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Self-diffusion in dilute colloidal suspensions with attractive potential interactions

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The colloidal short-time self-diffusivity $D_s^s(\phi)$ is significantly retarded relative to hard sphere suspensions for the case of interparticle potential interactions induced by a nonadsorbing polymer. A comparison of diffusing wave spectroscopy measurements with direct calculations of $D_s^s(\phi)$ demonstrates that depletion effects on structure explain the observed retardation. We show that coexistence boundaries place unexpectedly severe constraints on the amount of $D_s^s(\phi)$ retardation possible for stable suspensions. The measured retardation is demonstrated to be an indicator of suspension metastability.

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The strength and range of interparticle interactions affect the phase behavior, equilibrium structure, and particle dynamics of colloidal suspensions. Such potential interactions between particles may be of electrostatic, dispersive, or steric origin [1]. Alternatively, a nonadsorbing polymer may give rise to a potential of mean force between particles due to the effects of entropic depletion [1]. While the role of interparticle potential in mediating the phase behavior and equilibrium structure of colloidal suspensions has been often studied, the effect of this quantity on colloidal dynamics is less well known. Dynamics in the limit of high scattering vector q are characterized by the time-dependent self-diffusivity $D_s(\phi,t)$, which is a function of particle volume fraction, hydrodynamic interactions, and suspension structure [1,2]. The suspension structure is in turn determined by the potential interactions between particles. A comparison of direct calculations of single-particle diffusion with experimental measurements in dilute, interacting systems can (1) provide insight into and tests of theories of hydrodynamic interaction; (2) form the basis of an analytical method to parameterize the interparticle interaction potential; and (3) shed light on the extent to which single-particle diffusion can be affected by potential interactions in stable and metastable solutions.

In this paper, we report diffusing wave spectroscopy (DWS) measurements that quantify the effect of attractive interparticle interactions on the short-time self-diffusivity of dilute colloidal suspensions interacting via the depletion potential. Because of the dilute conditions, we may directly compare the results to theoretical calculations of hydrodynamic interaction for the depletion potential. We find that the equilibrium phase diagram places stringent limits on the extent to which single-particle diffusion in stable solutions can be perturbed from that of hard sphere suspensions. If the phase boundary is crossed, the self-diffusivity in the resulting metastable solution may be impacted by attractive interactions to a substantial degree.

Although theoretical treatment of self-diffusion in dilute particle suspensions with variable interactions is available [2–4], corresponding experimental measurements are few [5–10]. DWS is a powerful experimental tool that has been used to characterize self-diffusion in aqueous polystyrene latex dispersions with screened electrostatic interactions [6–11]. Comparisons to theory [2,12] indicated a behavior consistent with hard sphere interactions. Inertial and memory effects on short-time diffusion agreed with the theory of Hinch [13].

We extend the DWS methodology to consider variable potential interactions in multiply scattering suspensions. In the short-time limit probed by DWS, the interaction potential between colloids affects self-diffusion only through its effect on suspension structure. Because DWS applies to highly multiply scattering suspensions, its application to characterize potential interactions and stability in turbid colloidal suspensions is of broad relevance.

The effect of attractive interactions on self-diffusion for dilute suspensions is a consequence of the dependence of particle dynamics in the limit of low volume fraction on two-sphere hydrodynamic interactions and equilibrium structure [2]:

$$D_s^s(\phi)/D_0 = 1 + \lambda_a \phi,$$

$$\text{where}\quad \lambda_a = -\int_2^\infty [3 - A_{11}(r) - 2B_{11}(r)] g(r) r^2 dr. \quad (1)$$

In Eq. (1), D_0 is the Stokes-Einstein diffusivity, $A_{ij}(r)$ and $B_{ij}(r)$ are scalar functions that characterize the mobility of two spheres parallel and perpendicular to their line of centers, respectively, and $g(r)$ is the pair correlation function [2]. Under the dilute conditions for which Eq. (1) is valid, $g(r) = \exp[-\Phi(r)/kT]$, where $\Phi(r)$ is the two-particle potential interaction and kT is the thermal energy. Here, the dimensionless separation r is relative to the sphere radius a. Physically, Eq. (1) indicates that the dilute self-diffusivity is retarded relative to D_0 by the passive hindrance of neighboring particles. Application of Eq. (1) is appropriate at dilute volume fractions where the effect of higher-order coefficients is small. For example, at $\phi = 0.20$, the error in Eq. (1) relative to a calculation of $D_s^s(\phi)/D_0$ valid to the order of ϕ^2 is 5.1% for hard spheres [14]

Suspensions with depletion interactions are a model system to examine the effect of interparticle interactions on single-particle diffusion. Here, the colloids are monodisperse polystyrene spheres (Seradyn, Inc., Indianapolis) of radius

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0.301 μm with induced depletion interaction through the addition of polyacrylic acid (PAA, available from Aldrich, Milwaukee). For pH>7 the polymer is nonadsorbing [15]. Although more comprehensive descriptions of the depletion interaction are available [16], for the dilute conditions of interest here, it is appropriate to model the resulting attractive potential of mean force with the Asakura Oosawa(AO) form [17]. In the AO form, the potential is a function of the polymer to colloid size ratio ξ and the volume fraction of the polymer in equilibrium with the suspension, $\phi_p^{(R)}$. We compute the former parameter using the penetrable hard sphere model with $\xi=(2/\sqrt{\pi})(R_g/a)$ [18], and the latter using the expression for free volume fraction α in Ref. [19]. Here, R_g is the radius of gyration of the polymer. At pH$=10$, we find by static light scattering and gel permeation chromatography that $M_w=1.7\times10^6$ g/mole, $R_{g,z}=96$ nm, and $M_w/M_n=1.9$ for PAA. For certain experiments, we maximize attractive interactions by adjusting pH<7 which induces additional attractive interactions due to polymer adsorption [15].

We measured the DWS intensity autocorrelation function ($\lambda_0=488$ nm) $g_2(\tau)$ in the point-source transmission mode for 3–12 h in 10-min intervals with sample mixing between each interval. The mean squared displacement $\langle\Delta r^2(t)\rangle$ was extracted by the method in Refs. [6] and [20]. The photon transport mean free path l^* was obtained from Mie theory and the equilibrium structure factor [21]. DWS measures the $q^3F(q)$-averaged time-dependent diffusivity $[D(t)]=\langle\Delta r^2(t)\rangle/6t$, where $F(q)$ is the form factor [6]. For particles sufficiently large, such that the qa probed exceeds the first primary structural peak ($qa>\pi$) [6], $[D(t)]$ approaches $D_s(t)$ [9]. We measured $[D(t)]/D_0$ for the polystyrene spheres, which probe qa to 10.3, with no added polymer and thin Debye layer ($\kappa^{-1}=4.5$ nm) and found, in agreement with prior experiment [8,9], that the measured $D_s^s(\phi)$ were consistent with the theoretical result for dilute hard spheres (relative error is 5.3%) [2,3]. This finding establishes that the spheres conform to the limit $[D(t)]\rightarrow D_s(t)$ for the dilute concentrations studied, so here we adopt the notation of self-diffusivity for DWS results.

Suspensions of polystyrene particles in which the polymer reservoir concentration $C_p^{(R)}$ [22] was varied from 0 to 0.21 mg/ml and the particle volume fraction, ϕ, was varied from 0.01 to 0.25 were studied. The qualitative effect of polymer at $C_p^{(R)}=0.11$ mg/ml is shown in Fig. 1(a). The significant reduction in magnitude of $D_s(t)/D_0$ at low ϕ is evidence that added polymer retards self-diffusion in the dilute suspension relative to the DWS determined infinite dilution diffusivity in the polymer solution. This attenuation is attributed to the role of equilibrium structure in determining the overall effect of two-sphere hydrodynamic interactions on colloidal mobility, as we demonstrate in Figs. 1(b) and 2.

We rescaled the results for suspensions with attractive interactions to the single-particle result of Hinch [13], as originally preformed for hard spheres [10,23]. The rescaling is a two-parameter fit of $D_s^s(\phi)/D_0$ and a characteristic time for propagation of hydrodynamic interactions, τ_v. The rescaled data are plotted in Fig. 1(b). The fit is satisfactory and establishes that the method for extracting $D_s^s(\phi)$ is extendable to suspensions of variable interaction potential. The inset of Fig. 1(b) shows that the magnitude of retardation in $D_s^s(\phi)/D_0$ extracted from this rescaling is significantly greater than the hard sphere prediction.

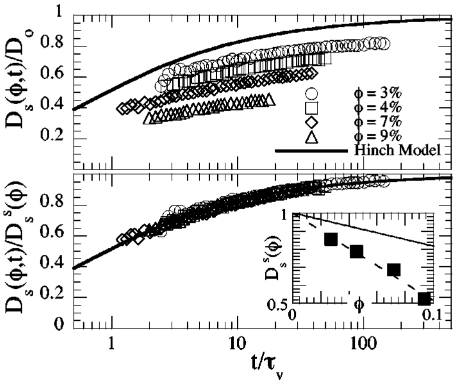

FIG. 1. (a) $D_s(\phi,t)/D_0$ for colloidal suspensions containing nonadsorbing polymer at $C_p^{(R)}=0.11$ mg/ml. The curve is the result of the Hinch model [13]. (b) Two-parameter fit of the data of (a) to the Hinch model. The inset shows that the attenuation of $D_s^s(\phi)/D_0$ at this $C_p^{(R)}$ is much more significant than for hard sphere colloids (solid curve).

The effect of $C_p^{(R)}$ on the self-diffusivity is plotted in Fig. 2. Measurements for 0.07, 0.09, and 0.21 mg/ml (open symbols) were conducted at high pH. Consistent with the results of Fig. 1, Fig. 2 shows that increased $C_p^{(R)}$ results in decreased $D_s^s(\phi)/D_0$ relative to the hard sphere result. Reduction of the solution pH (closed symbols) resulted in even greater retardation of the self-diffusivity. In addition, at these concentrations, phase instability was detected in the form of slowly increasing opalesence. The opalesence was reversible by shear melting. The magnitude of the experimental retardation in $D_s^s(\phi)/D_0$ is large. The values of λ_a obtained by fitting data to Eq. (1) are reported in Fig. 2. The coefficient λ_a is a convenient single-point characterization of potential interactions applicable to suspensions for which turbidity and virial coefficient measurements fail due to multiple scattering.

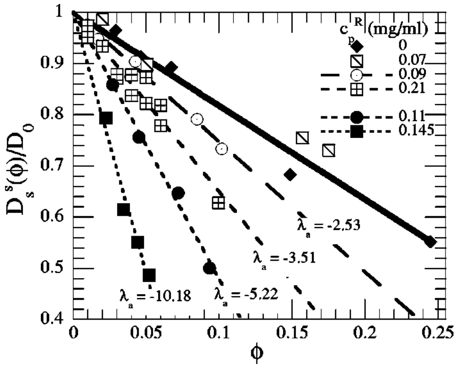

FIG. 2. $D_s^s(\phi)/D_0$ at a number of different polymer reservoir concentrations, $C_p^{(R)}$ as a function of colloid volume fraction. Open symbols are for nonadsorbing polymer (high pH), while filled symbols are for the polymer that adsorbs (low pH). The solid line is the theoretical result for hard spheres. The linear fits to the data are for Eq. (1). The extracted values of λ_a are listed.

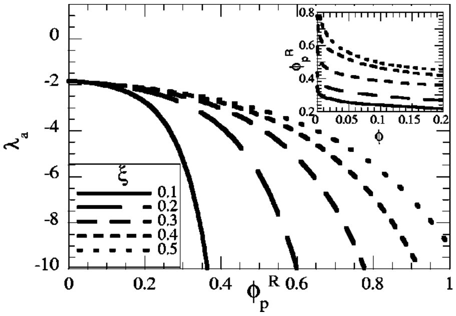

FIG. 3. The dependence of the linear coefficient λ_a on the AO depletion potential parameters of size ratio ξ and polymer reservoir volume fraction $\phi_p^{(R)}$computed for Eq. (1). The inset shows the depletion equilibrium phase diagram. The inset curves, from bottom to top, are for $\xi = 0.1 - 0.5$ in increments of 0.1.

A quantitative comparison to theory can be made for potential interactions due to the nonadsorbing polymer. To perform the comparison, we conducted measurements at $C_p^{(R)} = 0.21$ mg/ml and $p\text{H} = 10$ and computed λ_a for the case of the AO depletion interaction. In Eq. (1), the two-sphere mobility functions $A_{11}(r)$ and $B_{11}(r)$ were computed as in Ref. [24]. By varying the number of terms included in the far-field summation of $A_{11}(r)$ and $B_{11}(r)$, we estimate that the error in λ_a is no more than 1.0%. Applying Eq. (1), we find that the number average molar mass of a nonadsorbing polymer that is consistent with the experimental slope in the self-diffusivity of Fig. 2 differs from the value obtained by light scattering by 12%. This agreement is reasonable, given the experimental error of $\pm 10\%$, and the fact that these calculations did not account for polymer polydispersity.

We can understand the retardation in $D_s^s(\phi)/D_0$ by considering the effect of attractive interactions on suspension structure. Neighboring particles decrease the dilute self-diffusivity relative to infinite dilution because of their passive hindrance of colloidal mobility. In systems with depletion interactions, this passive hindrance is increased because attractive interactions induce increased probability for a neighboring particle to be found at close proximity.

In Fig. 3, we summarize the theoretical calculations of the effect of attractive interactions on self-diffusion for nonadsorbing polymer and demonstrate that the effect of attractive interactions on self-diffusion is significant. For the investigated level of depletion interaction (as parameterized by ξ and $\phi_p^{(R)}$), the absolute magnitude of λ_a may be more than five times greater than for hard sphere suspensions. In the inset of Fig. 3 and in Fig. 4, we address the extent to which the significant retardation predicted in Fig. 3 is experimentally realizable. That is, retarded self-diffusion requires strong short-range interparticle attraction; however, such interactions might also imply solution phase instability. To test this hypothesis, we estimated the phase diagram of the AO potential for the parameter range of interest by the theory of Lekkerkerker *et al.* [19] for colloid and nonadsorbing polymer mixtures, which has been found to approximate the phase behavior of depletion systems [22]. Since the region $\phi < 0.20$ is of particular interest, we reproduce the gas-liquid and fluid-solid coexistence lines in this dilute region in the inset of Fig. 3 for $\xi = 0.1 - 0.5$. The single-phase region is located below the coexistence curves. The phase boundaries place unexpectedly severe constraints on values of λ_a possible in stable suspensions. Indeed, as described earlier, metastability (phase instability) was observed in suspensions with sufficiently small self-diffusivity due to high $C_p^{(R)}$. We classified measurements of the self-diffusivity at various values of ϕ and $C_p^{(R)}$ based on the observed stability of the specimen and compared to the theoretical results, as plotted in Fig. 4. The agreement in Fig. 4 between the experimental observations and theory provides evidence that phase instability limits the amount of retardation of single-particle self-diffusion possible for stable suspensions. The constraint is severe because upon increasing $\phi_p^{(R)}$, phase instability occurs before λ_a decreases significantly. Thus, strong attractions that significantly retard $D_s^s(\phi)$ are sufficient to generate phase instability. The magnitude of retardation is in addition a reasonable indicator of suspension metastability.

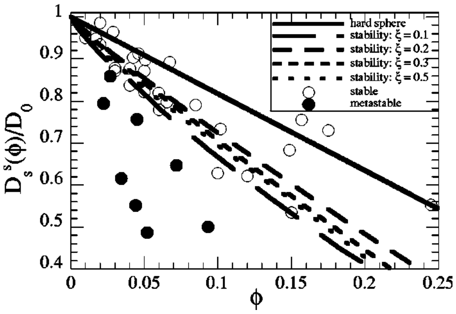

FIG. 4. Stability constraints for the AO depletion interaction for a number of size ratios compared to results for stable and metastable suspensions.

Previously, Kaplan *et al.* [25] found the effective diffusivity of multiply scattering binary hard sphere suspensions to be a function of interspecies hydrodynamic coupling. This study, by quantifying large particle hydrodynamics, has demonstrated that the coupling between size distributed particles affects even intraspecies hydrodynamic interactions in the way specified by Eq. (1).

Our approach of characterizing potential interactions by measuring its effect on self-diffusion differs from methods that accomplish the same goal by characterizing equilibrium structure from static light scattering [26], osmometry [27] or frequency-domain photon migration [28]. The method resembles the one based on the rheological measurement of the high-frequency viscosity [29], since both use the effect of suspension structure on hydrodynamic interactions to parametrize the interaction potential.

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