Concentration dependence of long-time tails in colloidal suspensions

Scott T. Milner and Andrea J. Liu
Exxon Research and Engineering, Annandale, New Jersey 08801
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Long-time tails in the velocity autocorrelation functions of colloidal particles immersed in fluid have been predicted for some time, and recently observed in experiments using diffusing-wave spectroscopy. We compute the linear effect of finite concentration of particles on the low-frequency ($\omega^{1/2}$) correction to the mobility of one colloidal particle, and hence the effect on the long-time tails, using a reflection method. The results are consistent with general arguments for the form of long-time tails in an effective medium.

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INTRODUCTION

Colloidal particles moving under the action of random thermal forces in viscous fluids exhibit Brownian motion, at sufficiently long times. That is to say, the growth of the mean-square position $\langle \delta r^2(t) \rangle$ is diffusive and grows as $6Dt$, while the velocity autocorrelation function (VAF) $\langle v(t)v(0) \rangle$ is often assumed to have only short-time correlations well represented by a delta function.

At shorter times, however, the behavior of such colloidal particles is richer. Hinch [1] and others [2,3] have shown theoretically that the VAF of single particles immersed in fluid have long-time tails which decay as $t^{-3/2}$, by relating the VAF to the mobility of the colloidal particle by fluctuation-dissipation arguments. The long-time tails may be regarded as a result of the hydrodynamic coupling of the colloidal particles to long-lived viscous diffusion modes in the fluid.

Recently, experiments have been performed using diffusing-wave spectroscopy [4,5] to probe early-time behavior of $\langle \delta r^2(t) \rangle$ in colloidal suspensions of latex spheres at a range of moderate concentrations and for varying particle radii [6]. It was found that for times less than the time $\tau_a = (a^2\rho/\eta)^{1/2}$ for vorticity to diffuse a distance of order the particle radius a, the random motions of the particles are not measurably affected by hydrodynamic couplings to other particles; the growth of the mean-square displacement was independent of concentration. In this time regime, the Hinch results [1] predict a characteristic crossover from ballistic motion towards diffusive behavior, which is observed [6]. At the longest times, when the particle motion is simply diffusive, a self-diffusion coefficient $D(\phi)$ depending on the volume fraction ϕ of particles was obtained in good agreement with predictions of Batchelor [7,8].

We are concerned with the concentration dependence of the long-time tail in the VAF, or equivalently with the power-law approach of $\langle \delta r^2(t) \rangle$ to a diffusive law. Previous calculations [9] of mobility tensors in colloidal suspensions have carried out expansions in (a/r) to third order, which is not sufficient to see the effect of a second particle on the mobility of a test particle (i.e., the response of its velocity to an external force acting on it alone).

In this paper, we employ a reflection method [10] adequate to compute the first-order correction in volume fraction of particles ϕ to the $O(\omega^{1/2})$ term in the low-frequency expansion of the self-mobility. We do this by computing [in a certain approximation sufficient to extract the $O(\omega^{1/2})$ term; see below] the shift, due to the presence of a sphere S_2, in the velocity of a sphere S_1, to which an external oscillating force F is applied. We may then average over the uniformly distributed locations of S_2 to get the desired $O(\phi)$ correction. We neglect here small effects on particle mobilities, etc. resulting from small deviations of the particle distribution from random isotropy caused by the drift of the test particles [7,8].

The reflection method consists of trying to find a flow field which may be added to that of a single oscillating sphere S_1 at the origin, which satisfies the no-slip boundary conditions on a second stress- and torque-free sphere S_2 at a position R. If the second sphere S_2 is far away, the unperturbed flow from the first sphere S_1 near S_2 may be expanded in a Taylor series about the location R of S_2. At zero frequency, we know the flow $v^{(0)}(r)$ falls off as $1/r$, the gradients $\nabla v^{(0)}(r)$ as $1/r^2$, and so forth. Each successive term in the Taylor series evaluated on the surface of S_2 is smaller by a factor of a/R.

We truncate the series after the first gradient, and seek a solution of the linearized incompressible Navier-Stokes equations which, when added to the truncated series, satisfies the no-slip and stress-free boundary conditions on S_2. This flow perturbation $v^{(1)}(r)$ is related to the flow around a sphere in a simple shear flow, and falls off as $(a/r)^2$. Back at S_1, we approximate this flow perturbation as a uniform flow (we take no gradient terms in a series about the location of S_1). This uniform-flow correction at S_1 is then of order $O(a/R)^4$; it gives no change in the fluid stresses acting on S_1, but alters its velocity.

When this procedure is extended to finite frequency, an additional length scale enters, namely the viscous wave number k such that $k^2 = i\omega\rho/\eta$. As we shall consider spheres at separations R large and small compared to k^{-1}, we make no assumption about the magnitude of kR. (Essentially, we assume k^{-1} and R are comparable in magnitude, so that ka and a/R are equivalently small quantities, as in Ref. [9].) We calculate the shift in mobility of the test sphere to order $(a/R)^4$ with a coefficient that is a function of kR.

For example, at finite frequency, the second sphere S_2 does not quite follow the mean unperturbed flow due to the first sphere. Inertial terms of $O(k^2)$ cause S_2 to lag this mean unperturbed flow a bit (if the sphere is denser than the fluid). The result is that S_2 moves relative to the mean flow from S_1, which creates a flow perturbation of order $1/R$ back at S_1. This gives a shift in the velocity of S_1 of order $O(k^2a^4/R^2)$. We write this as $O((kR)^2(a/R)^4)$ and see that it contributes at the order of our approximation.

Higher-order terms in a/R may be obtained in principle by considering both higher-order reflections, and higher-order gradients in the series expansion of the flow from one sphere at the location of the other. Higher-order terms in the volume fraction ϕ of the spheres require considering more than two spheres in a sequence of reflections. We shall not pursue such a systematic expansion. Rather, we show in the Appendix that the $O(\phi)$ correction to the $O(\omega^{1/2})$ term in the self-mobility depends only on the leading reflection, i.e., the $O(f(kR)/R^4)$ term.

This simplification works even though the $O(\phi)$ correction to the zero-frequency mobility has significant contributions from pairs of spheres that are too close for an expansion to some leading order in a/R to work. The intuitive reason for this is that spheres much closer than k^{-1} to the test sphere alter its mobility as if the frequency were zero; only spheres at distances of order k^{-1} contribute to the $O(k)$ mobility correction. At low frequencies, k^{-1} is large, and these contributing spheres are far enough away from the test sphere to be treated by the reflection method (expanding in a/R).

Our result at $O(\phi)$ for the amplitude of the long-time tail in the VAF is the same as that for a single particle immersed in fluid with viscosity $\eta(\phi)=\eta_0(1+5\phi/2)$ and density $\rho(\phi)=\rho_0[1+\phi(\rho_b-\rho_f)/\rho_f]$. We speculate in the Conclusion that the concentration dependence of the long-time tail may be given at higher concentration in terms of the properties of the effective medium, again because only distant ($R\sim k^{-1}$) particles alter the $O(k)$ mobility correction. At such distances, the surrounding fluid looks like an effective medium.

CALCULATION

The linearized Navier-Stokes equation for an incompressible fluid with velocity $v(r)$ and pressure $p(r)$ may be written

$$(k^2+\nabla^2)v(r)=\nabla p(r)\ ,\quad \nabla\cdot v=0\ ,\quad k^2=i\omega\ . \tag{1}$$

(We have chosen units in which the fluid density, particle radius, and fluid viscosity are equal to unity.) We construct solutions appropriate for spherical boundaries with the scalar wave solution $f(r;k)=\exp(ikr)/r$. Using linearity of the velocity field in the velocity u of the test sphere S_1 (located at the origin), the general homogenous solution of Eq. (1) for the sphere S_1 oscillating with velocity u (and frequency ω) may be written

$$v^{(0)}(r)=Auf(r;k)+Bu\cdot\nabla\nabla f(r;k)\ , \tag{2}$$

with the general solution for the pressure (which satisfies the Laplace equation) being

$$p(r)=Cu\cdot\nabla(1/r)\ , \tag{3}$$

leading to a particular solution of Eq. (1),

$$v(r)=\nabla p(r)/k^2\ . \tag{4}$$

Enforcing incompressibility leads to $A=Bk^2$; enforcing the no-slip boundary condition $v^{(0)}=u$ on $r=1$ leads to

$$A=\tfrac{3}{2}e^{-ik}\ ,\quad C=-\tfrac{3}{2}(1-ik-k^2/3)\ . \tag{5}$$

The force computed from $F_{\rm hyd}=\int\sigma\cdot\hat{n}dS$, with stress tensor $\sigma=\nabla v+(\nabla v)^T-p\mathbb{1}$, leads to the well-known result

$$F_{\rm hyd}(k)=-6\pi u(1-ik-k^2/9)\ . \tag{6}$$

Now consider the second sphere S_2, at location R; near it, the unperturbed flow $v^{(0)}$ from the first sphere S_1 may be expanded in a Taylor series,

$$v_i^{(0)}(r)\approx v_i^{(0)}(R)+E_{ij}(r-R)_j+\cdots\ , \tag{7}$$

where $E_{ij}=\nabla_j v_i^{(0)}(R)$ is the velocity gradient (unsymmetrized) at R. We now construct the flow field $v^{(1)}$ which satisfies Eq. (1) and no-slip, force-free boundary conditions on S_2 when added to the flow Eq. (7). We do this in two parts; first, we consider the flow perturbation $v^{(1)}$ which results from the presence of the gradient flow and the balance of torques on S_2. Then we shall consider the balance of forces on S_2 and the resulting motion of S_2 relative to the surrounding mean flow, which generates an additional flow $v^{(2)}$.

The flow $v^{(1)}$ is determined in a manner similar to that used in computing $v^{(0)}$. We write the general homogenous and particular solutions of Eq. (1) linear in E_{ij} in terms of the scalar wave solution $f(r;k)$. The homogenous solution is

$$v_i^{(1)}(r)=GE_{ij}\nabla_j f(r;k)+\overline{G}E_{ji}\nabla_j f(r;k)+HE_{jk}\nabla_j\nabla_k\nabla_i f(r;k)\ , \tag{8}$$

with particular solution

$$v_i^{(1)}(r)=\nabla_i p(r)/k^2\ ,\quad p(r)=JE_{ij}\nabla_i\nabla_j(1/r)\ . \tag{9}$$

Incompressibility leads to the condition $G+\overline{G}=Hk^2$. Constraining the velocity on the surface of S_2 to be that of a rotating sphere with its angular velocity in the appropriate direction leads to

$$G+\overline{G}=\frac{5e^{-ik}}{3(1-ik)}\ ,\quad J=-\frac{5(1-ik-2k^2/5+ik^3/15)}{3(1-ik)}\ . \tag{10}$$

By symmetry, there is no hydrodynamic force on S_2 from the gradient flow; we compute the torque in the usual way, and enforce the rotational equation of motion to obtain an equation for $G-\overline{G}$, evaluated at $r=1$,

$$(G-\overline{G})(f''+f'/r)=-(i\omega\rho/5)[1+(G-\overline{G})f']\ . \tag{11}$$

(Here ρ is the mass density of the sphere, and primes indicate differentiation with respect to r). When $G-\overline{G}=0$ (e.g., at $\omega=0$), we have the sphere S_2 rotating with precisely the angular velocity determined by the shear velocity of the flow of S_1.

Now we evaluate the gradients E_{ij} at sphere S_2 from the flow $v^{(0)}$, and the resulting flow $v^{(1)}$ back at sphere S_1, in more detail. It is convenient to expand the third-order gradient of $f(r;k)$ as follows:

$$\nabla_i\nabla_j\nabla_k f(r;k)=a(r;k)n_in_jn_k+b(r;k)(\delta_{ij}n_k+\delta_{ik}n_j+\delta_{jk}n_i)\ , \quad (12)$$

with n_i the radial unit vector, and $a(r;k)$ and $b(r;k)$ defined by

$$a(r;k)=-15\frac{f(r;k)}{r^3}(1-ikr-2k^2r^2/5+ik^3r^3/15)\ ,$$
$$b(r;k)=\frac{3f(r;k)}{r^3}(1-ikr-k^2r^2/3)\ . \quad (13)$$

Then we may write

$$v_i^{(1)}=-(E_{ij}+E_{ji})m_j[\tfrac{1}{2}(G+\overline{G})f'(r;k)+Hb(r;k)+Jb(r;0)/k^2]$$
$$-(E_{ij}-E_{ji})m_j[\tfrac{1}{2}(G-\overline{G})f'(r;k)]$$
$$-E_{jk}m_im_jm_k[Ha(r;k)+Ja(r;0)/k^2]\ , \quad (14)$$

where m_i is the unit vector pointing from S_1 to S_2. We evaluate the gradient factors using the flow $v^{(0)}$ of Eq. (2) as

$$(E_{ij}+E_{ji})m_j=u_i\{Af'(r;k)+2[Bb(r;k)+Cb(r;0)/k^2]\}$$
$$+u_lm_lm_i\{Af'(r;k)+4[Bb(r;k)+Cb(r;0)/k^2]+2[Ba(r;k)+Ca(r;0)/k^2]\}\ ,$$
$$(E_{ij}-E_{ji})m_j=Af'(r;k)[u_i-u_lm_lm_i]\ , \quad (15)$$
$$E_{jk}m_jm_k=u_lm_l\{Af'(r;k)+3[Bb(r;k)+Cb(r;0)/k^2]+[Ba(r;k)+Ca(r;0)/k^2]\}\ .$$

The change $v^{(1)}(0)$ in the velocity u of S_1 must be averaged over the direction and position of the second sphere S_2 to obtain the shift in the mobility $\delta\mu=\delta v/F$. Observe that $(G-\overline{G})f'(r;k)$ is $O(k^2/R^2)$ and $(E_{ij}-E_{ji})m_j$ is $O((a/R)^2)$. Thus, we drop the second term of Eq. (14), as it is of order $(kR)^2/R^6$. We then average the velocity correction at the location of the sphere S_1, denoted $v^{(1)}(0)$, over the direction m_i, and expand to leading (fourth) order in a/R where required, to obtain

$$\langle v_i^{(1)}(0)\rangle_{m_i}=u_i\frac{(1-ik)}{R^4}\left[\frac{75}{x^4}+\left[-\frac{150}{x^4}+\frac{150i}{x^3}+\frac{60}{x^2}-\frac{10i}{x}\right]e^{ix}+\left[\frac{75}{x^4}-\frac{150i}{x^3}-\frac{135}{x^2}+\frac{70i}{x}+\frac{45}{2}-5ix-\frac{5x^2}{6}\right]e^{2ix}\right]\ , \quad (16)$$

where $x=kR$.

Finally, we integrate over the distance R between S_1 and S_2, and multiply by the concentration c of spheres ($\phi=4\pi c/3$ since $a=1$) to obtain, to order k,

$$\langle v_i^{(1)}(0)\rangle=-u_i(1-ik)\phi\left[\frac{15}{8}+\frac{15ik}{4}+O(k^2)\right]\ . \quad (17)$$

Recall that at finite frequency, the second sphere does not quite follow the mean flow generated by the motion of the first sphere; this relative motion of S_2 to the mean background flow near it generates another flow perturbation back at S_1 which contributes to the velocity shift of S_1. The balance of forces on S_2 reads

$$-i\omega mu_2=F_{\rm hyd}=-6\pi(1-ik)[u_2-v^{(0)}(R)]-\tfrac{4}{3}\pi i\omega v^{(0)}(R)\ , \quad (18)$$

where $m=4\pi\rho/3$ is the mass of the sphere. (The first term on the right-hand side is the drag [to $O(k)$] on S_2 as it moves relative to the flow $v^{(0)}(R)$. The second term is the force due to the pressure gradient at S_2, which in the absence of S_2 would accelerate the fluid as its uniform velocity oscillates.) Hence we have

$$\delta u_2\equiv u_2-v^{(0)}(R)\approx\tfrac{2}{9}\delta\rho k^2v^{(0)}(R)(1+ik)\ , \quad (19)$$

where $\delta\rho=\rho-1$ is the difference in mass density of the sphere and fluid, relative to the fluid density.

This relative motion induces a flow at S_1 of the form

$$v_i^{(2)}=A(\delta u_2)_if(r;k)+B(\delta u_2)_l\nabla_l\nabla_if(r;k)+Ck^{-2}(\delta u_2)_l\nabla_l\nabla_i(1/r)\ , \quad (20)$$

with A,B,C as for the flow $v^{(0)}$. Evaluating the derivatives and substituting for δu_2 in terms of $v^{(0)}$, then averaging over the direction of m_i as before, gives

$$\langle\delta v_i^{(2)}(0)\rangle_{m_i}=u_i\frac{\delta\rho(1-ik)}{r^4x^2}[2+(-4+4ix+4x^2/3)e^{ix}+(2-4ix-10x^2/3+4ix^3/3+2x^4/3)e^{2ix}]\ . \quad (21)$$

Again we average over the distance between the two spheres and multiply by concentration to obtain

$$\langle \delta v_i^{(2)}(0) \rangle = u_i(1-ik)\frac{ik\phi\delta\rho}{2} + O(k^2) \ . \tag{22}$$

Now the hydrodynamic force on S_1 is just $F_i = -6\pi u_i(1-ik)$ to $O(k)$ [we are not concerned with $O(k^2)$ corrections to the mobility, so we may neglect inertial terms on S_1]. The mobility shift is given by the sum of the velocity shifts at fixed external force (which balances the hydrodynamic force). So we replace $u_i(1-ik)$ in Eqs. (17) and (22) with $-F_i/(6\pi)$; then we obtain our final result for the mobility to linear order in concentration ϕ and viscous wave number k,

$$\begin{aligned}\mu(k) &= (u + \langle \delta v^{(1)} \rangle + \langle \delta v^{(2)} \rangle)/F \\ &= -\frac{1}{6\pi}\{(1-15\phi/8) + ik(1-[15/4-\delta\rho/2]\phi)\} \ .\end{aligned} \tag{23}$$

DISCUSSION

The velocity autocorrelation function $S_{ij}(t) = \langle v_i(t)v_j(0) \rangle$ is obtained from a fluctuation-dissipation relation [1] of the form

$$S_{ij}(t) = T\delta_{ij}\tilde{\mu}(t) \ , \tag{24}$$

where $\tilde{\mu}(t)$ is the Fourier transform of $\mu([i\omega]^{1/2})$. The long-time tail in $S(t)$ comes from the low-frequency limit of μ obtained in Eq. (23); the power-law decay is $t^{-3/2}$ because the low-frequency correction in μ is $O(\omega^{1/2})$. The power-law behavior is not cut off, nor is the exponent changed, by the presence of other colloidal particles.

We may define a time-dependent diffusion coefficient $D(t)$ by the slope of the mean-square displacement as a function of time $6D(t) = \partial\langle \delta r^2(t) \rangle/\partial t$. Using the VAF and the fluctuation-dissipation relation, this gives

$$D(t) = D - 2\int_t^\infty dt'\tilde{\mu}(t') \ . \tag{25}$$

The limiting value D of $D(t)$ for times long compared to τ_a (and short compared to the time between collisions [8]) is just $\mu(0)$; performing the transform in the long-time limit yields

$$\begin{aligned}\tilde{\mu}(t) &= \{T/(12\pi^{3/2}\rho a^3)\}[\tau(\phi)/t]^{3/2} \ , \\ D(t) &= D(\phi)\{1-[4\tau(\phi)/\pi t]^{1/2}\} \ , \\ D(\phi) &= (6\pi)^{-1}[1-15\phi/8] \ , \\ \tau(\phi) &= \tau_a[1-(15/4-\delta\rho)\phi] \ .\end{aligned} \tag{26}$$

The above result for $D(\phi)$ from a single-reflection calculation is rather close to the result $D(\phi) = (6\pi)^{-1}(1-1.83\phi)$ of Ref. [7] $(15/8=1.875)$.

The result, Eqs. (23) and (26), for the concentration dependence of the long-time tail agrees with the following argument. With the factors of viscosity and particle radius made explicit, the result for $D(t)$ at $\phi=0$ is $D(t) = (6\pi\eta_0 a)^{-1}[1-(4a^2\rho_0/\pi\eta_0 t)^{1/2}]$, where η_0 and ρ_0 are the solvent viscosity and density. If we now replace η_0 with the Einstein result for suspension viscosity $\eta(\phi) = \eta_0[1+5\phi/2+O(\phi^2)]$ and ρ with the solution density $\rho(\phi) = \rho(1+\phi\delta\rho)$, the overall coefficient of the $t^{-1/2}$ term in $D(t)$ would be proportional to $(1+\phi\delta\rho)^{1/2}(1+5\phi/2)^{-3/2} \approx (1-[15/4-\delta\rho/2]\phi)$, as it is in Eq. (26).

It may seem surprising that macroscopic parameters $\eta(\phi)$ and $\rho(\phi)$ could appear in the context of the long-time tail in the VAF of a small particle. After all, the self-diffusion of a particle in the suspension is *not* given by $D(\phi) = 1/[6\pi\eta(\phi)a]$. The difference between these two quantities is (as discussed in the Introduction and Appendix) that while $D(\phi)$ depends strongly on nearby pairs of particles, the long-time tail of a test particle is affected mainly by distant particles. The self-diffusion of a *large* sphere of radius A in the suspension, for which the characteristic length scale of flow (the sphere radius) is much larger than the particles in the suspension, is indeed given by $D(\phi) = 1/[6\pi\eta(\phi)a]$. For such a large-scale flow relative to the particle size, the suspension looks like an effective medium.

Likewise, the $O(\phi)$ calculation explicitly shows that distant particles affect the frequency dependence of the mobility of a test particle by responding to the flow gradients set up by the moving test particle. Since their behavior in a flow gradient is directly related to the macroscopic suspension viscosity, it is not surprising that the suspension viscosity should enter into the result for the long-time tail. We may speculate that the long-time tail will have a coefficient proportional to $\rho(\phi)^{1/2}\eta(\phi)^{-3/2}$ at higher concentrations as well.

In fact, a rather general argument can be given to predict the form of the long-time tail in the VAF, on the basis of momentum conservation. The VAF has been shown in Ref. [1] to be just the response of the system to an initial condition in which the sphere is moving with a thermal initial velocity, $v^2 \sim T/m \sim T/(\rho a^3)$ (this is a consequence of the fluctuation-dissipation theorem). In their original discussion of long-time tails in simple fluids, Alder and Wainwright [2] pointed out that since momentum is conserved and propagates diffusively a length $(\eta t/\rho)^{1/2}$ in time t, the momentum originally confined to a volume of order a^3 is spread at long times over a volume $(\eta t/\rho)^{3/2}$. Hence the velocity of the sphere should be reduced from its initial value by a factor $a^3(\eta t/\rho)^{-3/2}$, and the VAF should be of order $T\rho^{1/2}(\eta t)^{-3/2}$ at late times.

This result should hold even in a concentrated suspension, with η and ρ replaced by the macroscopic suspension viscosity $\eta(\phi)$ and density $\rho(\phi)$, when momentum has diffused a sufficient distance from the sphere. For a single sphere this is clearly a sphere radius (the characteristic time is τ_a); for a concentrated suspension in which the sphere spacing is comparable to the sphere radius, the same length and time scales must emerge.

Note that the long-time tail of the VAF, in Eq. (26), is independent of sphere radius, since $(\tau_a)^{3/2} = (\rho a^2/\eta)^{3/2} \propto a^3$. This suggests we may think of applying Eq. (26) either to large spherical regions of fluid, or to rather small particles, down to nearly molecular size. Indeed, Alder and Wainwright were concerned with the

VAF not of colloidal particles but molecules in a single-component (simulated, two-dimensional) fluid.

Thus it is noteworthy that in simple incompressible, viscous fluids described by linearized hydrodynamics with Gaussian fluctuations, the autocorrelation function of the space- and time-dependent velocity field, $\langle v(rt)v(00)\rangle$, also has long-time tails. For $r^2 \ll \eta t/\rho$ it is easy to show [11] that $\langle v_i(rt)v_j(00)\rangle = [T/(12\pi^{3/2}\rho)](\eta t/\rho)^{-3/2}\delta_{ij}$, which agrees exactly with Eq. (26). In this context, the long-time tails arise because the VAF of nearby points in space has contributions from shear modes with long wavelengths and hence long decay times.

Again, we may think of the velocity field autocorrelation function of a suspension, and replace η and ρ by $\eta(\phi)$ and $\rho(\phi)$ in the above expression. The connections between long-time tails in simple fluids and colloidal suspensions are then the following: (i) at sufficiently long times, the momentum diffusing away from a colloidal particle moving in a suspension behaves as if it were in an effective medium; (ii) the long-time tail in the VAF of a colloidal particle is independent of its size, suggesting that the description may apply to rather small particles ($\approx$ molecules); and (iii) a continuum calculation of the correlation function of a simple fluid at nearby points and long-time delays is consistent with the long-time tail of spheres moving in such a fluid.

The arguments presented in the Appendix suggest that the present calculation of the linear dependence on ϕ of the long-time tail amplitude is exact, despite the fact that a far-field expansion was used to calculate it. In the limit of low frequencies, only far-away spheres respond to the motion of a driven sphere in a way different from their zero-frequency response, and so a far-field expansion is valid for the present calculation, even though it is not valid, e.g., for computing the zero-frequency mobility of a test sphere in a suspension [7]. The present calculation of concentration-dependent long-time tails may be compared both to a recent calculation of mobilities in dilute colloidal suspensions [12], and to recent experiments [6] that employ diffusing-wave spectroscopy [4,5] to determine the mean-square displacement $\langle r^2(t)\rangle$ of particles in a colloidal suspension.

The experiments of Ref. [6] were performed using micrometer-sized polystyrene latex particles, with volume fractions ranging from $\phi=0.02$ to 0.3. The experimental results for $D(t)$ cover a temporal range of roughly two decades above and one decade below τ_a. Data at both the earliest and latest times is less reliable, because of poor counting statistics and baseline subtraction uncertainties, respectively. The data appear to collapse for all volume fractions, over the entire temporal range, with a scaling like Eq. (26), except that the characteristic time $\tau(\phi)$ is reported to be consistent with $\tau(\phi)=a^2\rho_0/\eta(\phi)\approx\tau_a[1-5\phi/2+O(\phi^2)]$, rather than the expression in Eq. (26). The master curve is in good agreement with the calculated $D(t)$ curve for a *single* sphere in fluid, based on the results of Ref. [1] for the VAF.

It is worth noting that the best data of the experiments correspond to intermediate times, at which $D(t)$ is not well described simply in terms of a power-law correction to the long-time value. It is thus possible that the characteristic time $\tau(\phi)$ extracted by collapsing the data is biased by early times, at which the data should not scale the same way as at long times.

Clercx and Schram [12] compute the mobility matrix by expanding the flow field around the two particles in vector spherical harmonics centered on the two particles, relating the two sets of basis functions, and enforcing the boundary conditions on the spheres to some finite order in the expansion. The result is a numerical calculation of the mobility $\mu(\omega)$, which the authors present (after numerical Fourier transforms, etc.) in terms of $\bar{D}(t)=\partial\langle r^2(t)\rangle/\partial t$. Analytical results for the concentration dependence of the long-time tail are not presented.

Numerical results are given in Ref. [12] for ϕ=0,0.1,0.2,0.3, and mass density ratios 0.1,0.2,1,5,10. The numerical results cannot be collapsed into a single master curve throughout the temporal range, in contrast to the experimental data. In particular, for volume fraction $\phi=0.3$, $\bar{D}(t)$ is not monotonic increasing (which may be the result of difficulties with the numerical Fourier transform [12]). We find that the portion of the $\bar{D}(t)$ data reasonably well described by a long-time tail (sufficiently late times) appears to scale as in Eq. (26), for all mass density ratios presented, and for the lower concentrations ($\phi\leq 0.2$). Thus the two theoretical approaches seem consistent where both are expected to apply, but neither appears to agree with the experimental data obtained so far. It would be interesting to pursue experiments in which the particles are not so closely density matched, as in Ref. [6] to study the experimental dependence on $\delta\rho$ of the long-time tail.

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APPENDIX

Consider the shift in velocity of a test sphere S_1 at fixed external force due to the presence of a second sphere S_2 at a distance r. When expanded in powers of a/r and averaged over the direction from S_1 to S_2, we have some expression

$$\delta v(k)=4\pi cu\int_{2a}^{\infty}dr\, r^2\sum_{n=4}^{\infty}(a/r)^n f_n(kr)\ . \tag{A1}$$

[We have computed explicitly $f_4(kr)$.] It appears that for $kr\to 0$, all the $f_n(kr)$ begin as $f_n(0)+\frac{1}{2}f_n''(0)(kr)^2+\cdots$. Then for $n>4$, the expansion to $O(k^2)$ may be carried out under the integral sign without creating divergent integrals (up to the logarithmic divergence for $n=5$). Hence, for $n>4$, the small-k limit of the contributions to δv begins at $O(k^2)$.

Now consider $n=4$. We cannot expand to $O(k^2)$ as we did for $n>4$; we may instead rescale the integral as

$$k\int_{2ka}^{\infty}dy\, y^{-2}[f_2(y)-f_2(0)]+\tfrac{1}{2}f_2(0)a^3\ . \tag{A2}$$

Now $f_2(y)-f_2(0)$ goes as $\frac{1}{2}f_2''(0)y^2$ for small y, so we may take the lower limit of integration to zero without trouble. Hence the $O(k)$ contribution to $\delta v(k)$ is

$$\delta v(k)=4\pi cuk\int_0^\infty dy\, y^{-2}[f_2(y)-f_2(0)]\ . \qquad \text{(A3)}$$

We may ask about the self-consistency of keeping only the $(a/r)^4$ term in another way; namely, where in the domain of integration does the largest contribution to $\delta v(k)$ come from?

For small k, we may choose a length L much greater than a but much less than k^{-1}; for $r<L$, we may expand $f_2(kr)$. The domain of integration $\int_{2a}^{L}$ gives only constant and $O(k^2)$ contributions to the integral. Beyond $r=L$, expansions in a/r are justified. The $O(k)$ contribution to Eq. (29) comes from a range of integration roughly $\int_L^{k^{-1}}$, as we anticipated in the Introduction.

[1] E. J. Hinch, J. Fluid Mech. **72**, 499 (1975).
[2] B. J. Alder and T. E. Wainwright, Phys. Rev. A **1**, 18 (1970).
[3] R. Zwanzig and M. Bixon, Phys. Rev. A **2**, 2005 (1970).
[4] D. J. Pine, D. A. Weitz, J. X. Zhu, and E. Herbolzheimer, J. Phys. (Paris) **51**, 2101 (1990).
[5] P. E. Wolf and G. Maret, in *Scattering in Volumes and Surfaces,* edited by M. Nieto-Vesperinas and J. C. Dainty (Elsevier, Amsterdam, 1990), p. 37.
[6] J. X. Zhu, D. J. Durian, D. A. Weitz, and D. J. Pine, Phys. Rev. Lett. **68**, 2559 (1992).
[7] G. K. Batchelor, J. Fluid Mech. **74**, 1 (1976).
[8] The time regime probed by the experiment is not so long that concentration-gradient effects on $D(\phi)$ are relevant; i.e., the assumption of randomly distributed colloidal particles is justified in the experiment.
[9] W. van Saarloos and P. Mazur, Physica A **120**, 77 (1983).
[10] J. Happel and H. Brenner, *Low-Reynolds-Number Hydrodynamics* (Prentice-Hall, Englewood Cliffs, NJ, 1965), Chap. 6.
[11] R. F. Fox, Physica A **118**, 383 (1983).
[12] H. J. H. Clercx and P. P. J. M. Schram, Physica A **174**, 325 (1991).