

Measurement of the (quasi)-self-diffusion coefficient of solutions of Brownian macroparticles^{a)}

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D_s of a dilute suspension of 0.15μ polystyrene spheres moving through concentrated suspensions of 0.038μ polystyrene spheres was determined with light scattering spectroscopy. Solutions from which small ions had been rigorously excluded were compared with suspensions containing such ions. If the concentration dependence of D_s is $D_s = D_0(1 + \lambda\phi)$, ϕ being the volume fraction of 0.038μ spheres, removal of the small ions makes λ more negative. This behavior of λ agrees qualitatively with a dynamic friction model for D_s , but is inconsistent even as to sign with calculations based on the generalized Smoluchowski equations, as recently summarized by Evans and James [J. Chem. Phys. **79**, 5553 (1983)].

I. INTRODUCTION

Methods for computing the concentration dependence of the self-diffusion coefficient D_s were recently summarized and elegantly extended by Evans and James.¹ Namely, for a monodisperse suspension D_s may be expanded

$$D_s = D_0(1 + \lambda\phi), \quad (1)$$

D_0 being the diffusion coefficient of an isolated particle and ϕ being the volume fraction of solute particles in solution. For a model hard-sphere system, most calculations find $0 > \lambda \geq -2.7$ (Ref. 1, Table I; Refs. 2–12). From this agreement, Evans and James draw the reasonable conclusion that the calculation of λ is “basically well understood,” and proceed to extend the calculation to include correlations in the soft and hydrodynamic forces between suspended macroparticles.

The numerical concordance of Refs. 2–12 masks certain fundamental underlying disagreements in their methods. For example, Mazo² and this author³ have found a concentration dependence for D_s due entirely to non-hydrodynamic interactions between the macroparticles; in contrast, many calculations based on the Smoluchowski equation or its equivalents^{4–9} appear to indicate that D_s is independent of concentration if hydrodynamic interactions are not present.

This paper presents an experimental study of the self-diffusion coefficient of Brownian macroparticles in a concentrated suspension, using our optical probe technique^{13–17} to measure D_s with quasielastic light scattering spectroscopy. Our major result is that the generalized Smoluchowski equation

$$\frac{\partial P(\mathbf{r}^n, t)}{\partial t} = \sum_{ij} \nabla_i \cdot \mathbf{D}_{ij} \cdot [\nabla_j - \beta \mathbf{F}_j] P(\mathbf{r}^n, t) \quad (2)$$

as interpreted in Ref. 1, is experimentally incorrect as to sign in its prediction of the effect of electrostatic intermacromolecular interactions on the concentration dependence of D_s . Comparison will also be made with theoretical treatments of D_s in terms of fluctuation–dissipation relations and memory-function formalisms. Many of these calculations, while

suggestive, do not treat precisely the problem which is studied experimentally here.

Section II gives our experimental methods. The data is presented and interpreted in Sec. III. Theoretical predictions for λ are presented in Sec. IV, and specialized to bidisperse solutions in Sec. V. A discussion and conclusions are found in Sec. VI.

II. EXPERIMENTAL

Our equipment is largely as described in Ref. 17. A 25 mW HeNe laser was used to illuminate 1 cm (square) sample cells. The light scattered through 90° was analyzed with a 128 channel Langley–Ford Instruments digital correlator. For the studies on systems from which ions had not been rigorously excluded, the samples were suspensions of carboxylate-modified polystyrene latex spheres in conventional 14 M Ω deionized water. The nominal sphere diameters, provided by the manufacturer, were 0.038 and 0.15μ ; the actual radii obtained by light scattering spectroscopy were 204 and 815 \AA , respectively. The concentration of the 0.15μ spheres was 6×10^{-5} by volume, while the concentration of 0.038μ spheres ranged from 0% to 0.6% by volume. In some cases, the light scattering spectrum of a single sample of 0.15μ spheres was studied while the concentration of 0.038μ spheres was progressively increased. In other cases, mixtures were prepared to a given, high concentration of 0.038μ spheres. These two approaches gave consistent results.

Data analysis of a multiexponential spectrum can be relatively complicated; however, here the exponential time constants are sufficiently different that they can be studied separately. Graphical analysis (Fig. 1) reveals that scattering by the smaller spheres is imperceptible for $t > 1$ mS, even when their concentration is as high as 0.25%. Single-exponential fits were therefore made to the measured $S(k, t)$ for $t > 1$ mS. As $S(k, t)$ decays by more than one decade in 1 mS, the accuracy in D is significantly less accurate ($\pm 5\%$) than would normally be acceptable for a modern QELSS measurement on a simple, strongly scattering, system.

For systems from which small ions were excluded, data were taken from our previous experimental study on interacting spherical polyelectrolytes.¹⁷ Those samples were pre-

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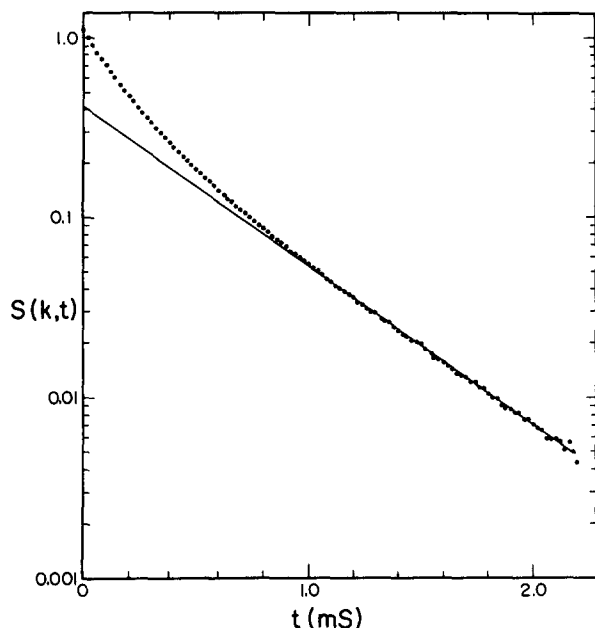


FIG. 1. Spectrum of a bidisperse suspension of 0.25 volume A% 0.038 μ and trace amounts of 0.15 μ polystyrene spheres. At $\tau \gtrsim 1$ mS, the spectrum exhibits a single slow exponential.

pared in quartz cells by suspending the spheres in deionized water and adding specially treated ion exchange resin. Several weeks were then allowed for small ions to be removed from solution. Data analysis for these samples, which has previously been described, is essentially similar to that of the nondeionized samples. However, ionic removal greatly reduces the scattering by the 0.038 μ spheres, thereby simplifying spectroscopic analysis. For example, at a 0.25% concentration of 0.038 μ spheres, ionic exclusion reduces the scattering intensity of the smaller spheres by a factor of 7.5 ± 2 .

III. RESULTS

The interpretation of spectra of interacting bidisperse suspensions is presented in Ref. 17, Appendix A. For the special case that one of the scattering species is highly dilute, the linewidth "corresponding" to that species has the form

$$\Gamma = 2D_s k^2 = 2 \frac{k_B T}{f_s} k^2, \quad (3)$$

where k is the scattering vector, k_B is the Boltzmann constant, and f_s is the drag coefficient of the dilute species in the bidisperse solution. D_s , as here defined, is the self-diffusion coefficient of the dilute species through the mixture. For the bidisperse solutions treated here, one expects to find a two-exponential spectrum; the slow exponential corresponds to the self-diffusion of the dilute large spheres through the non-dilute small spheres.

Figure 2 presents the major experimental result. The filled circles represent D_s in nearly ion-free solutions¹⁷; the open circles represent data for systems studied here, in which no particular effort was made to exclude small ions. If the volume concentration ϕ_{38} of 0.038 μ spheres is zero, the 0.15 μ spheres have a diffusion coefficient close to 0.30×10^{-7} cm²/s. For $0 < \phi_{38} < 0.003$, D for the samples

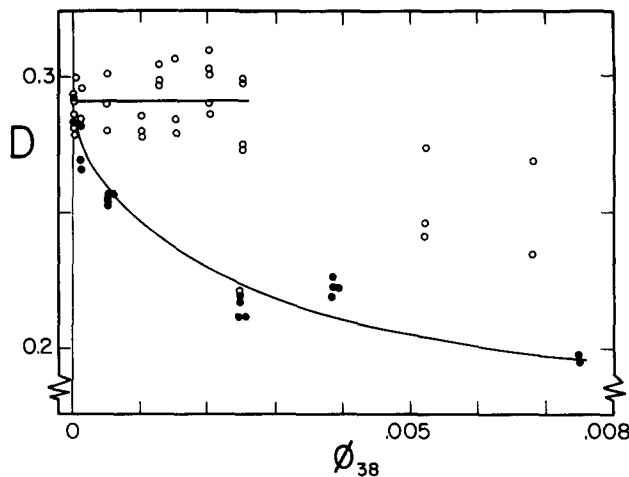


FIG. 2. Self-diffusion coefficient (in units 10^{-7} cm² sec⁻¹) of 0.15 μ polystyrene spheres, as a function of the concentration of 0.038 μ polystyrene spheres. Filled circles: systems from which small ions had been carefully excluded. Open circles: systems from which small ions have not been excluded. Removal of small ions has the effect of reducing D_s , contrary to the prediction of theories based on the generalized Smoluchowski equation.

studied here is independent of ϕ_{38} ; at substantially higher concentrations, D_s falls to approximately $0.25 (\pm 0.02) \times 10^{-7}$ cm²/s. In contrast, when small ions are removed, D is strongly dependent on ϕ_{38} . Even at $\phi_{38} = 1 \times 10^{-4}$, D_s is significantly less than at $\phi_{38} = 0$. At $\phi_{38} = 0.003$, D_s for the ion-removed systems has less than three-fourths of the value observed at $\phi_{38} = 0$.

While it would be possible to obtain substantially more information about these sphere suspensions, it is clear that treatment with ion exchange resin substantially increases the range and effective strength of electrostatic interactions in each solution. From Fig. 2, increasing the electrostatic interactions by removing small ions reduces D_s of the larger spheres. In terms of Eq. (1), treatment of a bidisperse polystyrene sphere suspension with ion exchange resin makes λ substantially more negative. (Treatment also appears to reduce the range over which D_s is linear in ϕ_{38} ; however, the sign of the change in λ is still apparent from the figure.)

IV. THEORETICAL PREDICTIONS FOR D_s

There is a large body of literature on the self-diffusion coefficient of a solution of interacting Brownian particles. The methods and results of these calculations divide them into three groups, namely:

(i) Calculations based directly or implicitly on the Smoluchowski equation, perhaps with the use of memory functions or the equivalent.

(ii) Calculations based on the Kirkwood formula

$$\zeta = \left\langle \frac{1}{3k_B T} \int_0^\infty \mathbf{F}(0)\mathbf{F}(t) dt \right\rangle \quad (4)$$

for the friction factor, where \mathbf{F} is the fluctuating force on the diffusing particle.

(iii) Calculations which refer directly to the velocities as well as the positions of the diffusing particles, as by starting with a Fokker-Planck equation or a generalized Langevin equation.

Within each group, calculations differ in the assumed form of intermacromolecular potential (hard sphere or screened Coulomb) and in the approximations used for the hydrodynamic interactions. As this is an experimental paper, not a review article, in this section we summarize results without discussing the details of all the calculations.

D_s has been calculated from a diffusion equation, without use of memory terms, by Batchelor,¹¹ Felderhof,⁷ Muthukumar and Freed,¹² and Beenacker and Mazur,¹⁹ among others. In these calculations, a concentration dependence of D_s arises from the hydrodynamic interactions between the Brownian particles.¹⁸ If the concentration dependence of D_s is written

$$D_s = D_0(1 + \alpha\phi), \quad (5)$$

ϕ being the solute concentration expressed as the volume fraction, then for hard spheres α is in the range -1.73 to -1.83 . From Refs. 7 and 19,

$$\alpha = N^{-1} \left\langle \sum_{i=1}^N \mathbf{T}_{ii} \right\rangle, \quad (6)$$

where \mathbf{T}_{ij} is the hydrodynamic interaction tensor, which includes nonzero reflection ($i = j$) terms. Felderhof shows

$$\mathbf{T}_{11} = -\frac{15}{4} \sum_{l>1} \left(\frac{a}{r_{1l}} \right)^4 \hat{r}_{1l} \hat{r}_{1l} + \dots, \quad (7)$$

a being the hydrodynamic radius of a particle and \hat{r}_{1l} being the unit vector between 1 and l . The addition of a long-range repulsive interaction to the hard core potential will increase the typical distance r_{1l} between pairs of particles, thereby reducing the magnitude of $\langle \mathbf{T}_{ii} \rangle$. A solution of neutral hard spheres will therefore have a more negative value of α than will a solution of hard spheres, all of which repel each other via the long-ranged Debye-Hückel potential.

Equation (6) follows from the Smoluchowski operator

$$L = \sum_{j,k=1}^N \nabla_j \cdot \mathbf{D}_{jk} \exp(-\beta U) \cdot \nabla_k [\exp(\beta U) \dots], \quad (8)$$

where U is the intermacromolecular potential energy, $\beta = (k_B T)^{-1}$, the diffusion tensor \mathbf{D}_{jk} is

$$\mathbf{D}_{jk} = \mathbf{D}_0 \delta_{jk} + \mathbf{T}_{jk}, \quad (9)$$

and \mathbf{T}_{jk} is the hydrodynamic interaction tensor between particles j and k . \mathbf{T}_{jk} includes both interactive ($j \neq k$) and reflective ($j = k$) terms.

Equation (6) is a relatively short-time result, in the sense that Eq. (6) is evaluated by approximating all particles to occupy their initial positions. If one measures D_s on a long time scale, it is insufficient to approximate the positions of all particles, other than the particle of interest, as being constant. To obtain long time values for D_s from Eq. (7), the Smoluchowski equation must be integrated. Ackerson and Fleishman²⁰ have integrated the Smoluchowski equation for a system of two hard spheres with no hydrodynamic interactions (obtaining $\alpha = -2$). Their calculation is the exact analytic result for all times for their boundary conditions. However, in this work the boundary condition satisfied by each sphere at the surface of the other sphere was the boundary condition for a Brownian particle confronted by an infinitely massive, nonmoving wall; the use of this boundary condition

for collisions between a pair of Brownian particles is not justified in the classical literature.²¹

As an alternative to a full integration of Eq. (7), one could apply a memory function formalism or do a perturbation expansion of the Liouville operator $\exp(tL)$, as has been done by Evans and James,¹ Hanna *et al.*,²² Jones and Burfield,²³ Marqusee and Deutch,²⁴ and Tough.⁸ In these calculations, α is found to be the sum of the $\langle \mathbf{T}_{ii} \rangle$ term of Eq. (6) and a memory function (time integral) term. For hard spheres with no hydrodynamic interactions, Tough obtained $\alpha = -4/3$. For hard spheres, Hanna *et al.* found $\langle \mathbf{T}_{ii} \rangle = -1.89\phi$, while the memory term contributes a -2ϕ to α if hydrodynamic effects were ignored. If hydrodynamic interactions were included, the memory term was reduced to -0.16ϕ . Similarly, in a hard sphere system with hydrodynamic interactions, Jones and Burfield²³ found that the $\langle \mathbf{T}_{ii} \rangle$ term contributed -1.73ϕ to α , while the memory term contributes only -0.08ϕ to α .

Marqusee and Deutch²⁴ studied a hard sphere system, and used the Oseen tensor approximation for \mathbf{T}_{ij} . In the Oseen approximation, $\langle \mathbf{T}_{ii} \rangle = 0$, while α is -0.07 if hydrodynamics are included, but $-4/3$ if hydrodynamics are neglected. These results are all in good agreement with those of Evans and James, who used a more accurate form for \mathbf{T}_{ij} , and found α to be incremented by $-111/64$ by the $\langle \mathbf{T}_{ii} \rangle$ term, and by -0.011 by the memory function term, respectively. There is thus reasonable agreement that the memory term is in the range -1 to -2 if hydrodynamics are ignored, but approximately -0.1 if hydrodynamic interactions are included.

Evans and James, and Marqusee and Deutch are apparently the only workers to have obtained the effect of a screened Coulomb (Debye-Hückel) interaction on D_s , based on the Smoluchowski equation and a memory integral. By neglecting hydrodynamics Marqusee and Deutch found a frequency dependent form for α ; this form is negative, and could be large. Evans and James¹ obtained the effect of superposing a Debye-Hückel potential on a hard sphere core, for a system in which $\mathbf{T}_{ij} \neq 0$. As also seen for hard spheres, including hydrodynamics in the calculation greatly changes the value of the memory integral. As shown in Ref. 1, if $\mathbf{T}_{ij} \neq 0$ the electrostatic contribution to α tends to *cancel* the effect of hard sphere forces on α , thereby making α *more positive*. This change in α might not have been expected intuitively. For hard spheres at constant number density, increasing the range of the interaction makes α more negative, regardless of whether or not hydrodynamic interactions are included. For charged spheres, adding hydrodynamic interactions reverses the *sign* of the memory integral. Since Evans and James are in good agreement with other calculations on hard spheres, this surprising result seems unlikely to be a calculational artifact.

Mazo,² Schurr,² and this author³ have all used the Kirkwood formula (4) to obtain the effect of direct interactions on the self-diffusion coefficient or the Stokes' Law drag coefficient. Mazo and this author showed, in the absence of hydrodynamic effects, that hard sphere and screened Coulomb interactions both reduce D_s , a long-range Coulomb interaction having a far larger effect on α than hard sphere

forces. Mazo successfully used his results to interpret data on micelle diffusion.²⁶ Schurr used Eq. (4) to calculate the effect of small ions on the self-diffusion of an isolated macroion. In the absence of hydrodynamic interaction terms, the effect of the small ions is to retard the motion of the macroion by an amount proportional to C_0/K^3 , where C_0 is the ion concentration and K is the Debye length.

Finally, Harris,²⁷ Hess and Klein,⁴ and this author³ have calculated the effect of fluctuation forces on the friction factor of the diffusion coefficient, using approaches which initially refer to the velocities as well as the positions of the diffusing macroparticles. In all three calculations, the unperturbed displacement of a Brownian macroparticle is taken to be given by the free particle Brownian motion propagator; that is, the calculations are taken out to the time scale appropriate for the description of self-diffusion. These calculations all found that electrostatic interactions and a memory term serve to reduce D_s . Harris²⁷ considered the interactions between a macroion and its ionic atmosphere. For a model system without hydrodynamic interactions, he found as the limiting law behavior that a weak long-range intermacromolecular potential acts to reduce D_s and D_m . Hess and Klein⁴ present the calculations most relevant to the problem at hand. On including both electrostatic and hydrodynamic forces, the former by using realistic parameters for a suspension of charged colloids, Hess and Klein computed the concentration dependence of D_s . It was predicted at low concentration that D_s falls very sharply with increasing macroion concentration C , but at higher C , D_s is nearly independent of C , with $D_s \sim D_0/2$.

In summary, calculations of the effect of concentration on D_s fall into three major classes; within each class, there appears to be reasonable agreement between the work of different authors. Calculations based on a diffusion equation^{1,7,11,12,19,20,22-24} find that hydrodynamic interactions by themselves reduce D_s , but that the reduction in D_s is less if the diffusing particles repel each other than if the particles have only a hard-core potential. Memory integral effects also change α , the change in α due to the memory function being negative for hard sphere interactions, and less negative if a screened Coulomb repulsion is superposed on the hard sphere interaction. Regardless of whether or not one includes a memory function term, it found from the diffusion equation (8) that electrostatic repulsions between hard spheres increase D_s over its value for uncharged spheres. On the other hand, calculations^{2,3,25} which use the Kirkwood integral (4), or which initially consider the velocities as well as the positions of the diffusing particles,^{3,4,27} find that D_s is reduced when Coulomb interactions are added to a hard sphere force.

V. APPLICATION TO BIDISPERSE SYSTEMS

The theoretical results noted in Sec. IV primarily apply to the true self-diffusion coefficient of a monodisperse suspension. The experimental data reported here actually gives the (quasi)-self-diffusion coefficient of a dilute solution of large spheres through a concentrated solution of smaller spheres. From the spectrum shown in Fig. 1, it appears (at least for the k vector being studied) that concentration fluctuations of the smaller spheres decay away well before fluc-

tuations in the larger spheres have relaxed. We therefore are looking at D_s in a long-time limit, suggesting that it is inadequate to calculate D_s from the initial positions of all spheres in solution. A long-time expansion is therefore probably necessary. The memory integral expansion for D_s includes effects due to the motion of small spheres around a larger sphere. The published results are a low-concentration expansion, in the sense that the results of multiple simultaneous encounters between a large sphere and smaller spheres are not taken into account.

The results of Schurr²⁵ and Harris²⁷ may be applied to this data in two ways. First, if ϕ_{38} is zero, the large spheres interact with their ion clouds, but not with each other. The macroion-small ion interactions should reduce D_s , the reduction being $\sim C^{-1/2}$, where C is the small-ion concentration. Our best estimate of D_s , with $\phi_{38} = 0$, was reduced when ion exchange resin was added, though the effect is small. This reduction agrees in sign with Schurr's prediction. Second, given the difference in their diffusion coefficients, one might treat 0.038μ spheres as another species of small ion. With this interpretation, the concentration of 0.038μ spheres and the Debye length K are independent; from Ref. 25, one concludes that the fall in D_s is $\sim C/K^3$, which is qualitatively consistent with our data. Since Ref. 25 does not consider hydrodynamic forces, numerical comparison is not useful.

To apply the results of Evans and James¹ to our data, their calculation must be extended to bidisperse sphere suspensions, as is done in the Appendix. It is found that the transformation from a monodisperse to a bidisperse suspension has a numerical effect on α , but does not alter the sign of any term which modifies α . In a bidisperse suspension, if the electrostatic interactions between the suspended particles are enhanced, the diffusion equation (4) therefore predicts that D_s should increase.

Hess and Klein's form for D_s appears to remain valid in bidisperse suspensions, except that (i) in their Eq. (28) the propagators $G(k,t)$ and $S(k,t)$ for the probe particle and the background particles would refer to the motion of particles of different types, and (ii) one must distinguish between the probe-background potential and the potential between pairs of background particles. These changes will lead to small numerical difference in the concentration dependence of D_s . However, after making these changes the effect of the memory term on D_s will still be much larger than the (slight) effect of the $\langle T_{ii} \rangle$ term on D_s , so from the work of Hess and Klein one concludes that enhancing electrostatic interactions will make α more negative and reduce D_s .

VI. DISCUSSION

In the above, experimental and theoretical results on the self-diffusion of interacting Brownian macroparticles were presented. Experimentally, light scattering spectroscopy was used to measure the self-diffusion of a dilute suspension of 0.15μ polystyrene spheres through a concentrated suspension of 0.038μ polystyrene spheres. These spheres, being carboxylate modified, are negatively charged. If no special precautions are taken to exclude small ions from the samples, the sphere-sphere electrostatic interactions are rel-

atively weak; D_s is nearly independent of the concentration ϕ_{38} of the 0.038μ spheres. However, if rigorous measures are taken to exclude small ions, long-range electrostatic interactions between the spheres become stronger; under these conditions, D_s is found to fall substantially with increasing concentration of the 0.038μ spheres.

In Secs. IV and V, theoretical calculations of D_s due to a series of authors were reviewed. There are several ways of approaching the problem. In particular, Evans and James have integrated the Smoluchowski operator (8); it is shown in the Appendix that their calculation is readily extended to bidisperse suspensions. Their calculation predicts that D_s is concentration dependent and that $\lambda = dD_s/dc$ changes in a positive direction if long-range electrostatic interactions between the spheres are enhanced. This prediction of the dependence of λ on long-range sphere-sphere interactions disagrees *as to sign* with experiment; experimentally, λ becomes more negative, not more positive, when electrostatic interactions are enhanced.

It is not claimed here that the theoretical results of Ref. 1 are incorrect, or that they are not a reasonable representation of published predictions of the generalized Smoluchowski equation (GSE). For hard spheres, Ref. 1 is in good agreement with other papers which report the same computation. Instead, it was here sought to test experimentally whether or not the predictions of the GSE correspond to reality. A major disagreement between theory and experiment is here found, under circumstances in which it seems unlikely that the theory is not applicable.

Another method of calculating D_s is through the Kirkwood formula (4) for the friction factor. The use of Eq. (4) in this problem has been justified by Mazo.²⁸ These calculations are typified by the work of Schurr,²⁵ whose calculation correctly predicts that D_s falls if ϕ_{38} is increased or if the small ions are removed.

Finally, it is possible to calculate D_s from a Fokker-Planck equation or a generalized Langevin equation. Numerical results for D_s , at low and high concentrations, were obtained by Hess and Klein.⁴ Our data resembles their numerical predictions, in that D_s at first falls rapidly with increasing ϕ_{38} , and then approaches $D_s \sim D_0/2$ at large ϕ_{38} . The Fokker-Planck and Langevin approaches thus are in reasonable qualitative agreement with the data presented here.

One way to eliminate the discrepancy between the theories is to modify the generalized Smoluchowski equation (GSE) until it predicts the right sign for the dependence of λ on the ionic strength of the solution. A rational modification to the GSE is suggested by the work of Mazo,² Hess and Klein,⁴ and this author,³ which shows that correlations of the random motions and the direct interactions of Brownian macroparticles can increase the drag coefficient, thereby tending to reduce the diffusion coefficient. This frictional effect acts³ by dispersing the random Brownian force on each macroparticle over all the particles in an interacting cluster. Since the fluctuating forces on the particles in a moving cluster are random and add incoherently, while the frictional forces add coherently, by dispersing the Brownian forces over a cluster, the diffusive motions of each particle in

a cluster can be reduced. In terms of the Smoluchowski equation, the friction term acts by replacing the hydrodynamic diffusion operator $\nabla \cdot \mathbf{D}_{ij} \cdot \nabla$ with a dressed diffusion operator $\nabla \cdot \hat{\mathbf{D}}_{ij} \cdot \nabla$, $\hat{\mathbf{D}}$ having been modified from \mathbf{D} by the inclusion of correlations between the Brownian motions of a probe particle and the subsequent forces on that particle due to its neighbors.

APPENDIX: GENERALIZATION OF THE CALCULATION OF EVANS AND JAMES TO BIDISPERSE SYSTEMS

Evans and James¹ show how D_s of a monodisperse system may be computed by use of the Smoluchowski operator (4). It is here shown that the methods of Ref. 1 may be extended to treat a model for bidisperse suspensions.

By dividing the Smoluchowski operator L into single particle and interactive parts

$$L = L_0 + L_1, \quad (\text{A1})$$

where

$$L_0 = D_0 \sum_{k=1}^N \nabla_k^2, \quad (\text{A2})$$

Evans and James demonstrate that D_s may be written as a sum of two terms D_s^0 and D_s^1 . One has

$$D_s^0 = D_0 + \frac{N-1}{V} \int dr_{12} \text{Tr}[\mathbf{T}_{11}(r_{12})] g^{(2)}(r_{12}), \quad (\text{A3})$$

where $g^{(2)}(r_{12})$ is the pair distribution function for particles 1 and 2, and $\text{Tr}[\dots]$ denotes the trace operator. D_s^0 is $D_0 + \langle \mathbf{T}_{ii} \rangle$. For D_s^1 , one has

$$D_s^1 = \frac{V}{3} \int_0^\infty d\tau \{ \langle \nabla_k \text{Tr}[\hat{\mathbf{D}}_{11}] \exp(L_0\tau) \mathbf{D}_{km} \cdot \beta \mathbf{F}_m \rangle + \langle \hat{\mathbf{D}}_{1k} \cdot \beta \mathbf{F}_k \exp(L_0\tau) \mathbf{D}_{1m} \cdot \beta \mathbf{F}_m \rangle - \langle \nabla_k \cdot \mathbf{D}_{k1} \exp(L_0\tau) \nabla_m \cdot \mathbf{D}_{m1} \rangle \}; \quad (\text{A4})$$

where $\hat{\mathbf{D}}_{ik} = \mathbf{D}_{ik} \exp(-\beta U)$ and \mathbf{F}_k is the force on the k th macroparticle. For \mathbf{T}_{11} , one has

$$\mathbf{T}_{11} = \frac{-15}{4} \sum_{l>1} \left(\frac{a}{r_{1l}} \right)^4 \hat{\mathbf{r}}_{1l} \hat{\mathbf{r}}_{1l} + \dots \quad (\text{A5})$$

As seen in Ref. 1, both hard-sphere and long-range interactions contribute to D_s^0 , but only long-range interactions contribute substantially to D_s^1 . If the long-range force is a screened Coulomb interaction, D_s^1 is positive; furthermore, a long-range repulsive interaction will reduce the magnitude of the integral in D_s^0 .

In order to apply these arguments to the system studied here, Eqs. (A1)-(A5) must be modified to describe a bidisperse suspension. This can be done by rewriting L_0 as

$$L_0 = \sum_{k=1}^N D_{0k} \nabla_k^2, \quad (\text{A6})$$

D_{0k} being the free-particle diffusion coefficient of the k th particle. The suspensions studied here are well approximated as containing a single large particle 1, and smaller particles 2, 3, ..., N . Mazur and van Saarloos have obtained \mathbf{T}_{jk} for a pair of spheres of unequal size; the coefficients of the terms \mathbf{T}_{jk} are changed, but its functional form remains the same as

when the spheres are the same size. With these modifications, the derivations of Ref. 1 can be repeated with only minor alterations. Equation (A3) for D_s^0 [whose kernel is essentially the same as Eq. (B4b), Ref. 17] is unaltered if D_0 and \mathbf{T}_{11} are interpreted as the bare diffusion coefficient and the reflection term of \mathbf{T}_{ij} for the probe particle. Since D_{ij} ($i \neq j$) is symmetric in the radii a_i and a_j of the two interacting macroparticles the method of finding Eq. (A4), as shown in Ref. 1, is still valid. Furthermore, to obtain from Eq. (A4) the assertion that $D_s^1 > 0$, one reduces from a complex form to the consideration of the changing distance r_{12} between the particles of an isolated pair. Even if these particles are not the same size, their relative motion is still described by a single diffusion coefficient, which is an average over the two particles in the pair, so the transition from a monodisperse to a bidisperse suspension will alter the calculated magnitude of D_s^1 but not change its sign.

It is thus possible to obtain from the generalized Smoluchowski equation a prediction of the concentration dependence of D_s in a bidisperse suspension. In terms of Eq. (1), increasing the electrostatic repulsions in the suspension acts in two ways to make λ less negative. First, the typical distance between each pair of particles is increased, so the integral in D_s^0 , whose sign is negative, is reduced in magnitude. Second, D_s^1 is a positive number, whose magnitude increases when the strength and range of the screened Coulomb interaction is increased.

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