of dilute dispersions of large particles is backscattering.²¹ Backscattering occurs due to reflection of the primary beam at the solution-glass boundary and (more important) at the glass-air boundary of the refractive index matching bath (exit window). Sometimes even the reflection of scattered light must be taken into account. Its influence can be estimated as follows. The normalized field autocorrelation function at angle θ and wave vector q for a monodisperse sample is $\exp(-q^2 Dt)$. Let q and q^* be the scattering vectors at angles θ and $180 - \theta$, respectively, and α be the ratio of the reflected to the primary intensity.

For a monodisperse dilute sample the normalized field autocorrelation function will take the form

$$g_1(t) = [P(q) \exp(-q^2 Dt) + \alpha P(q^*) \exp(-q^{*2} Dt)] / [P(q) + \alpha P(q^*)]. \quad (25)$$

At those angles θ where $\alpha P(q^*)$ is not negligible with respect to $P(q)$, the measured autocorrelation function will definitely be double exponential. The apparent diffusion coefficient D_{app} will be

$$D_{app} = \frac{P(q) + \alpha P(q^*) (q^*/q)^2}{P(q) + \alpha P(q^*)} \cdot D. \quad (26)$$

At $\theta > 90^\circ$ D_{app} will be less than D because $q > q^*$. We noticed this sudden decrease in D_{app} at angles larger than 135°. The effect is different from multiple scattering.

IV. RESULTS

A. Dilute samples

Because of the perfect matching it was difficult to study dilute samples in pure THFA. Therefore, effective diffusion coefficients $D_0(q)$ were obtained from measurements on dilute systems in THFA ($\phi = 0.0017$) to which 1 vol. % of toluene was added to enhance the particle scattering and thereby the signal to noise ratio of the measured autocorrelation function. The viscosity of the mixture is less than the viscosity of pure THFA, but the induced error in $D_0(q)$ is less than 1%. The mean value of $D_0(q)$ was taken as a first estimate of D_0 .

At 35 °C it was still hardly possible to measure a good field autocorrelation function and we got the impression that the value we found for D_0 was too high.

Therefore we extrapolated values of D_s^{short} of the lowest concentrations, calculated by the procedure discussed in Sec. IV B, to zero concentration. This extrapolation can be linear or quadratic. Both methods give the same intercept. The extrapolation showed that at 35 °C the diffusion coefficient of the dilute sample was indeed overestimated and so we used the extrapolated value of the lowest concentrations (shown in Fig. 1) as an estimate of D_0 . At the other temperatures there was no real distinction between the extrapolated value and the measured value. The best estimate of D_0 is then probably obtained by a fit through the lowest concentrations and the dilute ($\phi = 0.0017$) sample (shown in Fig. 1). As a consistency check we calculated the hydrodynamic radius of the particles from these values of D_0 , as listed in Table I. The

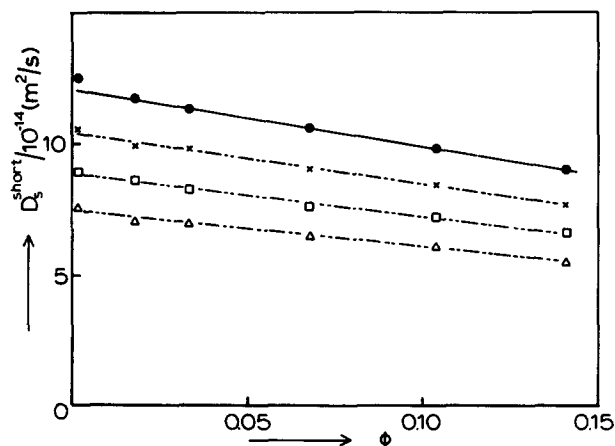


FIG. 1. Short-time self-diffusion coefficients for the double-coated silica as a function of volume fraction for the five lowest concentrations and a dilute sample (volume fraction $\phi = 0.0017$). Measurements were made at four temperatures: Δ —20 °C, \square —25 °C, \times —30 °C, \bullet —35 °C. Solid line is a linear fit through the five lowest concentrations (35 °C). Dashed line is a linear fit through the five lowest concentrations and the dilute sample (20, 25, and 30 °C). Intercepts are listed in Table I.

agreement is very good, in view of the errors in D_0 and η (about 1%–2%).

B. Concentrated samples

At each volume fraction the double coated system was measured at the four temperatures (20, 25, 30, and 35 °C). At the highest volume fractions the influence of multiple scattering became evident in static light scattering. At 35 °C the $P(q)S(q)$ structure was clearly visible, but at 25 °C it was completely smoothed out. The light scattered by these particles is strongly peaked in the forward direction. So the dominant effect of multiple scattering on DLS data is probably in that direction, where it leads to an increase in the apparent diffusion coefficient. On the other hand, at very high angles ($\theta > 135^\circ$) the backscattering effect leads to a decrease in the apparent diffusion coefficient, as discussed in Sec. III B. In the intermediate range $70^\circ < \theta < 130^\circ$ ($10 < qa < 15$) $D_{\text{eff}}(q)$ was almost independent of q (within 5%) and the mean value was taken as an estimate of D_s^{short} . The values of D_s^{short}/D_0 so obtained were independent of temperature, indicating that this value is not influenced very much by multiple scattering. At the temperatures 30 and 35 °C this procedure for finding D_s^{short} even improved for lower concentrations. As expected $D_{\text{eff}}(q)$ remained almost independent of q , at least for $qa > 8$, and from these data an unambiguous estimate of D_s^{short} could be obtained by taking their mean value. These estimates of D_s^{short} , divided by D_0 , are listed in Table II and plotted in Fig. 2 as a function of volume fraction. Within the measurement errors D_s^{short}/D_0 is independent of temperature.

However, at 20 and 25 °C this procedure for finding D_s^{short} could not be followed in the intermediate concentration region. The mean value of $D_{\text{eff}}(q)$ taken from data at $qa > 8$, was smaller than the values for $qa > 12$. Strictly speaking, in order to make the high- qa limit we should only use the latter data and, as Fig. 3 shows, they nicely agree with the data at 30 and 35 °C. Nevertheless, we prefer to use only the data obtained at 30 and 35 °C, which are far more reliable. Finally, we measured D_s^{short}/D_0 for the charged (single-coated) system at 30 °C. The results are listed in Table III and plotted in Fig. 4.

TABLE II. Normalized short-time self-diffusion coefficients D_s^{short}/D_0 vs volume fraction ϕ for the double-coated silica at 30 and 35 °C.

ϕ	D_s^{short}/D_0 at 30 °C	D_s^{short}/D_0 at 35 °C
1.8 ₀	0.95 ± 0.03	0.97 ± 0.03
3.3 ₅	0.94 ± 0.03	0.93 ± 0.03
6.8	0.86 ± 0.03	0.87 ± 0.03
10.4	0.80 ± 0.03	0.81 ± 0.03
14.1	0.74 ± 0.03	0.74 ± 0.03
18.0	0.67 ± 0.05	0.67 ± 0.03
21.3	0.61 ± 0.04	0.63 ± 0.03
25.3	0.56 ± 0.04	0.56 ± 0.03
27.6	0.52 ± 0.03	0.54 ± 0.02
32.2	0.46 ± 0.03	0.49 ± 0.03
41.1	0.37 ± 0.03	0.39 ± 0.03

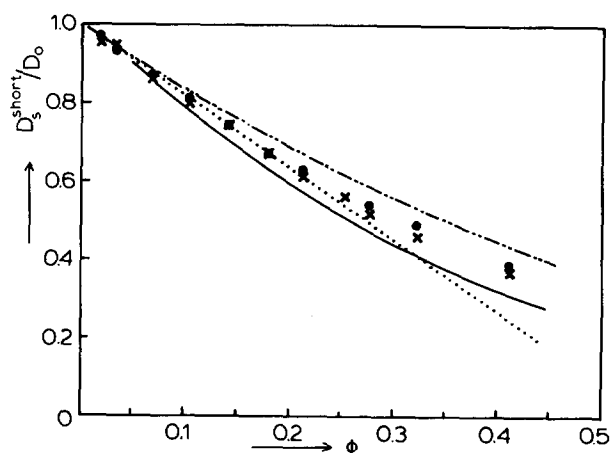


FIG. 2. Normalized short-time self-diffusion coefficients as a function of volume fraction for double-coated silica particles at 30 °C (\times) and 35 °C (\bullet). The dotted line is the $O(\phi)$ result [Eq. (22)], the dashed line is the $O(\phi^2)$ result [Eq. (23)], and the solid line represents the many-body result of Beenakker and Mazur (Refs. 13 and 14).

V. DISCUSSION

We have measured the short-time self-diffusion coefficient for two colloidal systems, differing only in particle interactions, both for semidilute as well as for concentrated dispersions. By comparing data obtained at different temperatures, and therefore different levels of scattering, we were able to estimate the possible influence of multiple scattering on these data. From this we concluded that the data obtained at 30 and 35 °C are very reliable and virtually not affected by multiple scattering.

Our data agree with those of earlier work,^{2,3} where short-time self-diffusion coefficients for sterically stabilized polymethylmethacrylate (PMMA) particles were presented. These studies were restricted to volume fractions $\phi > 0.2$, where it is generally assumed that density expansions like those given by Eqs. (22) and (23) are no longer valid. Furthermore, the ambiguities concerning the hard sphere nature

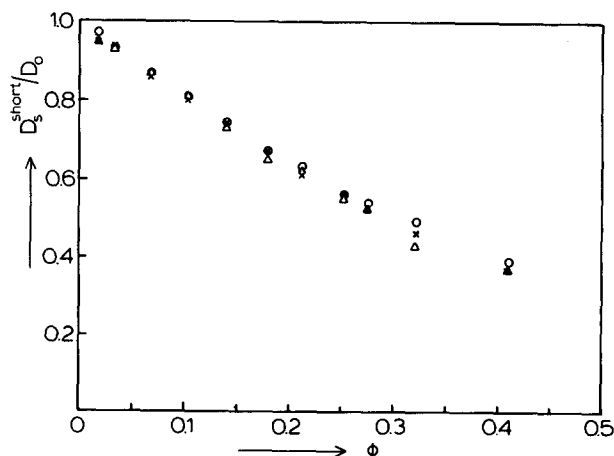


FIG. 3. Normalized short-time self-diffusion coefficients as a function of volume fraction for double-coated silica. Comparison of data obtained at 20 °C (Δ) at $qa > 12$ with the data obtained at 30 °C (\times) and 35 °C (\circ).

TABLE III. Normalized short-time self-diffusion coefficients D_s^{short}/D_0 vs volume fraction ϕ for the single-coated silica at 30 °C.

ϕ	D_s^{short}/D_0 at 30 °C
3.4	0.94 ± 0.03
7.0	0.86 ± 0.04
10.3	0.79 ± 0.04
17.7	0.67 ± 0.03
26.6	0.53 ± 0.04
37.3	0.39 ± 0.03
47.2	0.28 ± 0.02

of the PMMA particles and the determination of the “effective hard sphere” volume fraction remain a point of concern. In view of this there was a clear need for measurements with other types of particles, with different interactions and preferably also at volume fractions $\phi < 0.2$.

In Fig. 2 we compare the experimental data from the uncharged system with the various theoretical results described in Sec. II C. We note that the first-order expansion in ϕ describes the data remarkably well up to $\phi \sim 0.20$. In fact, up to $\phi \sim 0.25$ deviations from Eq. (22) are within the experimental errors (Fig. 5). This close agreement is quite surprising because, although Batchelor did use accurate numerical values for the two sphere hydrodynamic mobility functions and so his order ϕ term is quite accurate, this expansion is generally assumed not to be valid up to such high volume fractions. Here three- and more-body hydrodynamics become of importance and together with higher-order density contributions to the two particle distribution they will lead to correction terms of order ϕ^2 and higher.

The $O(\phi^2)$ density expansion of Beenakker and Mazur, Eq. (23), describes the data qualitatively correctly. We wish to point out that the difference between the $O(\phi)$ terms of Eqs. (22) and (23) is rather large. Actually up to $\phi \sim 0.1$ this difference is even larger than the contribution of the $O(\phi^2)$ in Eq. (23). Once more this emphasizes the importance of using accurate hydrodynamic mobility functions.

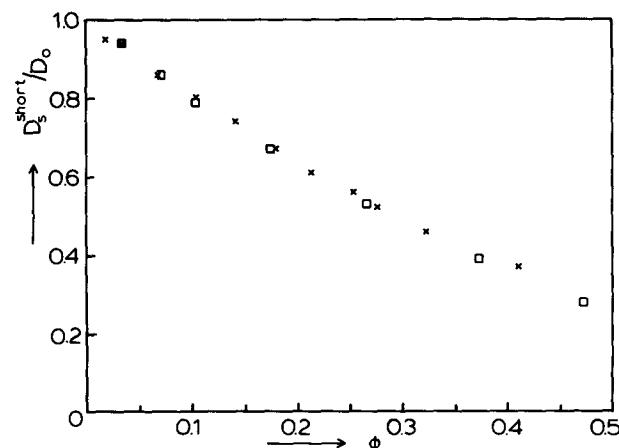


FIG. 4. Normalized short-time self-diffusion coefficients as a function of volume fraction for single- (\square) and double- (\times) coated silica particles at 30 °C.

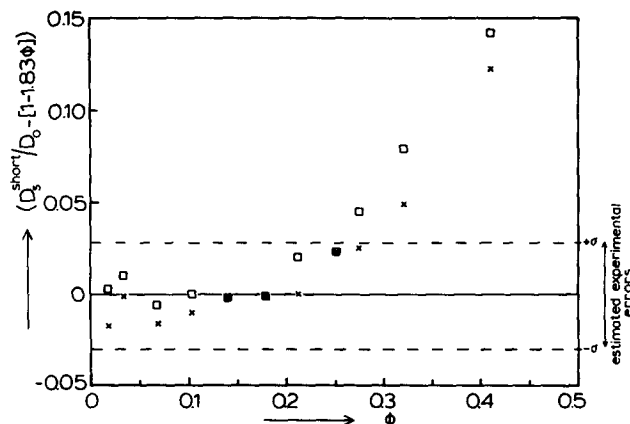


FIG. 5. Deviations between the measured normalized short-time self-diffusion coefficients and the $O(\phi)$ result [Eq. (22)] for the double-coated silica at 30 °C (\times) and 35 °C (\square), as a function of volume fraction.

It seems attractive to extend Eq. (22) as follows:

$$D_s^{\text{short}} = D_0 [1 - 1.83\phi + \epsilon(\phi)], \quad (27)$$

where $\epsilon(\phi)$ is of order ϕ^2 and higher.

It is difficult to estimate the form of $\epsilon(\phi)$ from our measurements. If $\epsilon(\phi) = K_2\phi^2$ is used, $K_2 = 0.7 \pm 0.3$ seems a reasonable estimate. This is in agreement with the ϕ^2 term of Eq. (23). There is obviously a clear need for accurate hydrodynamical calculations to order ϕ^2 .

For the higher concentrations the calculations of Beenakker and Mazur,^{13,14} using a resummation of the multiparticle hydrodynamic interactions, come close to the experimental points.

In Fig. 4 we compare data obtained from the charged system with data obtained from the uncharged system. There appears to be remarkably little difference between them. This indicates that the short-time self-diffusion is mainly determined by hydrodynamic interactions and is apparently little affected by direct particle interactions. This is in agreement with the evaluation of the theoretical expressions in Ref. 2, where it appeared that the use of different approximations for the two- and three-particle distribution functions was less important than the use of correct (many-body) hydrodynamics.

This is not *a priori* clear if we follow the approach of Sec. II C where the configuration dependent mobility function $\mathbf{b}_{11}\{\mathbf{r}^N\}$ is averaged over the appropriate many particle distribution functions. However, in the approach of Beenakker and Mazur,¹⁴ using an expansion of D_s^{short} in correlations of renormalized density fluctuations, one finds (adopting their notation)

$$D_s^{\text{short}} = D_s^{(0)} + D_s^{(2)}. \quad (28)$$

The zeroth-order term $D_s^{(0)}$ contains the many-body hydrodynamic interactions between an arbitrary number of spheres, but is independent of the particle distribution functions. $D_s^{(2)}$ is the correction to $D_s^{(2)}$ resulting from two-point correlations and only involves the two-particle distribution function $g(r)$. Both $D_s^{(0)}$ and $D_s^{(2)}$ are evaluated and tabulated in Ref. 14. It turns out that due to the special resuma-

tion the lowest-order correction $D_s^{(2)}$ is at most 8% of $D_s^{(0)}$ and so D_s^{short} is almost completely described by the zeroth-order result $D_s^{(0)}$. We may conclude from this that the detailed form of the particle distribution functions, and therefore the particle interactions, have no significant effect on D_s^{short} .

ACKNOWLEDGMENTS

The silica spheres coated with TPM and TMHS were synthesized by Mr. A. P. Philipse and Mr. V. de Leeuw. We are grateful to them for providing these systems to us. We thank Mrs. M. Uit de Bulten for typing the manuscript. This work is part of the research program of the Foundation for Fundamental Research of Matter (FOM) with financial support from the Netherlands Organisation for Pure Research (ZWO).

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