Diffusion of colloids at short times

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Abstract

We study the combined effects of electrostatic and hydrodynamic interactions (HI) on the short-time dynamics of charge-stabilized colloidal spheres. For this purpose, we calculate the translational and the rotational self-diffusion coefficients, \( D_t^s \) and \( D_r^s \), as function of volume fraction \( \phi \) for various values of the effective particle charge \( Z \) and various concentrations \( n_s \) of added 1–1 electrolyte.

Our results show that the self-diffusion coefficients in deionized suspensions are less affected by HI than in suspensions with added electrolyte. For very large \( n_s \), we recover the well-known results for hard spheres, i.e. a linear \( \phi \)-dependence of \( D_t^s \) and \( D_r^s \) at small \( \phi \). In contrast, for deionized charged suspensions at small \( \phi \), we observe the interesting non-linear scaling properties \( D_t^s \propto 1 - a_t \phi^{4/3} \) and \( D_r^s \propto 1 - a_r \phi^2 \). The coefficients \( a_t \) and \( a_r \) are found to be nearly independent of \( Z \). The qualitative differences between the dynamics of charged and uncharged particles can be well explained in terms of an effective hard sphere (EHS) model.

 normalized diffusion coefficients \( H_t^s \) and \( H_r^s \) are given by

\[
H_t^s = \frac{D_t^s}{D_0^s} = 1 - 1.831\phi + 0.88\phi^2 + \mathcal{O}(\phi^3) \quad (1)
\]

and by

\[
H_r^s = \frac{D_r^s}{D_0^s} = 1 - 0.630\phi - 0.67\phi^2 + \mathcal{O}(\phi^3), \quad (2)
\]

respectively. Here, \( D_0^s \) and \( D_0^r \) are the Stokesian diffusion coefficients for a colloidal sphere of radius \( a \) dispersed in a solvent of viscosity \( \eta \).

The possibility to express \( H_t^s \) and \( H_r^s \) in terms of a power series in \( \phi \) arises from the fact that hard sphere suspensions at small \( \phi \) can be considered as dilute both with respect to the particle hydrodynamics and to the microstructure. For charge-stabilized suspensions, however, this is not possible in general. Especially deionized, i.e. salt-free suspensions exhibit pronounced spatial correlations even at very small \( \phi \), so that these systems are diluted only as far as the HI is concerned. The corresponding radial distribution function \( g(r) \) has a pronounced \( \phi \)-dependence, a well developed first maximum, and it shows a correlation hole, i.e. a spherical region with zero probability for finding another particle, which usually extends over several particle diameters.

In contrast, the \( g(r) \) of hard spheres is nearly a unit step function \( g(r) \simeq \Theta(r - 2a) \) for \( \phi \leq 0.05 \). Therefore, the calculation of \( H_t^s \) and \( H_r^s \) at small \( \phi \) is more demanding for charged suspensions than for hard spheres, because for the charged particles it is necessary to use distributions functions generated from computer simulations or integral equation methods.

We will show subsequently, that it is essentially the presence of the correlation hole for charged suspensions, which causes large and interesting differences in the short-time diffusion of charged and uncharged suspensions.

1 Introduction

Since several years, the effect of HI on the short-time self-diffusion coefficients of hard sphere suspensions has been investigated in detail by various authors. For the calculation of the first and second virial coefficients of \( D_t^s \) and \( D_r^s \) in an expansion in terms of the volume fraction \( \phi \), both the influence of two-body and three-body HI was taken into account. At small \( \phi \), the currently established results for the

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2 Calculation of $H^t_s$ and $H^t_r$

In the following, we shortly summarize the main expressions needed to calculate $H^t_s$ and $H^t_r$ for charge-stabilized suspensions. A more detailed description of the method used by us for the calculation of short-time diffusion coefficients is given in Refs. [3,4].

As shown in Refs. [3,4], both $H^t_s$ and $H^t_r$ can be measured using depolarized dynamic light scattering (DDLS) from suspensions of optically anisotropic colloidal spheres. On the time scales, which are accessible by DDLS, the theoretical expression for $H^t_s$ is given by [3]

$$H^t_s = \frac{1}{3D_0} \langle \text{Tr} D^{tt}_{11}(rN) \rangle.$$ (3)

The corresponding expression for $H^t_r$ is obtained from eq. (3) by simply replacing the superscript $t$ by $r$. The hydrodynamic diffusivity tensors $D^{tt}_{11}$ and $D^{tt}_{11}$ relate the force/torque exerted by the solvent on an arbitrary particle 1 with its translational/angular velocity [3,4]. A due to the many-body character of HI, both tensors depend on the particle configuration $r^N = (r_1, \ldots, r_N)$ of all N interacting particles, and in principle the full N-particle distribution function is needed to perform the ensemble average $\langle \ldots \rangle$. $\text{Tr} D^{tt}_{11}$ denotes the sum over the diagonal elements of $D^{tt}_{11}$.

For an appropriate evaluation of eq. (3), we use a rooted cluster expansion [3,4,5], which leads to a "hydrodynamic virial expansion" of $H^t_s$:

$$H^t_s = 1 + H^t_{s1} \phi + H^t_{s2} \phi^2 + O(\phi^3).$$ (4)

Here, the coefficient $H^t_{s1}$ is given by an integral over the product of $g(r)$ with a translational hydrodynamic mobility function, which depends only on the distance $r$ of two spheres [3,6]. The second coefficient $H^t_{s2}$ accounts for three-body HI. For evaluating $H^t_{s2}$, one needs therefore an expression for the static triplét correlation function $g^{(3)}(r, r')$ which appears as part of the integrand of a three-fold integral.

A similar analysis is used to calculate $H^t_r$, leading to results which involve now rotational hydrodynamic two-body and three-body mobility functions [3,4,5,6].

The results for $H^t_s$ and $H^t_r$ depicted in eq. (4) and (5) were derived from eq. (3) by using in $H^t_{s1}$ and $H^t_{s2}$ the $g(r)$ of hard spheres evaluated up to linear order in $\phi$, whereas the vanishing density form of $g^{(3)}(r, r')$ was used in calculating the coefficients $H^t_{s2}$ and $H^t_{s2}$. In these results, exact two-body HI is accounted for $H^t_{s1}$ and $H^t_{s1}$, whereas only the leading long-distance contribution to the three-body mobility functions was used for the calculation of $H^t_{s2}$ and $H^t_{s2}$ [3,4,5,6].

For charged suspensions, however, it is not possible to use in eq. (4) low-order virial expressions of the two-body and three-body static distribution functions. In this study, we use instead results for $g(r)$, which are obtained from the rescaled mean spherical approximation (RMSA), as applied to the one-component macrofluid model of charge-stabilized colloidal suspensions [3]. The effective pair potential $u(r)$ acting between two particles is modelled by the repulsive part of the famous DLVO-potential, i.e. $\beta u(r) = K \exp[-\kappa(r - 2a)] \phi$, for $r > 2a$. Here, $\beta = (k_B T)^{-1}$, $K = Z^2 (L_B/a)(1 + \kappa a)^{-2}$, $L_B = \beta \epsilon^2/\epsilon$, and $\epsilon$ denotes the dielectric constant of the solvent. The screening parameter $\kappa$ is given by $\kappa^2 = L_B [3Z|\omega/a^3 + 8\pi n_s/\kappa^2)]$, where $n_s$ is the concentration of added 1-1 electrolyte, and the counterions are assumed to be monovalent [3,4]. Moreover, we use Kirkwood's superposition approximation for $g^{(3)}(r, r')$, inserting again the RMSA-$g(r)$. Further details concerning the numerical calculation of $H^t_{s1}$, $H^t_{s2}$, and $H^t_{s2}$ are given in Refs. [3,4,5].

3 Results and discussion

We focus first on the short-time diffusion coefficients of deionized charged suspensions, i.e. where $n_s = 0$. Our results for $H^t_s$ and $H^t_r$ are shown in figs. 1 and 2. The used system parameters are typical for systems which have been under experimental study [4].

Obviously, the effect of HI on the self-diffusion coefficients is less pronounced for charged suspensions than for hard spheres at the same $\phi$. Furthermore, we find a quite different volume fraction dependence of $H^t_s$ and $H^t_r$ for charged and uncharged particles. Whereas for hard spheres the $\phi$-dependence of $H^t_s$ and $H^t_r$ is linear at small $\phi$ (cf. eqs. (4) and (5)), we obtain from a least-square fit of our numerical results (shown as crosses in figs. 1 and 2) the following results for deionized charged suspensions for $0 \leq \phi \leq 0.05$ [3,4]:

$$H^t_s = 1 - a_t \phi^{1.30}, \quad a_t = 2.59,$$ (5)
\[ H^r_s = 1 - a_r \phi^{1.99}, \quad a_r = 1.28. \] (6)

The coefficients \( a_t \) and \( a_r \) are found to be nearly independent of the effective particle charge when \( Z \geq 200 \). From fig. 3 that eq. (6) constitutes the best fit function for \( H^r_s(\phi) \) even in the extended interval \( 0 \leq \phi \leq 0.15 \). In case of \( H^t_s \) however, the parametric form \( H^t_s = a_t \phi^s \) provides no good fit for values of \( \phi \) extending beyond 0.05.

There is a simple physical explanation for the weaker influence of HI on the self-diffusion coefficients of charged suspensions as compared to uncharged ones. As already mentioned, the \( g(r) \) of deionized suspensions displays a pronounced correlation hole, resulting form the strong electrostatic interparticle repulsion. Consequently, the hydrodynamic coupling between the translational or rotational motions of two spheres becomes rather small, thus giving rise to the observed weak influence of HI. Unlike charged particles, the influence particularly of the short-range part of HI is rather strong for hard sphere suspensions at small \( \phi \). This is due to the large probability of finding hard sphere particles at contact or close to the contact distance \( r = 2a \).

Along this type of arguments, it is also possible to explain the differences of \( H^t_s(\phi) \) and \( H^r_s(\phi) \) in deionized suspensions and suspensions with nonvanishing \( n_s \). We only show here the results of our calculations of \( H^r_s(\phi) \) for example. From these results in fig. B we notice that \( H^r_s \) becomes more and more affected by HI when \( n_s \) is increased. For very large \( n_s \), \( H^r_s \) of charged particles approaches the result for hard sphere suspensions, obtained semianalytically in Ref. [7] (cf. eq. (3)).

This finding is easily explained by noticing that the extension of the correlation hole decreases with increasing \( n_s \), leading to a stronger hydrodynamic coupling of the particles. Upon addition of electrolyte, the electrostatic repulsion of the particles becomes more and more screened and short-ranged, resulting in a pure hard-core repulsion for \( n_s \rightarrow \infty \). Therefore, the microstructure of the suspension gradually transforms to that of hard spheres, with \( H^r_s \) approaching the parametric form given in eq. (6).

We mention, that our results for \( H^s \) show similar trends, i.e. a gradual transformation of the \( \phi \)-dependence of \( H^s \) from eq. (3) to eq. (6) with increasing \( n_s \).

In the remainder of this article, we focus on the qualitatively different \( \phi \)-dependencies of \( H^s \) and \( H^r_s \) found in case of deionized charged and uncharged suspensions. For an intuitive physical explanation, we use an effective hard sphere model (EHS model) [7], describing the actual \( g(r) \) as a unit step function \( g_{EHS}(r) = \Theta(r - 2a_{EHS}) \). The EHS radius \( a_{EHS} > a \) accounts in a crude fashion for the correlation hole, observed in the actual \( g(r) \). We identify \( 2a_{EHS} = r_m \), where \( r_m \) is the position of the first maximum of \( g(r) \). It is now crucial to notice that \( r_m \) shows an interesting scaling property when \( n_s \). Due to the strong electrostatic repulsion, \( r_m \) has the same \( \phi \)-dependence as the average geometrical distance \( \bar{r} \) between two spheres. Hence

\[ a_{EHS} \propto r_m \propto \bar{r} = a \sqrt{4\pi/3\phi^{-\frac{3}{2}}} . \] (7)

Using the approximation \( g_{EHS}(r) \) of \( g(r) \), it is easy to calculate the coefficients \( H^t_{s1} \) and \( H^r_{s1} \) in an approximative way. By using far-field expansions of the hydrodynamic two-body mobility functions \( [8, 9] \), one obtains the following results from the leading terms of these expansions

\[ H^t_{s1} = -\frac{15}{8} \left( \frac{a}{a_{EHS}} \right) + \mathcal{O}(a_{EHS}^{-3}) , \] (8)

\[ H^r_{s1} = -\frac{5}{16} \left( \frac{a}{a_{EHS}} \right)^3 + \mathcal{O}(a_{EHS}^{-5}) . \] (9)
This leads together with eq. (3) and (7) to the expressions

\begin{align}
    H_s^t &= 1 - A'\phi^3 + O(\phi^4), \quad A' > 0, \quad (10) \\
    H_s^r &= 1 - A'\phi^2 + O(\phi^3), \quad A' > 0, \quad (11)
\end{align}

with exponents which are in good agreement with our numerical findings given in figs. 1 and 2 (cf. eqs. (5) and (6)).

Therefore we have shown by a simple analytic calculation based on the EHS model, that the observed differences in the functional forms of $H_s^t(\phi)$ and $H_s^r(\phi)$ between charged and uncharged suspensions are mainly caused by the leading terms of the hydrodynamic two-body mobility functions in combination with the scaling property $r_m \propto \phi^{-1/3}$, valid for deionized suspensions. The higher order terms in the hydrodynamic far-field expansions only give rise to minor corrections to the observed scaling properties depicted in eq. (3) and (6). These terms become increasingly important for larger volume fractions $\phi \geq 0.05$ (cf. eqs. (5) and (6) in the EHS model).

When electrolyte is added to the suspension, eq. (6) becomes invalid because of the enhanced screening of the direct particle interactions. This causes a change in the functional behaviour of $H_s^t(\phi)$ and $H_s^r(\phi)$, as can be seen both from the EHS model and from our numerical results (cf. fig. 3 in case of $H_s^r$).

Using the EHS model, it is also possible to motivate the nearly $Z$-independence of $a_t$ and $a_r$ in eqs. (3) and (6). Since $r_m$ is nearly independent of $Z$ for $Z \geq 200$, the EHS model predicts charge independent results for the short-time diffusion coefficients of deionized suspensions, in agreement with our numerical results.

We mention, that it is also possible to deal with $H_{s2}^t$ and $H_{s2}^r$ within the EHS model, giving further insight in the volume fraction dependence of the diffusion coefficients of deionized suspensions. It is then possible to explain qualitatively the surprising fact that $H_s^r(\phi)$ is well parametrized up to $\phi = 0.15$ by the functional form $H_s^r = 1 - a_r\phi^2$, obtained in the EHS model by using only the leading term in the far-field expansion of the rotational two-body mobility functions.

\section{Conclusion}

We have presented calculations of the translational and rotational short-time self-diffusion coefficients for charge-stabilized suspensions. The self-diffusion coefficients of charged suspensions are less affected by hydrodynamic interactions than the corresponding coefficients of hard spheres. As a major result we have found substantially different volume fraction dependencies of $H_s^t$ and $H_s^r$ for (deionized) charged and uncharged suspensions. The observed differences are well explained in terms of an effective hard sphere model by observing the big differences in the microstructure of suspensions of charged and uncharged particles.

We note finally that recent DDLS measurements of $H_s^t$ in deionized suspensions of charged fluorinated polymer particles compare favourably with our results in eq. (6). On the other hand, to our knowledge, no experimental data of $H_s^r$ for deionized charge-stabilized suspensions are accessible so far. We further point out that the interesting qualitative differences between charge-stabilized suspensions and hard spheres exist also with respect to sedimentation and long-time self-diffusion.

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