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Long-Time Self-Diffusion in Concentrated Colloidal Dispersions

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A theory of self-diffusion in concentrated dispersions is presented, in which the effects of hydrodynamic and direct interactions between macroparticles are virtually decoupled. The long-time self-diffusion coefficient D_s^L is written in terms of the radial distribution function of the suspended particles and of their short-time self-diffusion coefficient D_s^S . The predictions for the volume fraction dependence of D_s^L in hard-sphere suspensions are in excellent agreement with available experimental results.

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The direct-interaction forces between colloidal particles in suspension (Coulombic, van der Waals, etc.) constitute a fundamental relaxation mechanism in these systems,¹ in complete analogy with the role of intermolecular collisions in simple liquids.² Thus, the theoretical description of the dynamic effects of the direct interactions in colloidal dispersions has paralleled,^{1,3} to a large extent, corresponding developments in the theory of simple fluids. Unfortunately, this analogy breaks down under circumstances which happen to be of enormous practical interest, namely, when concentrated dispersions of uncharged colloidal particles are considered. For these systems, the nonconservative hydrodynamic interactions constitute another essential feature,¹ whose description requires the solution of a highly nontrivial many-body hydrodynamic problem.⁴ Thus, the fundamental analysis of the coupled effects of the direct and hydrodynamic interactions between colloidal particles constitutes a major goal of the current theoretical research on the dynamic properties of concentrated dispersions.

In recent theoretical^{5,6} and experimental^{7,8} studies of self-diffusion phenomena in concentrated dispersions, the effects of the hydrodynamic interactions have been singled out by the study of the self-diffusion properties in the short-time regime, i.e., for times much shorter than τ_I , the time one colloidal particle needs to diffuse a mean separation distance between suspended particles. (Even these short times, however, should always be much

longer than the typical relaxation time τ_B of the macroparticle's velocity. A simple estimate of τ_I and τ_B is given by $\tau_I \cong n^{-2/3}/D^0$ and $\tau_B \cong M/\zeta^0$, where M is the mass of the particles, n their number concentration, $D^0 = k_B T/\zeta^0$ their free-diffusion coefficient, and ζ^0 their Stokes friction coefficient. Here, T is the temperature, and k_B is Boltzmann's constant.) For such short times ($t \ll \tau_I$), the dissipative effects of the direct-interaction forces between the suspended particles are still negligible, and each macroparticle undergoes diffusive motion in the essentially static field of its neighbors. This short-time diffusive motion is characterized by a short-time self-diffusion coefficient D_s^S , which is found to be smaller than D^0 as a result of the hydrodynamic interactions. The ratio D_s^S/D^0 depends on the concentration of colloidal particles, and it has been measured in suspensions of hard-sphere-like particles as a function of their volume fraction $\phi = \eta n \sigma^3/6$ (σ being their hard-sphere diameter). The dependence of D_s^S/D^0 on ϕ is illustrated in Fig. 1, where an empirical fit of the experimental data of Ref. 7 is included. Theoretical results for this quantity are available,⁵ and it is fair to say that their agreement with the experimental observations requires only quantitative improvements.

In contrast, there is a virtual absence of quantitative theoretical predictions at arbitrary concentrations regarding the true *long-time* self-diffusion coefficient D_s^L , which describes the Brownian motion of a tracer particle

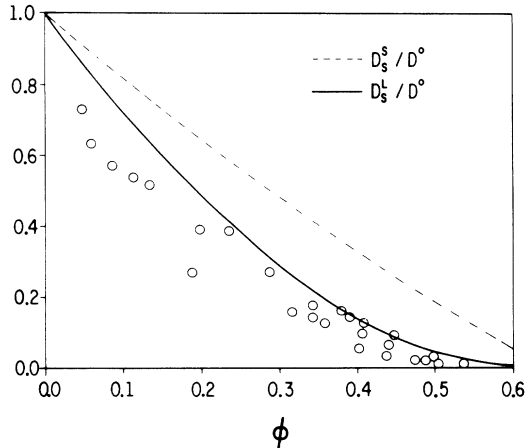


FIG. 1. Volume-fraction dependence of the short-time and long-time self-diffusion coefficients D_s^S and D_s^L for a suspension of hard-sphere-like particles. The broken line is an empirical fit of the experimental data reported in Fig. 3 of Ref. 7, whereas the points represent the experimental results for D_s^L , as read from Fig. 4 of the same reference. The solid line is the result of my theory for D_s^L calculated according to Eq. (6), in which the Percus-Yevick approximation for $g(r)$ was employed, and with D_s^S determined from the empirical fit in this figure.

in the asymptotic regime $t \gg \tau_I$. For such long times, each macroparticle has collided very many times with the other diffusing particles, and this produces an additional frictional effect. As a result, D_s^L is found to be even smaller than D_s^S . This is also illustrated in Fig. 1, where the results of the experimental measurements of D_s^L in hard-sphere suspensions, as reported in Ref. 7, are also exhibited. The main purpose of the work described in this Letter is to provide the first theoretical interpretation of these results, and in general, of the intermediate- and long-time self-diffusion properties of concentrated dispersions. This work is an extension of recent work^{9,10} on the theory of tracer-diffusion phenomena in suspensions without hydrodynamic interactions.

Let us consider a suspension of identical spherical colloidal particles interacting via a pair potential $\psi(r)$. [The actual functional form of $\psi(r)$ is unknown, and depends on the system. It includes short-range steric repulsions, van der Waals attractive forces, and possible Coulombic interactions. Simple functional forms of $\psi(r)$ for each of these forces have been employed in the literature.³] In self-diffusion experiments, the Brownian motion of a very small fraction of such particles is recorded, and each of these tracer particles may be regarded as diffusing independently of the others. Thus, the state of this system may be represented by an equilibrium ensemble of identical systems each containing only one tracer particle. Let the state of the system be defined by the variables $\mathbf{V}(t)$ and $n(\mathbf{r}, t)$, the tracer's velocity and the local concentration of the other colloidal

particles at a position \mathbf{r} referred to the center of the tracer, respectively. *The fundamental assumption of my theory is the existence of well-separated time scales as indicated above, i.e., in terms of the short and long times relative to τ_I . The Brownian motion of the tracer may then be described by the following Langevin equation:*

$$M d\mathbf{V}(t)/dt = -\zeta^S \mathbf{V}(t) + \mathbf{f}^S(t) + \int [\nabla\psi(r)] n(\mathbf{r}, t) d^3r, \quad (1)$$

This equation expresses the total force on the tracer as the sum of the direct-interaction forces exerted by the other particles on the tracer (the third term on the right-hand side), plus the hydrodynamic forces exerted by the supporting solvent, represented as a dissipative friction term plus the δ -correlated stochastic force $\mathbf{f}^S(t)$, related to the friction coefficient ζ^S by a fluctuation-dissipation relation.

The direct-interaction term represents the collisions of the tracer with the other diffusing particles. It constitutes a nondissipative, purely mechanical coupling between the velocity of the tracer and the instantaneous local concentration $n(\mathbf{r}, t)$. At very short times ($t \ll \tau_I$), $n(\mathbf{r}, t)$ does not change appreciably, and this force term constitutes an essentially static external field on the tracer. Thus, in the short-time regime ($M/\zeta^S \ll t \ll \tau_I$) Eq. (1) describes an ordinary diffusive phenomenon, which is characterized¹¹ by the diffusion coefficient $k_B T/\zeta^S$. Since the definition of the short-time self-diffusion coefficient given above is precisely that, i.e., the coefficient describing the diffusive motion of the tracer in the short-time regime, we must then have that ζ^S is given by $\zeta^S = k_B T/D_s^S$. Let me stress that the present theory does not attempt to calculate D_s^S , for which well established theories^{5,6} are available. Instead, it attempts to express D_s^L in terms, among other things, of D_s^S , which is regarded here as determined from experimental measurements^{7,8} or from independent theoretical calculations.⁵

Of course, it is only in the short-time regime where $n(\mathbf{r}, t)$ may be viewed as an essentially static quantity. For later times, $n(\mathbf{r}, t)$ obeys a diffusion equation of the type

$$\partial n(\mathbf{r}, t)/\partial t = \mathbf{V}(t) \cdot \nabla n(\mathbf{r}, t) - \nabla \cdot \mathbf{J}(\mathbf{r}, t) - \nabla \cdot \mathbf{J}_{\text{fluct}}(\mathbf{r}, t). \quad (2)$$

The first term on the right-hand side is a streaming term deriving from the fact that the position \mathbf{r} in $n(\mathbf{r}, t)$ is referred to the tracer's position, which moves with velocity $\mathbf{V}(t)$. Thus, this is an exact mechanical term. The other two terms represent the diffusive fluxes, which include a dissipative $[-\nabla \cdot \mathbf{J}(\mathbf{r}, t)]$ and a fluctuating $[-\nabla \cdot \mathbf{J}_{\text{fluct}}(\mathbf{r}, t)]$ component, related to each other by a fluctuation-dissipation relation.⁹

Equations (1) and (2) are, hence, quite general, and specific approximations are only required in the defini-

tion given to $\mathbf{J}(\mathbf{r}, t)$. For the sake of concreteness, let us consider the approximation provided by Fick's diffusion law, according to which

$$\mathbf{J}(\mathbf{r}, t) = -bn(\mathbf{r}, t)\nabla\mu[\mathbf{r}; n], \quad (3)$$

where b is the mobility of the diffusing particles as observed from the reference frame of the tracer (which has its own mobility). $\mu[\mathbf{r}; n(t)]$ is the local electrochemical

potential at position \mathbf{r} , and is, in general, a *functional* of the instantaneous local concentration profile $n(\mathbf{r}, t)$.

In recent work,⁹ the procedure has been established which, starting from the linearization of Eqs. (1) and (2) around the equilibrium averages $\langle \mathbf{V}(t) \rangle^{\text{eq}} = \mathbf{0}$ and $\langle n(\mathbf{r}, t) \rangle^{\text{eq}} = ng(r)$ [where $g(r)$ is the radial distribution function of the suspended particles], leads, after the elimination of $n(\mathbf{r}, t)$, to the following generalized Langevin equation for the velocity of the tracer:

$$M d\mathbf{V}(t)/dt = -\zeta^S \mathbf{V}(t) + \mathbf{f}^S(t) - \int_0^t \Delta\zeta(t-t') \mathbf{V}(t') dt' + \mathbf{F}(t). \quad (4)$$

In this equation, $\mathbf{F}(t)$ is a (colored) random force deriving from the thermal departures of $n(\mathbf{r}, t)$ from its radial equilibrium average $ng(r)$. It can be shown⁹ that $\mathbf{F}(t)$ satisfies a fluctuation-dissipation relation with the time-dependent friction function $\Delta\zeta(t)$, for which a general expression can be written in terms of $g(r)$ and of the Green's function of the linearized version of Eq. (2). The specific result obtained for $\Delta\zeta(t)$ from the use of Fick's law [Eq. (3)], under the additional simplification in which the field of the tracer is ignored in the calculation of n^{eq} and of the functional derivative $\{\delta\mu[\mathbf{r}; n]/\delta n(\mathbf{r}')\}_{\text{eq}}$ appearing in the linearization of Eq. (2), may be written as

$$\Delta\zeta(t) = (k_B T n / 24\pi^3) \int d^3k \{ [kh(k)]^2 / S(k) \} \exp[-2D_s^S k^2 t / S(k)]. \quad (5)$$

In this equation, $S(k) = 1 + nh(k)$ is the static structure factor of the suspended particles. In the derivation of this result, an important additional approximation was employed, namely, the substitution of the relative mobility b by the sum of the short-time mobility $D_s^S/k_B T$ of the diffusing particles and of the tracer; i.e., b was approximated by $b = 2(D_s^S/k_B T)$.

Equations (4) and (5) provide about the simplest description of the intermediate and long-time self-diffusion properties of a monodisperse suspension in terms of the static quantity $S(k)$ and of the short-time self-diffusion coefficient D_s^S . From those equations one can derive expressions for the relevant self-diffusion properties (velocity autocorrelation function, mean squared displacement, etc.). In particular, the long-time self-diffusion coefficient is given by

$$D_s^L = D_s^S [1 + (n/48\pi^3) \int d^3k h^2(k)]^{-1}. \quad (6)$$

The application of these results to specific systems is rather straightforward, as long as D_s^S is available. For hard-sphere suspensions the Percus-Yevick approximation¹² provides a convenient analytic expression for $S(k)$, whereas D_s^S may be determined from the empirical fit in Fig. 1. In such a figure I plot the results thus obtained for D_s^L from Eq. (6). Although a more natural comparison would be to display the ratio D_s^L/D_s^S of the two experimentally determined self-diffusion coefficients along with the calculated ϕ -dependent factor in Eq. (6), it is clear from the comparison in Fig. 1 that the trends observed in the experimental results for D_s^L are predicted by the results of my theory, especially at high volume fractions. Given the simplicity of the theory, and the fact that it does not involve any adjustable parameter at

all, one may say that, except at small volume fractions, there is a remarkable quantitative agreement between theory and experiment for D_s^L .

The comparison in Fig. 1 for D_s^L is intended to illustrate the type of predictions which can be drawn from my theory, as well as their relevance concerning the interpretation of particular experimental results. Let me mention, in this respect, that in a real suspension of uncharged particles it is impossible to get rid entirely of van der Waals interactions between the particles. Hence, I have applied Eq. (6) to a hard-sphere plus attractive Yukawa potential, and compared with the experimental data in Fig. 1. Although a seemingly perfect fit of the long-time data can be achieved for reasonable values of the Yukawa parameters, such an observation is not particularly relevant, given the current uncertainties in the experimental results and in the details of the approximations. More interesting is the fact that refinements in the specific approximations and simplifications introduced here are certainly possible. For example, the question concerning the description of the diffusion of the other particles as observed from the reference frame of the tracer (which is itself undergoing Brownian motion) may be given an alternative treatment.⁹ I have found that this also leads to a better quantitative agreement with the experimental data in Fig. 1, especially at high volume fractions.

The results presented here can also be extended in several interesting directions. As an example, let us consider the case in which there are more than one (say ν) species of diffusing particles with arbitrary direct interactions. Then the extension of Eq. (6) for the long-time self-diffusion coefficient D_s^L of a tracer particle of

species i , reads

$$D_i^L = D_i^S \left\{ 1 + \sum_{j=1}^v [n_j D_j^S / 3(D_i^S + D_j^S)] \int d^3r [g_{ij}(r) - 1]^2 \right\}^{-1}, \quad (7)$$

where D_j^S is the short-time self-diffusion coefficient of a particle of species j , whose number concentration is n_j , and whose radial distribution function around the tracer is $g_{ij}(r)$. The experimental measurements needed to test this result are probably not much more involved than those employed in Fig. 1, but they are not yet available. Thus, for the time being let me discuss the physical picture behind the theoretical scheme introduced in this paper.

The classical concept of Brownian motion¹¹ can be viewed in terms of the random trajectories available to a Brownian particle (as generated by the Langevin equation). The statistical properties of these trajectories differ qualitatively if the particle diffuses freely, or if it is one of many interacting particles in a suspension; in the latter case, collisions between particles hinder the motion of each other, and the effects of such collisions are only appreciable over times much longer than the "mean collision time" τ_I . However, in between collisions, the mechanism of transport is still essentially free diffusion. In the absence of hydrodynamic interactions, this free diffusion is characterized by the same diffusion coefficient, $D^0 = k_B T / \zeta^0$, as in truly free diffusion. In its simplest version, my theory assumes that when hydrodynamic interactions are present, their effects are established within a very short time (compared with τ_I), and that they only modify the effective friction which the Brownian particle feels at any instant during its "free" diffusion between collisions. Thus the trajectories available to this Brownian particle should not differ from those of a tracer particle in an identical (but idealized) suspension without hydrodynamic interactions, except that the diffusion coefficient governing this "free" diffusion is no longer D^0 , but $D_j^S = k_B T / \zeta^S$. Within this simplified picture, many ideas and techniques developed for systems of interacting Brownian particles without hydrodynamic interactions^{2,3} could be translated essentially without change, except for the replacement of D^0 by D_j^S . Equation (6) is a good example of this type of result. Of course, there may be systems and conditions where this simple picture of hydrodynamic interactions will not

hold. The comparison in Fig. 1 suggests, however, that at least for the system we have considered, this is an idea worth pursuing.

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