

Self-diffusion coefficients of charged particles: Prediction of nonlinear volume fraction dependence

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We report on calculations of the translational and rotational short-time self-diffusion coefficients D_s^t and D_s^r for suspensions of charge-stabilized colloidal spheres. These diffusion coefficients are affected by electrostatic forces and many-body hydrodynamic interactions (HI). Our computations account for both two-body and three-body HI. For strongly charged particles, we predict interesting nonlinear scaling relations $D_s^t \propto 1 - a_t \phi^{4/3}$ and $D_s^r \propto 1 - a_r \phi^2$ depending on volume fraction ϕ , with essentially charge-independent parameters a_t and a_r . These scaling relations are strikingly different from the corresponding results for hard spheres. Our numerical results can be explained using a model of effective hard spheres. Moreover, we perceptibly improve the known result for D_s^t of hard-sphere suspensions. [S1063-651X(97)05307-5]

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Self-diffusion of spherical colloidal particles has been studied experimentally over a wide range of time scales by means of various scattering techniques, in particular by polarized and depolarized dynamic light scattering (DLS). At short times on the scale of DLS, the particles have only moved a small fraction of their diameter σ , and the particle motion is determined by solvent-mediated many-body hydrodynamic interactions (HI) weighted by the equilibrium microstructure. The latter is determined by direct potential forces arising, e.g., for hard-sphere particles from the steric repulsion between the particles, and, in the case of charge-stabilized particles, from the electrostatic repulsion of overlapping double layers [1]. The configuration-averaged effect of HI gives rise to values of the translational and rotational diffusion coefficients D_s^t and D_s^r that are smaller than their respective Stokesian values at infinite dilution, i.e., $D_0^t = k_B T / (6\pi\eta a)$ and $D_0^r = k_B T / (8\pi\eta a^3)$. Here, a is the particle radius and η is the shear viscosity of the suspending fluid.

The properties of hard spheres are in various respects easier to describe quantitatively than those of charge-stabilized particles. As a consequence, there are many experimental [2–4] and theoretical [3,5,6] results available on the short-time self-diffusion coefficients of hard spheres. With regard to the computation of the first and second virial coefficients of D_s^t and D_s^r in an expansion in terms of the volume fraction ϕ , the currently established results for the normalized diffusion coefficients H_s^t and H_s^r are given by [3,6]

$$H_s^t = \frac{D_s^t}{D_0^t} = 1 - 1.831\phi + 0.88\phi^2 + O(\phi^3), \quad (1)$$

$$H_s^r = \frac{D_s^r}{D_0^r} = 1 - 0.630\phi - 0.67\phi^2 + O(\phi^3). \quad (2)$$

The possibility to expand H_s^t and H_s^r in powers of ϕ arises from the fact that hard-sphere suspensions at small ϕ are dilute both with respect to HI and to the microstructure.

While the short-time dynamics of hard spheres is well understood, far less is known thus far about charge-stabilized suspensions. The purpose of this letter is to show that there are striking differences in the ϕ dependence of H_s^t and H_s^r between charged and uncharged suspensions, and also to provide quantitative predictions. These unexpected differences are most pronounced for deionized, i.e., salt-free suspensions of charged particles. For such systems, our numerical results for H_s^t and H_s^r are well represented by the parametric form $1 + p\phi^\alpha$, where α is an exponent larger than one. Due to the strong direct interparticle interactions, deionized suspensions especially exhibit pronounced spatial correlations even for very small ϕ , say $\phi \leq 10^{-4}$, so that, contrary to hard spheres, these systems are dilute only with regard to HI. The corresponding radial distribution function (rdf) $g(r)$ has a well-developed first maximum and it exhibits a so-called correlation hole, i.e., $g(r)$ is essentially zero up to a well-defined nearest-neighbor separation larger than σ [7]. In comparison, the rdf of hard spheres is nearly equal to a unit step function $\Theta(r - \sigma)$ for $\phi \leq 0.05$, and an analytical expression for $g(r)$ of hard spheres is known up to first order in ϕ [8]. Therefore, the calculation of H_s^t and H_s^r at small ϕ is more demanding for charged suspensions, because it is necessary to use static distribution functions generated by integral equation methods or computer simulations.

We base our calculations of H_s^t for charge-stabilized suspensions on the general expression $H_s^t = \langle \text{Tr} \mathbf{D}_{11}^t(\mathbf{r}^N) \rangle / (3D_0^t)$ as derived from the generalized Smoluchowski equation [9]. The corresponding expression for H_s^r is obtained by replacing the superscript t with r . The hydrodynamic diffusivity tensor $\mathbf{D}_{11}^t(\mathbf{r}^N)$ [$\mathbf{D}_{11}^{rr}(\mathbf{r}^N)$] relates the force (torque) exerted by the solvent on an arbitrary particle 1 with its translational (rotational) velocity. $\text{Tr} \mathbf{D}_{11}^t$ denotes the trace of \mathbf{D}_{11}^t , and the factor 1/3 accounts for spatial isotropy. Due to the many-body character of HI, both tensors depend on the instantaneous N -particle configuration $\mathbf{r}^N = (\mathbf{r}_1, \dots, \mathbf{r}_N)$, and

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in principle the full N -particle distribution function is needed to perform the equilibrium ensemble average $\langle \cdot \rangle$. Thus, it is not possible to perform an exact calculation of H_s^t and H_s^r that is valid for all particle concentrations. For small ϕ , however, when the mean particle distance gets sufficiently large, a good approximation for these quantities is obtained by considering only two-body and, to leading order, three-body contributions to the HI. For this reason, we use a rooted cluster expansion for the calculation of H_s^t [3,10], leading to the following series expansion of H_s^t :

$$H_s^t = 1 + H_{s1}^t \phi + H_{s2}^t \phi^2 + \dots, \quad (3)$$

which we truncate after the third term. Here, H_{s1}^t is given in terms of integrals

$$H_{s1}^t = \frac{1}{a^3} \int_{2a}^{\infty} dr r^2 g(r) 6 \pi \eta a [\alpha_{11}^t(r) + 2\beta_{11}^t(r)], \quad (4)$$

involving $g(r)$ and scalar two-body mobility functions $\alpha_{11}^t(r)$ and $\beta_{11}^t(r)$, whose expansions in powers of (a/r) are known, in principle, up to arbitrary order [11,12]. In our calculations, we include contributions to α_{11}^t and β_{11}^t up to $O(r^{-20})$. The coefficient H_{s2}^t is far more difficult to calculate since it involves three-body HI. By considering the leading term in the far-field expansion of the three-body part of \mathbf{D}_{11}^t [6], H_{s2}^t is approximated by the threefold integral

$$H_{s2}^t = \frac{225}{64} \int_0^1 dt_{12} \int_0^1 dt_{13} \int_{-1}^1 d\xi g^{(3)}(t_{12}, t_{13}, \xi) f_i(t_{12}, t_{13}, \xi),$$

$$f_i(t_{12}, t_{13}, \xi) = \frac{t_{12} t_{13}}{h^{7/2}} \xi \{ 11 t_{12}^2 t_{13}^2 - 2(t_{12}^4 + t_{13}^4) - 10 \xi t_{12} t_{13} \\ \times (t_{13}^2 + t_{12}^2) + \xi^2 [10 t_{12}^2 t_{13}^2 + 6(t_{13}^4 + t_{12}^4)] \\ - 6 \xi^3 t_{12} t_{13} (t_{13}^2 + t_{12}^2) + 3 \xi^4 t_{12}^2 t_{13}^2 \}, \quad (5)$$

with $h(t_{12}, t_{13}, \xi) = t_{12}^2 + t_{13}^2 - 2\xi t_{12} t_{13}$. This integral involves the static triplet correlation function $g^{(3)}$ expressed in terms of $t_{12} = 2a/r_{12}$, $t_{13} = 2a/r_{13}$, and $\xi = \mathbf{r}_{12} \cdot \mathbf{r}_{13} / (r_{12} r_{13})$, where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the relative vector between the particles i and j , and r_{ij} is its magnitude.

A similar analysis is used by us for calculating H_s^r , leading to expressions for the coefficients H_{s1}^r and H_{s2}^r , which appear in a series similar to Eq. (3) and which involve non-rotational two-body and three-body mobility functions. For conciseness, we will not quote here the expressions for H_{s1}^r and H_{s2}^r , since these are given in Ref. [3]. Once again, we account for terms up to $O(r^{-20})$ in the far-field expansion for the two-body mobility functions, and for the leading three-body part of \mathbf{D}_{11}^r .

For charge-stabilized suspensions, it is only necessary to account for the first few terms in the expansion of the two-body mobility functions, since the integrals in Eq. (4) converge rapidly because $g(r)$ is practically zero at small r [7]. On the other hand, many terms are needed for hard spheres to accurately obtain the first virial coefficients as depicted in Eqs. (1) and (2). Notice that the second virial coefficients for hard spheres are made up of two contributions. The first one

is due to H_{s1}^t and H_{s1}^r , with $g(r)$ expanded up to first order in ϕ , whereas the second one arises from three-particle HI as embodied in H_{s2}^t and H_{s2}^r [3,6]. The second virial coefficient of H_s^r in Eq. (2) was obtained by essentially accounting for all two-body contributions in H_{s1}^r , and also for the leading three-body contribution [3]. On the other hand, only two-body terms up to $O(r^{-7})$ plus the leading three-body term were used so far in calculating the second virial coefficient of H_s^t , as given by the value 0.88 in Eq. (1) [6]. By considering terms up to $O(r^{-20})$ in calculating H_{s1}^t , we obtain an improved value of -1.096 for the two-body part of the second virial coefficient. Together with the three-body contribution $H_{s2}^t = 1.81$, which is obtained by Monte-Carlo integration of Eq. (5), we get the improved result

$$H_s^t = 1 - 1.831\phi + 0.71\phi^2. \quad (6)$$

This result is in better agreement with experimental data [3,4] for hard-sphere suspensions than Eq. (1). The experimental data in Ref. [4] especially agree almost perfectly with Eq. (6).

However, for charge-stabilized suspensions, it is not possible to use low-order virial expressions of the static distribution functions. We use instead results for $g(r)$, obtained from the rescaled mean spherical approximation (RMSA), as applied to the one-component macroion fluid model (OCM) of charge-stabilized suspensions [7]. In the OCM, the effective pair potential $u(r)$ acting between two particles consists of a hard-core part with diameter σ , and of a screened Coulomb potential $\beta u(r) = K \sigma \exp[-\kappa(r-\sigma)]/r$ for $r > \sigma$. Here, $K = (L_B/\sigma) Z^2 (1 + \kappa\sigma/2)^{-2}$, $L_B = e^2/(\epsilon k_B T)$, ϵ is the dielectric constant of the solvent, and Z is the effective charge of a particle in units of the elementary charge e . κ is given by the Debye-Hückel relation $\kappa^2 = L_B [24|Z|\phi/\sigma^3 + 8\pi n_s]$, where n_s is the number density of added 1-1-electrolyte, and the counterions are assumed to be monovalent [7]. For computing H_{s2}^t and H_{s2}^r , $g^{(3)}(\mathbf{r}, \mathbf{r}')$ is needed as static input. To this end, we use for simplicity Kirkwood's superposition approximation for $g^{(3)}(\mathbf{r}, \mathbf{r}')$, with the rdf calculated in RMSA. The threefold integrals are calculated using a Monte Carlo method.

Since the observed qualitative differences in the short-time self-diffusion coefficients of charged and uncharged particles are most pronounced for deionized charged suspensions, we concentrate here on the case $n_s = 0$. The system parameters used in our calculations are typical for suspensions that have been under experimental study [3,13]. If not stated differently, two-body contributions to HI, including terms up to $O(r^{-20})$, are considered together with the leading three-body contribution. Figures 1 and 2 show our results for H_s^t and H_s^r as functions of ϕ (crosses). The corresponding results for hard spheres are also included in these figures. Evidently, the effect of HI on H_s^t and H_s^r is less pronounced for charged suspensions. Moreover, we find a qualitatively different ϕ dependence of H_s^t and H_s^r for charged and uncharged particles. Whereas for hard spheres the ϕ dependence of H_s^t and H_s^r is linear at small ϕ , we obtain for charged particles, from a least-square fit of our numerical results to the form $1 + p\phi^\alpha$, the following interesting results:

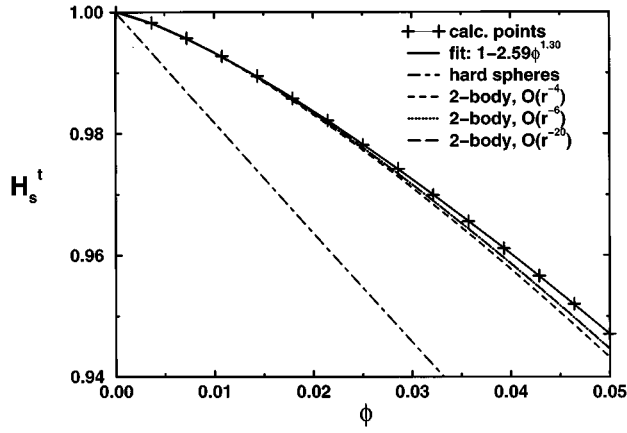


FIG. 1. H_s^t versus ϕ for a deionized charge-stabilized suspension with $\sigma=90$ nm, $Z=200$, $T=294$ K, and $\epsilon=87.0$. Solid line: best fit of the numerical results shows fractional ϕ dependence, i.e., $H_s^t = 1 - 2.59\phi^{1.30}$, with exponent $\approx 4/3$. Also shown is the dependence of H_s^t on various two-body contributions to the HI. Included are terms of the two-body expansion of \mathbf{D}_{11}^t as indicated in the figure. Dashed-dotted line: result for hard spheres according to Eq. (6).

$$H_s^t = 1 - a_t \phi^{1.30}, \quad a_t = 2.59, \quad (7)$$

$$H_s^r = 1 - a_r \phi^{1.99}, \quad a_r = 1.28, \quad (8)$$

with exponents close to $4/3$ and 2 , respectively. Equation (7) is valid for $\phi \leq 0.05$, whereas from Fig. 2 it is seen that Eq. (8) is valid even up to $\phi \leq 0.15$. The prefactors a_t and a_r are found to be nearly independent of Z for $Z \geq 200$. This fact is illustrated in Fig. 3, which shows results for $H_s^t(\phi)$ for various values of Z . Notice that due to the Z independence of H_s^t and H_s^r , the same Eqs. (7) and (8) are recovered when the accurate, but elaborate, Rogers-Young integral equation scheme [7] is used for $g(r)$ instead of the RMSA.

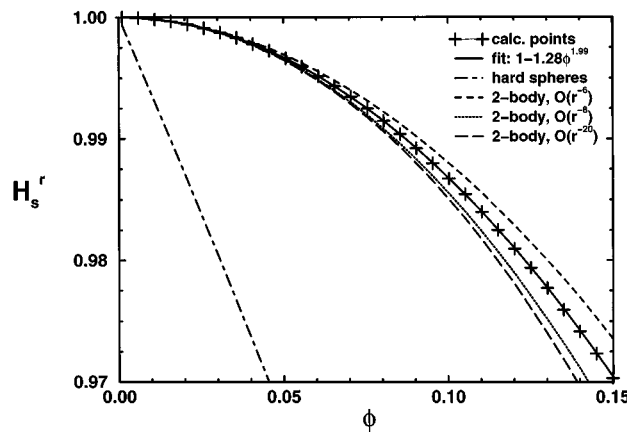


FIG. 2. Results for H_s^r obtained for a system with the same parameters as in Fig. 1 and compared with the corresponding result for hard spheres given in Eq. (2). Best fit of the calculated points (solid line) has nearly quadratic ϕ dependence, i.e., $H_s^r = 1 - 1.28\phi^{1.99}$, which extends to surprisingly large ϕ . Further shown is the dependence of H_s^r on various terms of the two-body series expansion of \mathbf{D}_{11}^r .

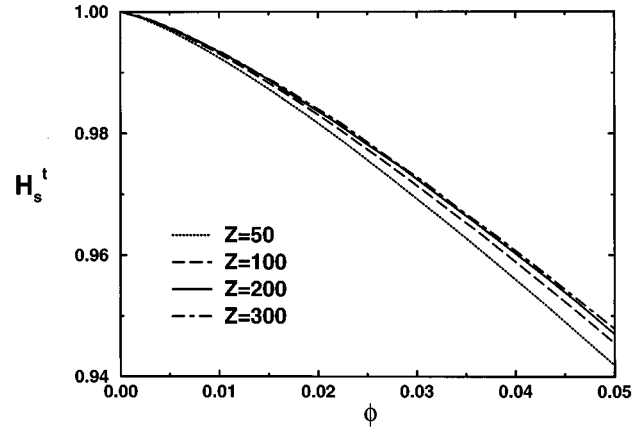


FIG. 3. H_s^t versus ϕ for various values of the effective charge number Z as indicated in the figure. All system parameters except Z are the same as in Fig. 1. Notice that H_s^t becomes nearly independent of Z at $Z \geq 200$.

We will now show that the occurrence of exponents close to $4/3$ and 2 and the Z independence of a_t and a_r can be understood in terms of a model of effective hard spheres (EHS) with density-dependent effective diameter $\sigma_{EHS} > \sigma$, which accounts for the extension of the correlation hole. We can identify $\sigma_{EHS} = r_m$, where r_m is the position of the principal peak of $g(r)$. It is now crucial to note for deionized suspensions that r_m as obtained from the RMSA coincides within 3% with the the average geometrical distance $\bar{r} = \sigma[\pi/(6\phi)]^{1/3}$ of two spheres. Thus, we have the scaling relation $r_m \propto \bar{r} \propto \phi^{-1/3}$. Here it is important that Z be chosen large enough that the physical hard core of a particle is completely masked by the electrostatic repulsion [7]. We now approximate $g(r)$ by the rdf $g_{EHS}(r; \phi_{EHS})$ of the EHS model, evaluated at the effective volume fraction $\phi_{EHS} = \phi(\sigma_{EHS}/\sigma)^3$. When this approximation for $g(r)$ is used, and if only the leading terms in the series expansions of the two-body mobility functions are retained, we obtain the results $H_s^t = 1 - a_t \phi^{4/3}$ and $H_s^r = 1 - a_r \phi^2$ with exponents very close to our numerical results. Here,

$$\begin{aligned} a_t &= \frac{15}{8} \phi_{EHS}^{-1/3} \int_1^\infty dx \frac{g_{EHS}(z; \phi_{EHS})}{x^2} \\ &= \frac{15}{16} \phi_{EHS}^{-1/3} \int_0^\infty dz z^2 G_{EHS}(z; \phi_{EHS}), \\ a_r &= \frac{15}{16 \phi_{EHS}} \int_1^\infty dx \frac{g_{EHS}(z; \phi_{EHS})}{x^4} \\ &= \frac{15}{384 \phi_{EHS}} \int_0^\infty dz z^4 G_{EHS}(z; \phi_{EHS}), \end{aligned} \quad (9)$$

and $G_{EHS}(z)$ is the Laplace transform of $xg_{EHS}(x)$ with $x = r/\sigma_{EHS}$. Notice that ϕ_{EHS} , and hence a_t and a_r , are independent of ϕ and Z (≥ 200) when σ_{EHS} is identified as r_m . To obtain a rough estimate of a_t and a_r , we can further approximate $g_{EHS}(x)$ by $\Theta(x-1)$, and σ_{EHS} by \bar{r} , giving $a_t = 2.33$ and $a_r = 0.60$. By employing the analytic expression for $G_{EHS}(z; \phi_{EHS})$ provided by the Percus-Yevick ap-

proximation [14], we obtain the values $a_t=3.02$ and $a_r=1.12$, where the value for a_r in particular is rather close to the numerical coefficient in Eq. (8).

Thus, the EHS model suggests that the scaling relations in Eqs. (7) and (8) found from our numerical calculations are caused mainly by the leading terms in the series expansions of the two-body mobility functions. To verify this assertion, we have included in Figs. 1 and 2 results for H_s^t and H_s^r obtained by neglecting three-body contributions and by truncating the two-body series expansions after various terms of increasing powers in (a/r) . These figures illustrate our finding that, up to $\phi=0.05$, the lowest order contributions to the translational and rotational two-body mobilities proportional to r^{-4} and r^{-6} , respectively, give by far the most important contributions to H_s^t and H_s^r . Higher-order two-body terms and the leading-order three-body term become significant only for $\phi \geq 0.05$. For H_s^t , these higher-order terms are of the same signature and sum up to increasing deviations in H_s^t from Eq. (7) when ϕ is enlarged beyond 0.05. With regard to H_s^r , however, we observe a fortuitous partial cancellation between the three-body contribution and the two-body terms of order $O(r^{-8})$, which are of opposite sign. As a result, Eq. (8) remains valid even up to $\phi \approx 0.15$. We mention that this cancellation can also be understood in terms of the EHS model by reasoning similar to that given above for the leading two-body contribution to H_s^r [17].

It is further interesting to investigate how H_s^t and H_s^r are influenced by added electrolyte. Our corresponding calculations show a gradual transition from the nonlinear scaling relations (7) and (8) to the expressions (2) and (6) when the amount of added salt n_s is increased and when the microstructure changes to a hard-sphere-like structure due to the screening of the electrostatic repulsion.

To summarize, we have calculated the translational and rotational short-time self-diffusion coefficient of charged suspensions by incorporating two-body and three-body contributions to the HI. As a major result, we have found for the first time substantially different volume fraction dependencies for charged and uncharged particles. We were also able to explain the observed differences in terms of an effective hard-sphere model. We mention that recent depolarized DLS experiments [13] on deionized suspensions of optically anisotropic particles are in good agreement with our predicted result for H_s^r in Eq. (8). With regard to H_s^t , we are not aware of experimental results that are sufficiently precise at low ϕ to distinguish the $\phi^{4/3}$ -behavior from the essentially linear ϕ dependence of hard spheres. Finally, we point out that interesting qualitative differences between suspensions of charged particles and hard spheres exist also with respect to sedimentation [15] and long-time self-diffusion [16].

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