J. Fluid Mech. (1993), *vol.* 257, *pp.* 607–636

The dynamic mobility of particles in a non-dilute suspension

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(Received 29 December 1992 and in revised form 6 July 1993)

When an alternating electric field is applied to a colloid the particles oscillate at a velocity proportional to the applied field strength. The complex constant of proportionality is termed the dynamic mobility (O'Brien 1988). Although this quantity can now be determined from electroacoustic measurements in suspensions of arbitrary concentration (O'Brien 1990), the theory for interpreting these measurements in terms of the size and charge of the particles is limited to dilute suspensions.

In this paper we derive an expression for the $O(\phi)$ correction to the dynamic mobility in a random suspension of uniform spheres with volume fraction ϕ. It is assumed that the particle radius is much greater than the double layer thickness but much smaller than the sound wavelength. The mobility is calculated using O'Brien's 1979 macroscopic boundary integral technique. This method ensures a correct mathematical formulation of the problem, and yields an absolutely convergent expression for the average particle velocity. The evaluation of this expression to $O(\phi)$ involves the determination of the velocities of an isolated pair of particles at various separations and frequencies of oscillation. These velocities are computed using the collocation technique and the $O(\phi)$ correction to the dynamic mobility is then obtained by numerically integrating over all particle separations.

1. Introduction

An alternating electric field causes colloidal particles to move with a sinusoidal velocity which depends on their charge and size, and on the frequency of the applied field. In this paper we are concerned with the calculation of the particle velocity in a non-dilute suspension of uniform, non-conducting spheres.

As in other suspension calculations (Batchelor 1974) we will represent macroscopic quantities as averages over a sample volume V containing a representative sample of suspension. These averages will be denoted by angle brackets. For example the macroscopic electric field $\langle \boldsymbol{E} \rangle$ is defined as

$$\langle \boldsymbol{E} \rangle = \frac{1}{V}\int \boldsymbol{E}\,\mathrm{d}V, \tag{1.1}$$

where $\boldsymbol{E}$ is the local electric field. The sample volume V can be any shape, but it must be small compared to the macroscopic dimensions of the suspension or the sound wavelength at the applied frequency.

In the analysis, all time-varying quantities will be written in complex form, with an $\mathrm{e}^{i\omega t}$ variation.

The average velocity $\langle \boldsymbol{U} \rangle$ of the particles in V depends on the electric field $\langle \boldsymbol{E} \rangle$, but it is not uniquely determined by $\langle \boldsymbol{E} \rangle$, for in addition to the motion driven by the local field, there is a component due to the local bulk motion of the suspension, which tends to convect the particle back and forth. This local bulk motion is characterized by the macroscopic momentum per unit mass in V, denoted by $\bar{\boldsymbol{u}}$, where (O'Brien 1990)

$$\bar{\boldsymbol{u}} = \frac{\langle \rho \boldsymbol{u} \rangle}{\langle \rho \rangle}.$$

Here ρ and $\boldsymbol{u}$ are the local density and velocity respectively.

From the linearity of the governing equations (see §3) it follows that the contributions from the electric field and the local bulk motion are independent and are proportional to the corresponding driving field. Hence for a statistically isotropic suspension the particle velocity $\langle \boldsymbol{U} \rangle$ is given by an expression of the form

$$\langle \boldsymbol{U} \rangle = \mu_D \langle \boldsymbol{E} \rangle + \gamma \bar{\boldsymbol{u}}, \tag{1.2}$$

where μ_D and γ are suspension transport properties.† μ_D is the dynamic mobility. The quantity γ is another type of mobility, associated with the particle motion in a macroscopic sound wave.

Our aim is to calculate μ_D correct to $O(\phi)$. From (1.2) it can be seen that μ_D is the velocity per unit electric field for $\bar{\boldsymbol{u}} = 0$. Although this definition appears to be a simple extension of the definition for the electrophoretic mobility μ in a static field, the latter quantity is different, for μ is defined under conditions of zero volume-average velocity $\langle \boldsymbol{u} \rangle$ (Chen & Keh 1988), rather than zero momentum. The two velocities $\bar{\boldsymbol{u}}$ and $\langle \boldsymbol{u} \rangle$ are not equal in general, for from the above definition of $\bar{\boldsymbol{u}}$ we see that

$$\bar{\boldsymbol{u}} = \frac{\rho_1 \langle \boldsymbol{u} \rangle + \phi \Delta\rho \langle \boldsymbol{U} \rangle}{\langle \rho \rangle}, \tag{1.3}$$

where ρ_1 is the liquid density and $\rho_1 + \Delta\rho$ is the particle density. In the zero frequency limit the coefficient γ in (1.2) approaches unity, since there are no inertia forces to cause the particles to lag the liquid motion, and thus from (1.2) and (1.3) we find that the static mobility is related to the dynamic mobility by

$$\mu = \lim_{\omega \to 0} \frac{\mu_D}{1 - \phi \dfrac{\Delta\rho}{\langle \rho \rangle}}. \tag{1.4}$$

As the particles oscillate backwards and forwards they generate macroscopic sound waves. This phenomenon of sound wave generation in a colloid by an applied electric field is called the electrokinetic sonic amplitude, or ESA effect (Oja, Petersen & Cannon 1985). The dynamic mobility can be determined experimentally by measuring the ESA or the reverse effect of electric fields generated by an applied sound wave. Formulae for determining μ_D from such measurements are given in O'Brien (1988; equations (4.4) and (5.6)) for the case of a dilute suspension in a parallel-plate electrode device. For concentrated suspensions the corresponding formula for μ_D can be obtained by solving the differential equations for $\langle \boldsymbol{E} \rangle$, $\bar{\boldsymbol{u}}$ and the macroscopic pressure distribution set out in §5 of O'Brien (1990).

Although it is now possible to determine μ_D from such measurements in suspensions of arbitrary concentration, the theory for determining particle size and charge from the

† By using similar arguments to those used in the derivation of the electroacoustic reciprocal relation in the Appendix to O'Brien (1990), it is possible to derive a macroscopic uniqueness theorem which proves that the average velocity $\langle \boldsymbol{U} \rangle$ is uniquely determined by the local macroscopic electric field and momentum per unit mass. Thus there are no other driving terms in equation (1.2).

measured μ_D is limited to dilute suspensions (O'Brien 1988; Loewenberg & O'Brien 1992). In this paper we take the first step towards a theory for concentrated suspensions by calculating the $O(\phi)$ correction to the dynamic mobility.

2. Outline of the paper

In the following section we set out the equations and boundary conditions for the local velocity, pressure and electric fields in the suspension.

The $O(\phi)$ correction for μ_D is obtained here using the macroscopic boundary integral technique devised by O'Brien (1979). The procedure begins, in §4, with a Green's function solution for the local velocity field in terms of integrals over the particles and over a macroscopic boundary enclosing the suspension sample. The integrals involve the local stress and velocity. In the macroscopic boundary integral these quantities can be replaced by the macroscopic pressure and velocity and the integral converted to a volume integral over the sample. A similar type of formula is also obtained for the local electric field. In §5 these expressions are combined with a Faxén formula for the motion of a sphere in ambient electric and flow fields. This yields an exact expression for the velocity of a particle in terms of integrals over the surfaces of the other particles in the suspension. The contribution from the particles, which would result in a non-convergent sum if taken in isolation, is cancelled at large distances by the contribution from the macroscopic boundary integral. In §6 we take the average of this formula over an ensemble of macroscopically identical suspensions to obtain the $O(\phi)$ correction to μ_D in terms of an integral involving the dynamic mobility of an isolated pair of spheres in an applied electric field. In §7 we show how the dynamic mobility of the sphere pair can be determined from the more familiar hydrodynamic resistance tensor of a pair of uncharged spheres. The calculation of this resistance tensor is described in the Appendix. The form of the dynamic mobility of a sphere pair as a function of separation and frequency is described in §8. Finally, in §9 we evaluate the integral of the dynamic mobility over all separations to obtain the $O(\phi)$ correction to μ_D.

3. The mathematical statement of the problem

As mentioned above, the colloidal particles move in an electric field because they are charged. This charge, which usually resides on the particle surface, is balanced by an equal and opposite charge on the ions in the surrounding electrolyte. These ions form a diffuse cloud around the particle. The combination of surface charge and an equal and opposite diffuse layer charge is called the electrical double layer (Hunter 1987).

The thickness of the double layer can be reduced by adding salt to the suspension. In our calculations it will be assumed that the double-layer thickness is much less than the particle radius, an assumption which is often satisfied in practice. For example, in 10^{-3} M KCl, the double-layer thickness is only 10 nm, so the thin double-layer constraint is satisfied by particles of a micrometre or more.

When an electric field is applied to a colloid a tangential flow is generated by the electrical forces on the diffuse part of the double layer. For the thin double-layer systems of interest here, the diffuse layer can be treated as an infinitesimally thin sheet, and this flow can be represented as a tangential velocity jump of

$$\frac{\epsilon\zeta}{\eta}\nabla_s\psi \tag{3.1}$$

at the particle surface (O'Brien 1988), where ϵ and η are the permittivity and viscosity of the solvent respectively, and ζ is the equilibrium voltage drop between the particle surface and the bulk electrolyte. $-\nabla_s \psi$ is the component of the local electric field tangential to the particle surface.

The particle Reynolds number Ua/ν for this motion is typically very small. For example a 1 μm diameter particle with a zeta potential of 50 mV has a Reynolds number of 2×10^{-5} in a field of 1000 V/m, where we have used the estimate $\epsilon\zeta E/\eta$ for the particle velocity. Thus we can neglect the inertia term $\rho \boldsymbol{u} \cdot \nabla \boldsymbol{u}$ in the Navier–Stokes equations, which then reduce to

$$\mathrm{i}\omega\rho\boldsymbol{u} = -\nabla p + \eta\nabla^2\boldsymbol{u}, \tag{3.2}$$

and

$$\nabla \cdot \boldsymbol{u} = 0, \tag{3.3}$$

where p and $\boldsymbol{u}$ are the fluid velocity and pressure. For convenience we have dropped the subscript 1 on the liquid density, which will henceforth be denoted simply by ρ. The incompressibility constraint (3.3) is invoked on the assumption that the particle radius is much smaller than the sound wavelength.

In most suspension calculations the linear inertia term $\mathrm{i}\omega\rho\boldsymbol{u}$ is also neglected. The ratio of the linear inertia term to the viscous stress is characterized by the dimensionless quantity $\omega a^2/\nu$. In this application, where the applied field may have a frequency of several MHz, $\omega a^2/\nu$ can be $O(1)$ or greater; in the case of a 1 μm diameter particle at 1 MHz, $\omega a^2/\nu = 1.6$.

The amplitude of the particle oscillations at these high frequencies is very small. For a 50 mV particle in a 1 MHz field of 1000 V/m, the amplitude is only 5×10^{-12} m. It is remarkable that such tiny motions can give rise to measurable macroscopic sound waves.

The expression (3.1) for the velocity jump involves the electrical potential ψ, and so this quantity must be evaluated before the velocity problem can be addressed. In our calculation of the potential, we will assume that the particle charge is small enough so that the condition

$$\frac{1}{\kappa a}\exp\left(\frac{e|z\zeta|}{2kT}\right) \ll 1 \tag{3.4}$$

is satisfied, where a is the particle radius, κ^{-1} is the double-layer thickness and z is the counterion valency. When this condition is satisfied the distortion of the diffuse layer does not have a significant effect on the field (O'Brien 1986), and hence the applied field distribution is the same as that for a suspension of uncharged particles.

Since the quantity κa is large for the thin double-layer systems of interest here, the condition (3.4) is satisfied for a realistic range of ζ potentials.

It will also be assumed that the particle permittivity is much less than that of the solvent, as is usually the case for aqueous suspensions. When this condition, and the constraint (3.4) are satisfied, the normal derivative of ψ at the particle surface is zero.

Thus the calculation of the particle motion involves the solution of Laplace's equation for ψ, and equations (3.2)–(3.3) for $\boldsymbol{u}$ and p, subject to the boundary conditions that there is a velocity jump (3.1) on the particle surfaces, that the normal component of the electric field at the particle surface is zero, and that the volume average field is $\langle \boldsymbol{E} \rangle$ while the momentum per unit mass $\bar{\boldsymbol{u}}$ is zero.

The electric force exerted by the applied field on each particle is balanced by an equal and opposite force on the diffuse layer. Thus the force and torque-balance equations for the particle and its double-layer take the form

$$\mathrm{i}\omega M\boldsymbol{U} = \boldsymbol{F}, \tag{3.5}$$

and
$$\mathrm{i}\omega I_M \boldsymbol{\Omega} = \boldsymbol{T}, \tag{3.6}$$

where $\boldsymbol{U}$ and $\boldsymbol{\Omega}$ are the translational and angular velocity of the body, and $\boldsymbol{F}$ and $\boldsymbol{T}$ are the hydrodynamic force and torque on the particle and diffuse layer. Since the double-layer is thin we can represent $\boldsymbol{F}$ and $\boldsymbol{T}$ as integrals over the particle surface and take M and I_M to be the mass and moment of inertia of the particle respectively.

In the zero frequency limit the unsteady Stokes equations (3.2) and (3.3) are satisfied by the fluid velocity field

$$\boldsymbol{u} = \frac{\epsilon\zeta}{\eta}\nabla\psi + \boldsymbol{U}, \tag{3.7}$$

with a uniform particle velocity $\boldsymbol{U}$. The term $(\epsilon\zeta/\eta)\nabla\psi$ represents a steady potential flow and hence it does not contribute to the hydrodynamic force or torque on the particle. Thus the solution (3.7) also satisfies the conditions (3.5) and (3.6) that the particles are force and torque-free at zero frequencies. The particle velocity $\boldsymbol{U}$ in this limit is determined from the zero momentum flux requirement. From (1.3) it follows that

$$\frac{\phi\,\Delta\rho}{\rho}\boldsymbol{U} = -\langle \boldsymbol{u}\rangle$$

for zero momentum flux. On evaluating the quantity $\langle \boldsymbol{u}\rangle$ using the form (3.7) for local velocity $\boldsymbol{u}$ we find that

$$\lim_{\omega\to 0}\mu_D = \frac{\epsilon\zeta}{\eta}\frac{K^*/K}{1+\phi\,\Delta\rho/\rho}, \tag{3.8}$$

where K^* is the electrical conductivity of the suspension and K is the conductivity of the background electrolyte. In deriving this result we have replaced $\nabla\psi$ in the electrolyte by $-\boldsymbol{i}/K$, where $\boldsymbol{i}$ is the local electric current density, and we have used the fact that $\boldsymbol{i}$ is zero inside the particles.

4. The integral expression for the velocity and electric field

The Green's function $\boldsymbol{G}$ for the unsteady Stokes equations (3.2) and (3.3) has the form (Williams 1966)

$$G_{ij} = \frac{1}{8\pi\eta}\left(\delta_{ij}\frac{A(R)}{r} + x_i x_j \frac{B(R)}{r^3}\right), \tag{4.1}$$

where
$$\left.\begin{aligned} A &= 2\,\mathrm{e}^{-R}\left(1+\frac{1}{R}+\frac{1}{R^2}\right) - \frac{2}{R^2}, \\ B &= -2\,\mathrm{e}^{-R}\left(1+\frac{3}{R}+\frac{3}{R^2}\right) + \frac{6}{R^2}, \end{aligned}\right\} \tag{4.2}$$

$$k^2 = \mathrm{i}\frac{\omega}{\nu}, \quad R = kr \tag{4.3}$$

and ν is the kinematic viscosity.

$G_{ij}(\boldsymbol{x})$ is the ith component of the fluid velocity at $\boldsymbol{x}$ due to a unit point force in the x_j direction acting at the origin in an infinite liquid.

As $r\to 0$ with k held fixed, $\boldsymbol{G}$ diverges like $1/r$. This is a consequence of the fact that the viscous terms in the unsteady Stokes equations dominate the inertia terms at small

r; the equations in this case reduce to the steady Stokes equations, which have a Green function proportional to $1/r$. At large r the inertia terms dominate in the equations of motion, the flow is irrotational and G decays like $1/r^3$.

The Green's function representation for the solution $\boldsymbol{u}$ of the unsteady Stokes equations take the form

$$\boldsymbol{u}(\boldsymbol{x}_0) = \sum_p \boldsymbol{u}_p(\boldsymbol{x}_0) + \int_\Gamma (\boldsymbol{G}\cdot\boldsymbol{\sigma} - \boldsymbol{u}\cdot\boldsymbol{T})\cdot \mathrm{d}\boldsymbol{S}, \tag{4.4}$$

where Γ is a closed surface and $\mathrm{d}\boldsymbol{S}$ points out of Γ. $\boldsymbol{T}$ is a third-order tensor, with T_{ijk} representing the ik component of the stress tensor associated with the flow field G_{ij}. $\boldsymbol{u}_p$ is the contribution to the velocity at $\boldsymbol{x}_0$ from the pth particle within Γ, given by

$$\boldsymbol{u}_p = \int_{A_p} (\boldsymbol{G}\cdot\boldsymbol{\sigma} - \boldsymbol{u}\cdot\boldsymbol{T})\cdot \mathrm{d}\boldsymbol{S}, \tag{4.5}$$

where $\mathrm{d}\boldsymbol{S}$ points into the particle. The expression (4.4) is an extension of the result given by Ladyzhenskaya (1969) for Stokes flow to the oscillating case.

In the macroscopic boundary integral method (O'Brien 1979), the surface Γ is taken to be a 'macroscopic' surface, that is, one for which the radii of curvature are much greater than the average particle separation. Γ could, for example, be a sphere with a radius much greater than the average particle separation. Such a surface will pass through both fluid and particles. In writing (4.4) in this case we formally include the contribution to the integral over Γ from the portion lying inside the particles, so that the integral extends over all of Γ. The contribution from these portions of Γ is cancelled in (4.4) by the contribution to the $\boldsymbol{u}_p$ from the surfaces of intersection of the cut particles.

The terms $\boldsymbol{G}$ and $\boldsymbol{T}$ in the integral over Γ vary much more slowly with position than $\boldsymbol{\sigma}$ and $\boldsymbol{u}$, since the radii of curvature of Γ are much greater than the lengthscales for the microscopic fluctuations. Thus the fluctuations in $\boldsymbol{\sigma}$ and $\boldsymbol{u}$ cancel out on integration, and these terms can be approximated in the integral by their macroscopie averages $\langle\boldsymbol{\sigma}\rangle$ and $\langle\boldsymbol{u}\rangle$. Hence the integral over Γ in (4.4) becomes

$$\int_\Gamma (\boldsymbol{G}\cdot\langle\boldsymbol{\sigma}\rangle - \langle\boldsymbol{u}\rangle\cdot\boldsymbol{T})\cdot \mathrm{d}\boldsymbol{S}. \tag{4.6}$$

The velocity $\boldsymbol{u}$ is assumed to be a stationary random function of position within Γ, and thus the deviatoric part of the stress tensor $\boldsymbol{\sigma}_D$ is also a stationary function, with a constant mean. It follows that the product of $\boldsymbol{G}$ and $\langle\boldsymbol{\sigma}_D\rangle$ in (4.6) is $O(1/r^3)$, since G itself is $O(1/r^3)$ at large r. Thus as the radius of Γ becomes infinite the contribution to the surface integral from this term vanishes. We may therefore replace $\langle\boldsymbol{\sigma}\rangle$ in (4.6) by $-\langle p\rangle\boldsymbol{I}$ in this limit. On applying Gauss's divergence theorem to the integral (4.6) we then obtain

$$\int_V \boldsymbol{G}\cdot(-\boldsymbol{\nabla}\langle p\rangle - \mathrm{i}\omega\rho\langle\boldsymbol{u}\rangle)\,\mathrm{d}V + \langle\boldsymbol{u}(\boldsymbol{x}_0)\rangle. \tag{4.7}$$

Here V is the volume lying inside Γ and outside a vanishingly small sphere centred on $\boldsymbol{x}_0$. The term $\langle\boldsymbol{u}(\boldsymbol{x}_0)\rangle$ arises from the surface integral over the small sphere. In deriving this result we have used the fact that

$$\boldsymbol{\nabla}\cdot\boldsymbol{G} = 0,$$

and
$$i\omega\rho \boldsymbol{G} = \nabla\cdot \boldsymbol{T},$$

since the flow field $\boldsymbol{G}$ and the corresponding stress tensor $\boldsymbol{T}$ satisfy the unsteady Stokes equations.

In the dynamic mobility calculation the macroscopic momentum term $\bar{\boldsymbol{u}}$ is set to zero. Since the rate of change of this momentum is equal to the macroscopic pressure gradient in the suspension (see (3.5) in O'Brien 1990) we can set $\nabla\langle p\rangle$ to zero in the above integral.

As discussed in §1, the volume averaged velocity $\langle \boldsymbol{u}\rangle$ is related to $\bar{\boldsymbol{u}}$ by the formula (O'Brien 1988, p. 80)
$$\langle\rho\rangle \bar{\boldsymbol{u}} = \rho\langle \boldsymbol{u}\rangle + \phi\,\Delta\rho\langle \boldsymbol{U}\rangle. \tag{4.8}$$

On setting $\bar{\boldsymbol{u}}$ to zero we find that
$$\langle \boldsymbol{u}\rangle = -\frac{\phi\,\Delta\rho}{\rho}\langle \boldsymbol{U}\rangle. \tag{4.9}$$

Substituting this formula for $\langle \boldsymbol{u}\rangle$ in the expression (4.7) for the macroscopic boundary integral and combining with (4.4) we find that the velocity at a point in the suspension is given by
$$\boldsymbol{u}(\boldsymbol{x}_0) = \sum_p \boldsymbol{u}_p(\boldsymbol{x}_0) - \frac{\phi\,\Delta\rho}{\rho}\langle \boldsymbol{U}\rangle\cdot\left[\boldsymbol{I} - i\omega\rho\int_V \boldsymbol{G}\,\mathrm{d}V\right]. \tag{4.10}$$

From the formula (4.5) it follows that the contribution $\boldsymbol{u}_p$ from a distant particle is
$$-i\omega\,\Delta\rho v \boldsymbol{G}\cdot \boldsymbol{U} + O(1/r^4),$$

where v is the particle volume. The leading term in this formula is cancelled in (4.10) by the volume integral that arose from the macroscopic boundary term, and thus the formula converges as Γ becomes infinite.

By similar arguments it can be shown that the electric field at $\boldsymbol{x}_0$ can be written in the analogous form (O'Brien 1979, equation (3.11))
$$\boldsymbol{E}(\boldsymbol{x}_0) = \langle \boldsymbol{E}(\boldsymbol{x}_0)\rangle + \frac{n\langle \boldsymbol{S}\rangle}{3\epsilon} + \sum_p \boldsymbol{E}_p(\boldsymbol{x}_0) - \frac{1}{4\pi\epsilon}\int_V n\langle \boldsymbol{S}\rangle\cdot\nabla\nabla\frac{1}{r}\,\mathrm{d}V, \tag{4.11}$$

where n is the particle number density,
$$\boldsymbol{S} = \epsilon\int_{A_p}\left(\psi\boldsymbol{n} - \boldsymbol{x}\frac{\partial\psi}{\partial n}\right)\mathrm{d}A \tag{4.12}$$

is the electric dipole strength of the particle and
$$\boldsymbol{E}_p(\boldsymbol{x}_0) = \frac{1}{4\pi}\int_{A_p}\left(\psi\nabla\nabla\frac{1}{r} - \nabla\frac{1}{r}\nabla\psi\right)\cdot\boldsymbol{n}\,\mathrm{d}A \tag{4.13}$$

is the contribution to the field at $\boldsymbol{x}_0$ from the pth particle in Γ. In these formulae the unit normal $\boldsymbol{n}$ points out of the particle.

In the derivation of these results it has been assumed that the unsteady Stokes equations (3.2) and (3.3) apply everywhere in the fluid within Γ. In fact the incompressibility condition (3.3) is only approximately satisfied, and our results are valid only if Γ is much smaller than the wavelength of sound. The limit of infinite Γ

that we have taken is therefore not strictly valid. This limit should be interpreted as the limit as the dimensions of Γ grow much larger than the average particle separation while remaining much smaller than the sound wavelength.

5. A formula for the particle velocity in a suspension

For the next step in the macroscopic boundary integral method we require a Faxén formula for the velocity of a sphere placed in an infinite liquid with an ambient electric field $\boldsymbol{E}_a(\boldsymbol{x})$ and flow field $\boldsymbol{u}_a(\boldsymbol{x})$. This formula will be used for calculating the velocity of a test particle in a suspension, with the 'ambient' fields $\boldsymbol{u}_a$ and $\boldsymbol{E}_a$ given by the expressions (4.10) and (4.11), with the sums extending over all particles except the test particle.

The calculation of the particle velocity in these ambient fields involves the solution of Laplace's equation, and the unsteady Stokes equations (3.2) and (3.3) subject to the boundary conditions that $\boldsymbol{u}$ and $\boldsymbol{E}$ approach the ambient fields far from the particle and

$$\left.\begin{aligned} \boldsymbol{u} &= \boldsymbol{U}+\boldsymbol{\Omega}\times\boldsymbol{x}+\frac{\epsilon\zeta}{\eta}\nabla\psi, \\ \frac{\partial\psi}{\partial n} &= 0, \end{aligned}\right\} \tag{5.1}$$

at the particle surface. The translational velocity $\boldsymbol{u}$ and angular velocity $\boldsymbol{\Omega}$ are determined from the force and torque balance equations (3.5) and (3.6).

Pozrikidis (1989) has shown that the hydrodynamic force on a fixed sphere placed in an ambient flow field $\boldsymbol{u}_a$ is given by the Faxén formula

$$\boldsymbol{F} = (\alpha+\beta\nabla^2)\,\boldsymbol{u}_a(\boldsymbol{x}_0), \tag{5.2}$$

where $\boldsymbol{x}_0$ is the centre of the sphere,

$$\alpha = 2\pi\eta a(3+3\lambda+\lambda^2); \quad \beta = -2\pi\eta a\left(1+\frac{3}{\lambda}+\frac{3}{\lambda^2}-3\frac{e^{\lambda}}{\lambda^2}\right), \tag{5.3}$$

and

$$\lambda = (1+\mathrm{i})\left(\frac{\omega a^2}{2\nu}\right)^{\frac{1}{2}}. \tag{5.4}$$

The derivation of this formula assumes no-slip boundary conditions. In order to make use of this result we must convert our problem to one in which the sphere is held fixed and there is no slip at the surface. This is accomplished by setting

$$\boldsymbol{u} = \frac{\epsilon\zeta}{\eta}\nabla\psi+\boldsymbol{u}'+\boldsymbol{u}'', \tag{5.5}$$

$$p = -\mathrm{i}\omega\rho\frac{\epsilon\zeta}{\eta}\psi+p'+p'', \tag{5.6}$$

where $(\boldsymbol{u}'', p'')$ is the solution to the unsteady Stokes equations for a particle translating with velocity $\boldsymbol{U}$ and rotating with angular velocity $\boldsymbol{\Omega}$ in an infinite liquid at rest. Thus $\boldsymbol{u}''$ satisfies the $\boldsymbol{U}+\boldsymbol{\Omega}\times\boldsymbol{x}$ part of the boundary condition (5.1).

The hydrodynamic force on the particles due to the flow field (5.5) can be written as

$$\boldsymbol{F} = \boldsymbol{F}_{\psi}+\boldsymbol{F}'+\boldsymbol{F}'',$$

where $\boldsymbol{F}_\psi$ is the force due to the part of the flow field proportional to $\nabla\psi$, and $\boldsymbol{F}'$ and $\boldsymbol{F}''$ are the hydrodynamic forces due to the $\boldsymbol{u}'$ and $\boldsymbol{u}''$ flow fields respectively.

$\boldsymbol{F}''$ is given by (Lawrence & Weinbaum 1986)

$$\boldsymbol{F}'' = R\boldsymbol{U},$$

where the resistance coefficient R is given by

$$R = -6\pi\eta a(1+\lambda+\tfrac{1}{9}\lambda^2). \tag{5.7}$$

The flow field $(\epsilon\zeta/\eta)\nabla\psi$ gives rise to the pressure field $-\mathrm{i}\omega\rho(\epsilon\zeta/\eta)\psi$, and this exerts a hydrodynamic force

$$\boldsymbol{F}_\psi = \mathrm{i}\omega\rho\frac{\epsilon\zeta}{\eta}\int_{A_p}\psi\boldsymbol{n}\,\mathrm{d}A$$

on the particle. The viscous stresses do not contribute to this force because the flow field is irrotational.

By using the expression (4.12) for the electrical dipole strength $\boldsymbol{S}$, and the fact that $\nabla\psi\cdot\boldsymbol{n}$ is zero at the particle surface, we can write the above formula for the force as

$$\boldsymbol{F}_\psi = \mathrm{i}\omega\rho\frac{\zeta}{\eta}\boldsymbol{S}. \tag{5.8}$$

The dipole strength $\boldsymbol{S}$ can be calculated using the Faxén formula for a sphere in an ambient electric field, namely (O'Brien 1979, equation (3.14))

$$\boldsymbol{S} = -2\pi a^3\epsilon\boldsymbol{E}_a(\boldsymbol{x}_0).$$

Thus we have formulae for $\boldsymbol{F}_\psi$ and $\boldsymbol{F}''$. To complete the calculation of the force on the sphere we require $\boldsymbol{F}'$, and it is here that the Pozrikidis–Faxén formula is used.

By using the fact that ψ satisfies Laplace's equation we find that the $(\boldsymbol{u}', \boldsymbol{p}')$ field satisfies the unsteady Stokes equation (3.2) and (3.3) with the boundary conditions that $\boldsymbol{u}'$ is zero at the particle surface, while far from the particle,

$$\boldsymbol{u}' \to \boldsymbol{u}_a + \frac{\epsilon\zeta}{\eta}\boldsymbol{E}_a.$$

The Pozrikidis formula (5.2) for the force on a fixed sphere can be applied to this $\boldsymbol{u}'$ problem, giving the result

$$\boldsymbol{F}' = (\alpha+\beta\nabla^2)\,\boldsymbol{u}_a(\boldsymbol{x}_0) + \alpha\frac{\epsilon\zeta}{\eta}\boldsymbol{E}_a(\boldsymbol{x}_0), \tag{5.9}$$

where we have used the fact that $\boldsymbol{E}_a$ satisfies Laplace's equation.

The total force on the particle is obtained by summing the contributions (5.7), (5.8) and (5.9). Setting this sum equal to the mass times acceleration of the particle $\mathrm{i}\omega M\boldsymbol{U}$ and solving for the particle velocity $\boldsymbol{U}$ we obtain the required Faxén relation, namely

$$\boldsymbol{U} = \frac{(\alpha+\beta\nabla^2)}{\mathrm{i}\omega M - R}\boldsymbol{u}_a(\boldsymbol{x}_0) + \mu_0\boldsymbol{E}_a(\boldsymbol{x}_0), \tag{5.10}$$

where μ_0 is the dynamic mobility of an isolated sphere, given by

$$\mu_0 = \frac{\epsilon\zeta}{\eta}\left[\frac{\alpha - 2\mathrm{i}\omega\rho\pi a^3}{\mathrm{i}\omega M - R}\right]. \tag{5.11}$$

Although we have derived the Faxén law (5.10) for a sphere in an infinite liquid, the formula can also be applied to a sphere in a suspension. In the suspension problem we take the ambient fields $\boldsymbol{u}_a$ and $\boldsymbol{E}_a$ to be given by the formulae (4.10) and (4.11), where the sum now extends over all particles except the test sphere. Note that the stress and velocity in the integrals in these formulae are the stress and velocity when the test sphere is present; so these fields are not really the true ambient fields. However, for the derivation of the result all that is required is that the fields $\boldsymbol{u}_a$ and $\boldsymbol{E}_a$ satisfy the unsteady Stokes equations and Laplace's equation in the volume occupied by the test sphere, and this is the case here. The 'disturbance' velocity and electric fields in this case are given by the integrals (4.5) and (4.13) over the surface of the test sphere.

The substitutions (5.5) and (5.6) can be applied as before, and the formulae for the forces $\boldsymbol{F}'$ and $\boldsymbol{F}_\psi$ also hold for the suspension problem. The Pozrikidis result (5.2), which is used to calculate the force $\boldsymbol{F}'$, is valid provided the disturbance velocity

$$\boldsymbol{u}' - \boldsymbol{u}_a - (\epsilon\zeta/\eta)\,\boldsymbol{E}_a$$

satisfies the unsteady Stokes equations outside the test sphere and approaches zero far from the sphere; this is so because the disturbance velocity (4.5) and electric field (4.13) satisfy this criterion. Thus, the derivation of the Faxén relation carries over to the suspension problem.

In applying the Faxén law to the suspension, however, it is convenient to evaluate the term $\nabla^2 \boldsymbol{u}_a$ using the formula

$$\boldsymbol{u}_a(\boldsymbol{x}_0) = \sum_{p\neq j} \boldsymbol{u}_p(\boldsymbol{x}_0) + \int_\Gamma (-\langle p\rangle\, \boldsymbol{G} + \langle \boldsymbol{u}\rangle \cdot \boldsymbol{T})\cdot \mathrm{d}\boldsymbol{S} \tag{5.12}$$

instead of (4.10). Here the macroscopic boundary integral has been kept as a surface integral, rather than converting to volume integral form. When we take ∇^2 of this expression, the contribution from the macroscopic boundary can be ignored, for the integrand is then $O(r^{-4})$ and so the boundary integral vanishes as Γ tends to infinity. Combining the resulting formulae for $\boldsymbol{u}_a$, $\boldsymbol{E}_a$ and $\nabla^2\boldsymbol{u}_a$ with the Faxén formula (5.10) we obtain

$$\begin{aligned} \boldsymbol{U}_j = \sum_{p\neq j} \Delta \boldsymbol{U}_p - \frac{\alpha\phi\,\Delta\rho\langle \boldsymbol{U}\rangle}{\rho(\mathrm{i}\omega M - R)}\cdot\left[\boldsymbol{I} - \mathrm{i}\omega\rho\int_V \boldsymbol{G}\,\mathrm{d}V\right] \\ + \mu_0\left[\langle \boldsymbol{E}\rangle + \frac{n\langle \boldsymbol{S}\rangle}{3\epsilon} - \frac{1}{4\pi\epsilon}\int_V n\langle \boldsymbol{S}\rangle\cdot\nabla\nabla\frac{1}{r}\,\mathrm{d}V\right], \end{aligned} \tag{5.13}$$

where

$$\Delta \boldsymbol{U}_p = \frac{(\alpha+\beta\nabla^2)}{\mathrm{i}\omega M - R}\boldsymbol{u}_p(\boldsymbol{x}_0) + \mu_0 \boldsymbol{E}_p(\boldsymbol{x}_0). \tag{5.14}$$

This is the required result, expressing the velocity of the jth sphere in the suspension in terms of the contributions from the other particles and terms from the macroscopic boundary integral. This completes the second step of the macroscopic integral method.

6. The average particle velocity to $O(\phi)$

The average quantities that we have been dealing with so far are averages over a representative sample of a single suspension. Such averages can also be determined by sampling over an ensemble of macroscopically identical suspensions (Batchelor 1970).

On taking the ensemble average of (5.13) over all realizations in which there is a particle centred on x_0, we obtain

$$\langle U\rangle = \mu_0\langle E\rangle - \left[\frac{\alpha\phi\,\Delta\rho\langle U\rangle}{\rho(R-\mathrm{i}\omega M)} - \mu_0\frac{n\langle S\rangle}{3\epsilon}\right] + \int\left[\Delta U(x_0\,|\,x_0+r)\,p(x_0+r\,|\,x_0) - \frac{\mathrm{i}\omega\alpha\phi\,\Delta\rho\langle U\rangle\cdot G}{R-\mathrm{i}\omega M} - \frac{\mu_0 n\langle S\rangle}{4\pi\epsilon}\cdot\nabla\nabla\frac{1}{r}\right]\mathrm{d}V, \quad (6.1)$$

where $\Delta U(x_0\,|\,x_0+r)$ is the average of the contribution to the velocity at x_0 from a sphere at x_0+r averaged over all realizations in which there is a sphere at x_0 and one at x_0+r. $p(x_0+r\,|\,x_0)$ is the probability density for a sphere at x_0+r given that there is a sphere at x_0. The integral in (6.1) extends over all space outside a vanishingly small sphere centred on x_0. There are no problems with convergence for the macroscopic boundary integrals cancel out the r^{-3} contribution from ΔU at large r.

The quantities p and n in the integrand in (6.1) are $O(\phi)$ and thus the integral itself is $O(\phi)$. To get the $O(\phi)$ correction to $\langle U\rangle$ we can therefore use an $O(1)$ approximation for ΔU, that is, we can evaluate ΔU as if the spheres at x_0 and x_0+r were alone in an infinite electrolyte with an ambient uniform field $\langle E\rangle$. To the same accuracy we can also replace $\langle U\rangle$ on the right-hand side of (6.1) by $\mu_0\langle E\rangle$, the value for an isolated sphere, and we can approximate $\langle S\rangle$ by the isolated sphere value $-2\pi a^3\epsilon\langle E\rangle$.

By using the integral formulation (4.4) for the problem of two spheres in an ambient field $\langle E\rangle$ and following the same procedure as was used for deriving (5.13), we find that the velocity of one member of the pair is given by

$$U_1 = \Delta U_2 + \mu_0\langle E\rangle, \quad (6.2)$$

where the subscripts 1 and 2 denote the two spheres. The term $\mu_0\langle E\rangle$ comes from the integral over Γ, on the assumption that the radius of this surface is so large that it lies in the region where the field takes the uniform value $\langle E\rangle$. On rearranging the expression (6.2) we find that the term ΔU in (6.1) can be calculated using the formula

$$\Delta U(x_0\,|\,x_0+r) = U(x_0\,|\,x_0+r) - \mu_0\langle E\rangle, \quad (6.3)$$

where we have replaced ΔU_2 by $\Delta U(x_0\,|\,x_0+r)$ and U_1 by $U(x_0\,|\,x_0+r)$, where the latter symbol indicates the velocity of a sphere at x_0 when the other sphere is at x_0+r.

To determine the $O(\phi)$ correction to $\langle U\rangle$ using (6.1) and (6.3) we must calculate the velocity of a pair of spheres for all separations at the given frequency and evaluate the integral of the velocity over those separations.

From the linearity and symmetry of the two-sphere problem it follows that the velocity of the sphere-pair is given by an expression of the form

$$U = (\mu_\parallel ee + \mu_\perp[I - ee])\cdot\langle E\rangle, \quad (6.4)$$

where e is the unit vector parallel to r and $\mu_\parallel$ and $\mu_\perp$ are the dynamic mobilities of a sphere-pair aligned with and perpendicular to the applied field respectively.

To evaluate the $O(\phi)$ coefficient we also require a form for the pair distribution function p. In this paper we will assume that the suspension is random, that is $p = n$ for $r > 2a$ and zero for $r < 2a$. On substituting this form for p in (6.1) and integrating over all orientations we find that to $O(\phi)$, the dynamic mobility of the suspension is given by

$$\mu_0 = \mu_0(1 - \phi[\tfrac{1}{2} + H + \tfrac{2}{3}H(1 - (2\lambda+1)\,\mathrm{e}^{-2\lambda})]) + \phi\int_2^\infty \mathrm{d}r([\mu_\parallel + 2\mu_\perp - 3\mu_0]\,r^2 - \tfrac{2}{3}H\lambda^2 r\,\mathrm{e}^{-\lambda r}), \quad (6.5)$$

where
$$H = \frac{\alpha\,\Delta\rho}{\rho(R-\mathrm{i}\omega M)}.$$

The term multiplied by $\frac{2}{3}H$ comes from the integral of the $\langle \boldsymbol{U}\rangle \cdot \boldsymbol{G}$ term in (6.1) from $r=0$ to $r=2a$. The dipole term does not contribute to this formula, for the integral of $\nabla\nabla 1/r$ over a sphere is zero.

The next step in the calculation is the determination of the dynamic mobilities of an isolated pair of spheres.

7. The relationship between the dynamic mobility and the hydrodynamic resistance

In their paper on the dynamic mobility of a spheroidal particle, Loewenberg & O'Brien (1992) obtained a formula linking the dynamic mobility of an isolated particle to the hydrodynamic resistance coefficient of an uncharged, but otherwise identical particle, where the resistance coefficient is the hydrodynamic force on the particle translating with unit velocity. In this section we will derive similar relations between the dynamic mobility and resistance coefficients for a pair of spheres. Unlike μ_D, the resistance coefficients do not depend on the particle density, since they are determined by the flow field for a prescribed particle velocity. Thus by working in terms of the resistance coefficient instead of the dynamic mobility we reduce the number of variables to two, namely $(\omega a^2/\nu)$ and d/a, where d is the distance between the particle centres.

We begin by substituting the expressions

$$\boldsymbol{u} = \boldsymbol{v} + \frac{\epsilon\zeta}{\eta}(\nabla\psi + \langle \boldsymbol{E}\rangle), \tag{7.1}$$

$$p = p' - \mathrm{i}\omega\rho\frac{\epsilon\zeta}{\eta}(\psi + \langle \boldsymbol{E}\rangle\cdot\boldsymbol{x}), \tag{7.2}$$

$$\boldsymbol{U} = \boldsymbol{U}' + \frac{\epsilon\zeta}{\eta}\langle \boldsymbol{E}\rangle, \tag{7.3}$$

in the governing equations and boundary conditions. The variables $\boldsymbol{v}$ and p' satisfy the oscillatory Stokes' equations (3.2) and (3.3) subject to the same boundary conditions as that for uncharged spheres moving with velocity $\boldsymbol{U}'$ in an infinite liquid at rest far from the spheres. On substituting (7.2) and (7.3) in the force-balance formula (3.5) we get

$$\mathrm{i}\omega M\boldsymbol{U}' = \int_{A_p} \boldsymbol{\sigma}'\cdot\boldsymbol{n}\,\mathrm{d}A - \mathrm{i}\omega\frac{\epsilon\zeta}{\eta}\left[M\langle \boldsymbol{E}\rangle - \rho\int_{A_p}(\psi + \langle \boldsymbol{E}\rangle\cdot\boldsymbol{x})\boldsymbol{n}\,\mathrm{d}A\right], \tag{7.4}$$

where $\boldsymbol{\sigma}'$ is the stress tensor with pressure p' replacing the true pressure p.

Equation (7.4) has the same form as the force balance equation for a particle moving under the action of an external force

$$F_{ext} = -\mathrm{i}\omega\frac{\epsilon\zeta}{\eta}\left[M\langle \boldsymbol{E}\rangle - \rho\int_{A_p}(\psi + \langle \boldsymbol{E}\rangle\cdot\boldsymbol{x})\boldsymbol{n}\,\mathrm{d}A\right]. \tag{7.5}$$

The quantity $(\psi + \langle \boldsymbol{E}\rangle\cdot\boldsymbol{x})$ satisfies the same equations and boundary conditions as the velocity potential for two spheres moving with velocity $\langle \boldsymbol{E}\rangle$, and the integral involving this potential in (7.5) is the hydrodynamic force due to this potential flow. From potential flow theory it is known that the hydrodynamic force on oscillating particles (Batchelor 1967, §6.4, p. 407) is the same as if the particles had an extra mass M^a which depends on the radius and separation of the sphere pair. Thus the formula (7.5) for the effective force on either of the spheres can be written as

$$F_{ext} = -\mathrm{i}\omega(M^a + M)\frac{\epsilon\zeta}{\eta}\langle E\rangle. \tag{7.6}$$

Since the pressure does not contribute to the torque on a spherical particle, the torque-balance equation (3.6) is not altered by the substitution of the formula (7.2) for the pressure. Thus, there is an external force but no external torque in the transformed problem.

By using the substitution (7.1)–(7.3) we have removed the slip boundary condition from the problem and converted it to one of calculating the motion of a pair of uncharged, torque-free spheres owing to the external force (7.6) acting on each sphere.

In general M^a is a tensor, but if the field is aligned either parallel or perpendicular to the line of centres then the added mass force is parallel to the field and M^a reduces to a scalar in the above expression. We let $M^a_\parallel$ and $M^a_\perp$ be the added mass for the parallel and perpendicular motions, respectively.

From the fore and aft symmetry of this problem it follows that the application of an equal force to each sphere will cause them to translate with equal velocities and rotate with equal and opposite angular velocities. By using the rotational symmetry and linearity condition we find that the hydrodynamic force on either sphere owing to this motion has the form

$$\eta a F^U_\parallel\, \boldsymbol{U}\cdot\boldsymbol{ee} + \eta a F^U_\perp(\boldsymbol{U} - \boldsymbol{U}\cdot\boldsymbol{ee}) + \eta a^2 F^\Omega(\boldsymbol{\Omega}\times\boldsymbol{e}), \tag{7.7}$$

where $F^U_\parallel$ and $F^U_\perp$ are the non-dimensional force per unit velocity parallel and perpendicular to the centreline, and F^Ω gives the force per unit angular velocity.

Similarly the torque on the sphere moving with angular velocity $\boldsymbol{\Omega}$ is given by

$$\eta a^3 T^\Omega \boldsymbol{\Omega} + \eta a^2 T^U(\boldsymbol{U}\times\boldsymbol{e}) \tag{7.8}$$

where T^Ω is the torque per unit angular velocity and T^U gives the torque per unit translational velocity. By using the reciprocal relation (Goldman, Cox & Brenner 1966) for oscillatory Stokes flow it can be shown that

$$T^U = F^\Omega. \tag{7.9}$$

The F and T quantities in the above expressions are the resistance coefficients referred to earlier. If these coefficients are known then the particle velocity $\boldsymbol{U}'$ and $\boldsymbol{\Omega}$ can be obtained by substituting (7.7) and (7.8) in the force and torque balance equations (3.5) and (3.6), with the addition of the external force $\boldsymbol{F}_{ext}$ given by (7.6). In the case of motion along the centreline this yields

$$\mathrm{i}\omega M U_\parallel = \eta a F^U_\parallel U_\parallel - \mathrm{i}\omega(M^a_\parallel + \eta a F^U_\parallel)\frac{\epsilon\zeta}{\eta}E_\parallel, \tag{7.10}$$

where we have used the formula (7.3) to replace $\boldsymbol{U}'$ by the true velocity $\boldsymbol{U}$. For the perpendicular component of the motion we obtain

$$\mathrm{i}\omega M U_\perp = \eta a F^U_\perp U_\perp + \eta a^2 F^\Omega \Omega - \mathrm{i}\omega(M^a_\perp + \eta a F^U_\perp)\frac{\epsilon\zeta}{\eta}E_\perp, \tag{7.11}$$

from the force balance, and

$$i\omega I_M \Omega = \eta a^3 T^{\Omega}\Omega + \eta a^2 T^U \left(U_\perp - \frac{\epsilon\zeta}{\eta} E_\perp\right), \tag{7.12}$$

from the torque balance.

Solving equation (7.10) for $U_\parallel$ we find that the dynamic mobility for the aligned spheres is given by

$$\mu_\parallel = \frac{\epsilon\zeta}{\eta} \frac{\eta a F_\parallel^U + i\omega M_\parallel^a}{\eta a F_\parallel^U - i\omega M}. \tag{7.13}$$

In the case of transverse motion the calculation is more complicated, since the formulae (7.11) and (7.12) contain the two unknowns $U_\perp$ and Ω. The solution of these equations gives

$$\left.\begin{aligned} \mu_\perp &= \frac{\epsilon\zeta}{\eta} \frac{\eta a F_\perp^U + i\omega M_\perp^a - \eta a F^{\Omega}\alpha}{\eta a F_\perp^U - i\omega M - \eta a F^{\Omega}\alpha}, \\ \alpha &= \frac{T^U}{T^{\Omega} - \lambda^2 I_p}; \quad I_p = \tfrac{4}{5}\pi \frac{\rho_p}{\rho} \end{aligned}\right\} \tag{7.14}$$

and

$$\mu_R \equiv \frac{\Omega}{E} = \frac{\epsilon\zeta}{\eta a} \frac{T^U}{T^{\Omega} - \lambda^2 I_p}\left(1 - \frac{\mu_0}{\epsilon\zeta/\eta}\right), \tag{7.15}$$

where μ_R is the rotational dynamic mobility, that is the angular velocity per unit applied field.

Readers who are not familiar with the electrokinetics literature may be interested in the fact that in the low-frequency limit the velocity field reduces to a potential flow, even though the Reynolds number is zero (Morrison 1970). This can be seen from the fact that the force (7.6) that drives the flow field $\boldsymbol{v}$ is zero in this limit and thus only the potential flow component remains in the formula (7.1) for $\boldsymbol{u}$. The reason for this surprising result is that the double layer acts as a sink for the vorticity generated by the particle motion, and hence the vorticity is confined to the double layer instead of diffusing out to the surrounding liquid. Thus flow is irrotational beyond the double layer. As the frequency is increased the particle velocity drops owing to inertia, the cancellation of vorticities is incomplete, and the flow field is no longer irrotational.

To determine the dynamic mobilities of a pair of spheres using these formulae we must calculate the added masses and the resistance coefficients for pairs parallel and perpendicular to the applied field. In the following sections we will outline the numerical procedure for determining these quantities and present sample calculations.

8. Calculation of the dynamic mobility of a sphere pair

The calculation of the resistance coefficients and the added masses involves the solution of the unsteady Stokes equations and Laplace's equation for a sphere pair moving with a prescribed velocity. Of the various problems to be considered only the case of the potential flow field due to axisymmetric motion of two spheres can be solved exactly. This is done using the stream function expressed in bipolar coordinates (see the Appendix). For the other problems, general solutions can be written down, but the coefficients in the series must be determined numerically. It is, however, possible to obtain simple forms for the asymptotic behaviour of the dynamic mobility and resistance coefficients at low and high frequencies.

At low frequencies it can be shown (Pozrikidis 1989) that the resistance coefficient for translation motion is given by the asymptotic formula

$$F^U = -D_0 - \frac{D_0^2}{6\pi}\lambda + O(\lambda^2), \tag{8.1}$$

where D_0 is the Stokes drag coefficient. This formula applies to both the transverse and parallel motions, with the appropriate Stokes drag substituted for D_0.

At high frequencies the corresponding asymptotic form is (Pozrikidis 1989)

$$\frac{F^U}{\lambda^2} = -m^a - \frac{B}{\lambda} + O\left(\frac{1}{\lambda^2}\right). \tag{8.2}$$

$m^a = M^a/\rho a^3$, where M^a is the added mass of either sphere, defined by

$$-\mathrm{i}\omega M^a U_0 = \mathrm{i}\omega\rho \int_A \phi \hat{n}\, \mathrm{d}A.$$

In this expression ϕ is the velocity potential, A is the surface of either sphere, and the integral on the right-hand side extends over the surface of either sphere.

The coefficient B in (8.2) is called the Basset force coefficient. It can be calculated using the formula (Batchelor 1967, §5.13)

$$B = \frac{1}{a^2 U_0^2} \int_A U_s^2\, \mathrm{d}A, \tag{8.3}$$

where U_s is the tangential velocity of the fluid at the surface of either of the particles, obtained from the potential flow solution for two particles moving with equal velocities U_0.

By using the asymptotic form (8.1) with the formulae (7.13) and (7.14) for the dynamic mobilities we find that $\mu_\parallel$ and $\mu_\perp$ are both given by

$$\mu \sim \frac{\epsilon\zeta}{\eta} + O(\lambda^2) \tag{8.4}$$

for small λ. This is in agreement with Smoluchowski's formula for the static mobility, which is known to apply to any group of particles with thin double layers and uniform ζ potential (this may be deduced from the results in Morrison 1970). Thus each sphere moves as if it were alone in the zero frequency limit. The interactions cancel in this limit because the forces on each sphere owing to the electric field vary in exactly the same way with spacing as the resistance coefficients.

For the high-frequency limit, we substitute (8.2) in (7.13) and (7.14) to find that $\mu_\parallel$ and $\mu_\perp$ both have the asymptotic form

$$\mu \sim \frac{\epsilon\zeta}{\eta} \frac{B}{(m^a + \frac{4}{3}\pi\rho_p/\rho)\,\lambda} \tag{8.5}$$

at large λ. Thus the mobilities approach zero at high frequencies like $\omega^{-\frac{1}{2}}$, at a rate that depends on the particle density, the Basset force and the added mass.

The resistance coefficients used in §7 to derive expressions for the dynamic mobility of sphere pairs were calculated using the multipole collocation technique (Gluckman, Pfeffer & Weinbaum 1971; Kim & Russel 1985). The added mass and the Basset force

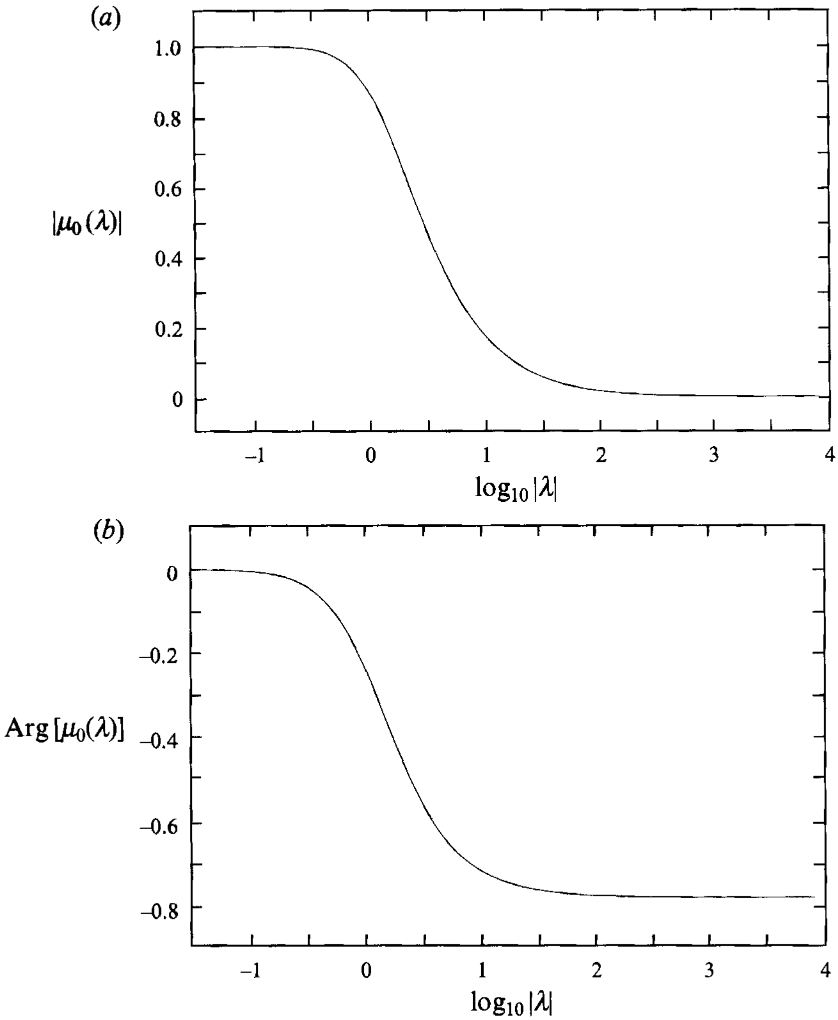

FIGURE 1. The dynamic mobility of an isolated particle as a function of frequency, for $\rho_p/\rho = 2$.

were calculated using bipolar coordinates. The added mass has been calculated by Jeffrey (1976) and will not be discussed here. The details of the resistance and Basset force calculations are outlined in the Appendix.

All results presented in this section are for the case of the particle to fluid density ratio, ρ_p/ρ, equal to 2. The mobilities will be normalized by dividing by the mobility for an isolated sphere, which is plotted as a function of frequency in figure 1.

The results for the normalized dynamic mobility of either sphere of an identical pair in axisymmetric motion are shown in figure 2. At low frequencies there is no interaction and for all separations the normalized mobility is equal to 1 in accord with the Smoluchowski formula, as discussed in §7. As the frequency increases the terms $\mathrm{i}\omega M^a$ and $\mathrm{i}\omega M$ in (7.13) become significant, and the mobility begins to decrease. The change with frequency is monotonic, rising to a limiting value of around 11% in the high-frequency limit.

From figure 2(*b*) it can be seen that the phase of $\mu_\parallel$ is quite insensitive to particle interactions. The change in the phase lag between the particle motion and applied field

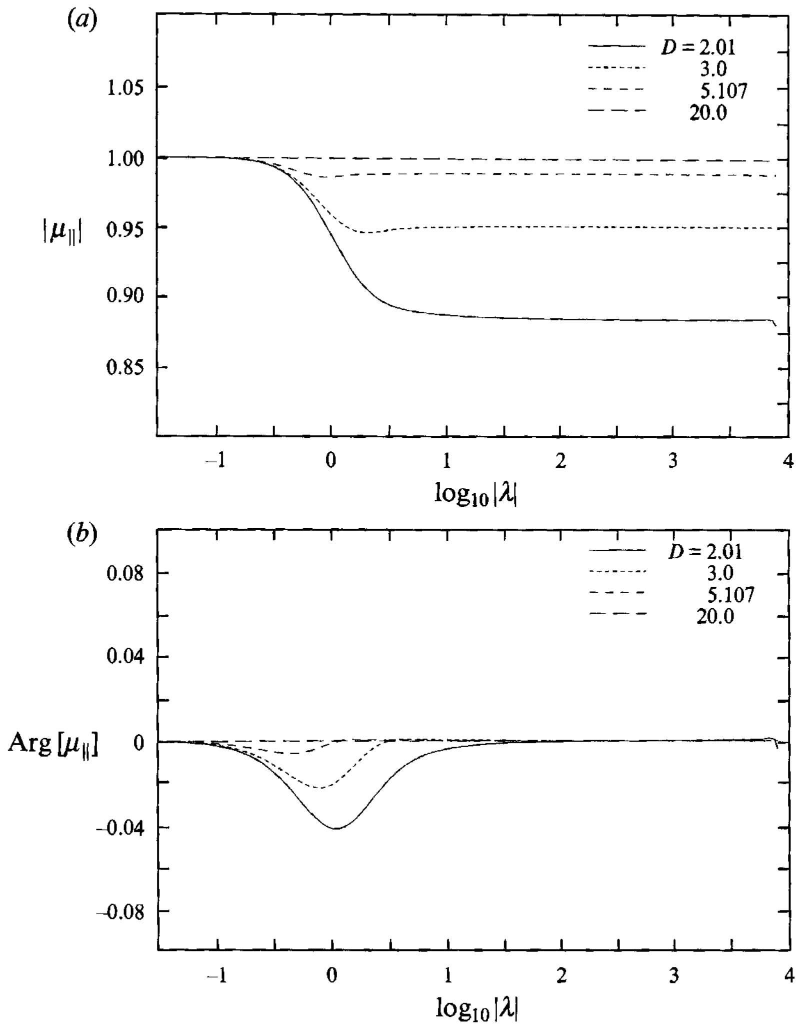

FIGURE 2. The dynamic mobility of either sphere of an identical pair in axisymmetric motion, as a function of frequency, at various centre to centre separations.

increases with decreasing separation, reaching a maximum of 2.3° for the closest spheres at $|\lambda| \sim 1$. At these frequencies an isolated particle lags the applied field by about 17° (figure 1*b*).

From the asymptotic forms (8.4) and (8.5) for $\mu_{\|}$ and $\mu_{\perp}$ it follows that the high-frequency limit of the normalized mobility is

$$\frac{1+2\rho_p/\rho}{m^a/\frac{2}{3}\pi+2\rho_p/\rho}\frac{B}{6\pi}, \tag{8.6}$$

where the m^a and B refer to the values appropriate to the transverse or axisymmetric motion. For $D = 2.01$, $B/B_{\infty} = 0.8334$ and $m_a/\frac{2}{3}\pi = 0.7077$, yielding a value of 0.885 for this ratio for the case of axisymmetric motion. This is in good agreement with the value in figure 2(*a*).

The electrostatic and hydrodynamic interactions between the spheres both decay as

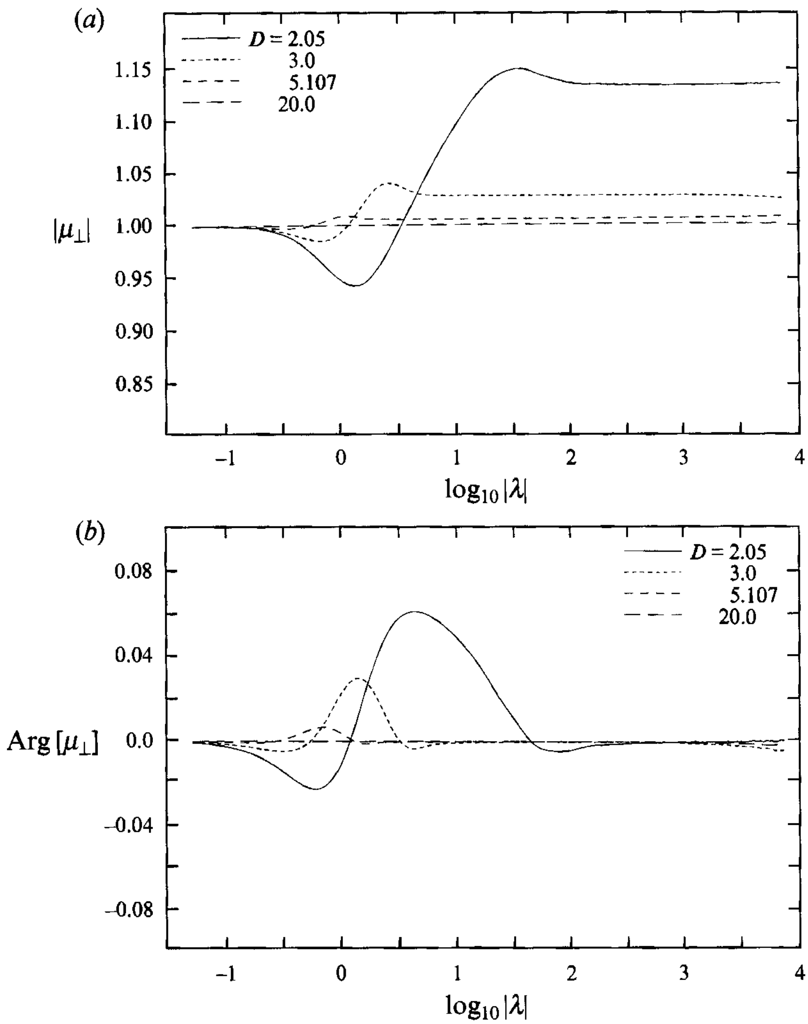

FIGURE 3. The dynamic mobility of either sphere of an identical pair in transverse motion, as a function of frequency, at various centre to centre separations.

r^{-3} at high frequencies, and for this reason the interactions shown in figure 2 are fairly short-ranged.

Results for the transverse mobility $\mu_\perp$ are shown in figure 3. Although the curves are very different from those of $\mu_\parallel$, the magnitude and phase vary by similar amounts. In this case the mobility magnitudes increase to a maximum with frequency and then level off. From figure 3(*b*) it can be seen that the interactions at low frequencies increase the phase lag between the particle motion and the applied field, but at higher frequencies the interactions reduce the phase lag. Both the phase and magnitude of $\mu_\perp$ agree with the asymptotic form (8.5) at high frequencies.

Although we do not need to know the rotational mobility μ_R for our $O(\phi)$ calculation, it is interesting to see how this quantity does vary with frequency and particle separation. In figure 4 we show $a\mu_R$ normalized by the mobility of an isolated sphere as a function of frequency at various centre to centre separations. This ratio is equal to the speed at a point on the surface of the particle owing to rotation, divided

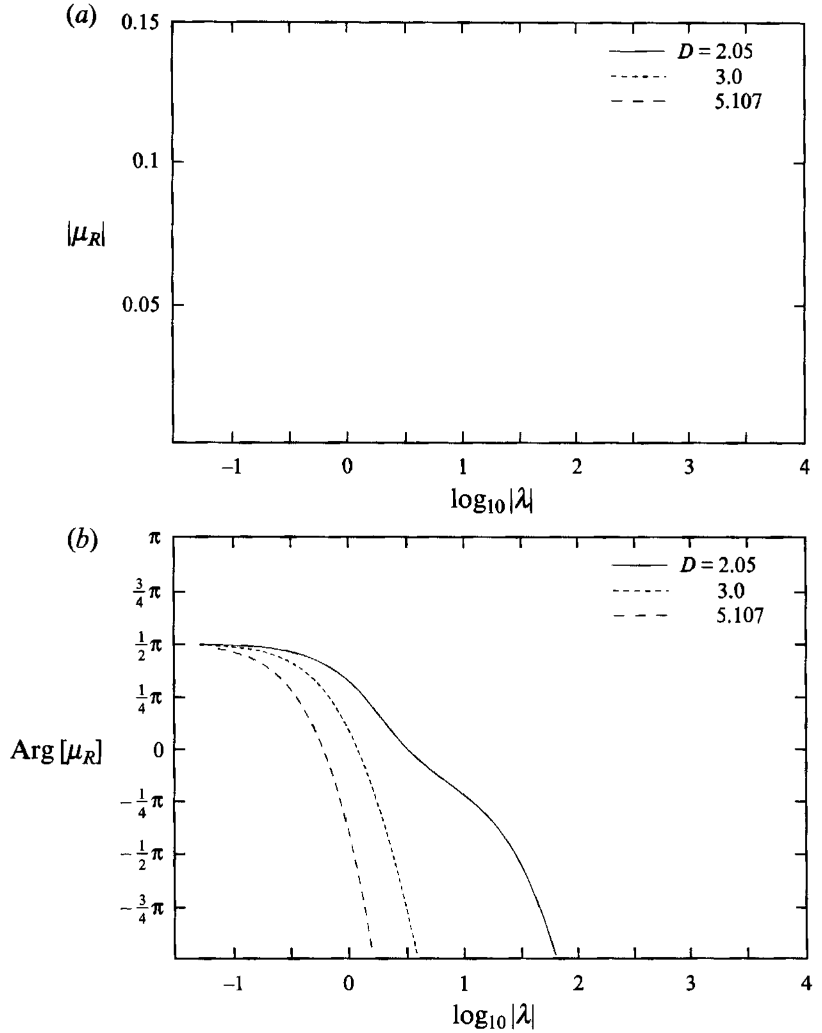

FIGURE 4. The rotational dynamic mobility of either sphere of an identical pair in transverse motion, as a function of frequency, at various centre to centre separations.

by the speed on a translating isolated particle. From figure 4(*a*), it can be seen that the rotational speed is only 15% of the translational speed at most, and that the greatest rotation occurs for the closest spheres, near $\lambda = 1$.

We plan to apply the two-sphere solution to study multiparticle interactions using Stokesian dynamics simulation (Brady & Bossis 1988). Such calculations would be greatly simplified if we could neglect the particle rotations. To get some idea of the errors incurred by such a step we have calculated $\mu_\perp$ with Ω set to zero. As would be expected, the error is worse in the case of close spheres, where the rotations are greatest, but even here the error in the magnitude of $\mu_\perp$ is only 1%, while the maximum phase error is 1°. Thus the rotation can safely be neglected in the calculation of the translational particle motion.

9. Calculation of the $O(\phi)$ coefficient

The integral in (6.5) was evaluated using a trapezoidal rule with an unevenly spaced grid, with the points packed close together near $r = 2$ where the mobility is most rapidly varying. For large separations r, where

$$\left|\frac{\mu_\parallel + 2\mu_\perp}{\mu_0} - 3\right| < 1.7 \times 10^{-4},$$

the contribution to the integral was calculated using the far-field form

$$\mu_\parallel + 2\mu_\perp - 3\mu_0 = 3\frac{(\mu_0 - \mu_s)}{1+\lambda+m^*\lambda^2}\frac{e^{\lambda(2-r)}}{r}, \tag{9.1}$$

where

$$m^* = \frac{1}{3} + \frac{2}{9}\frac{\Delta\rho}{\rho}$$

and $\mu_s = \epsilon\zeta/\eta$ is the Smoluchowski mobility. This far-field form is obtained by applying the Faxén relation (5.10) to one of the spheres, with the ambient electric and velocity fields given by the flow field due to the other sphere as if it were isolated.

In figure 5 we show the calculated values of the $O(\phi)$ coefficient $f(\lambda)$ for $\rho_p/\rho = 2$ and $\rho_p/\rho = 4$, where

$$f = \lim_{\phi \to 0} \frac{\mu_D/\mu_0 - 1}{\phi}.$$

These curves were obtained by passing a spline through the computed values, which are marked on the figure. It is apparent that the particle concentration effect increases with particle density.

This effect of particle concentration is most pronounced at low frequencies. From the formula (3.8) it follows that

$$\lim_{\omega \to 0} f = -\tfrac{3}{2} - \frac{\Delta\rho}{\rho},$$

where we have used the fact that the $O(\phi)$ coefficient for the conductivity is $-\frac{3}{2}$ for a suspension of non-conducting spheres (Maxwell 1873). It is not obvious from the form of the integral expression (6.5) that the computed f value should tend to this limit. The fact that it does provides another check on the validity of the computations.

It does not seem to be possible to derive a simple analytic form for the high-frequency limit of f. For $\rho_p/\rho = 4$ the computed values of f tend to -0.52, while for $\rho_p/\rho = 2$, the limiting value is -0.43. Clearly the $O(\phi)$ correction is smaller at high frequencies than at low frequencies and the effect of particle density is less pronounced.

For both $\rho_p/\rho = 2$ and 4, the contribution to $f(\lambda)$ from the term

$$\int_2^\infty (\mu_\parallel + 2\mu_\perp - 3\mu_0)\, r \,\mathrm{d}r$$

is between 51% and 67% for the frequencies shown in figure 5. Thus the particle interactions play an important role, at all frequencies. It is surprising that this contribution is so large at low frequencies, for there is no interaction between a pair of particles at zero frequency. From the asymptotic form (9.1) it can be seen that

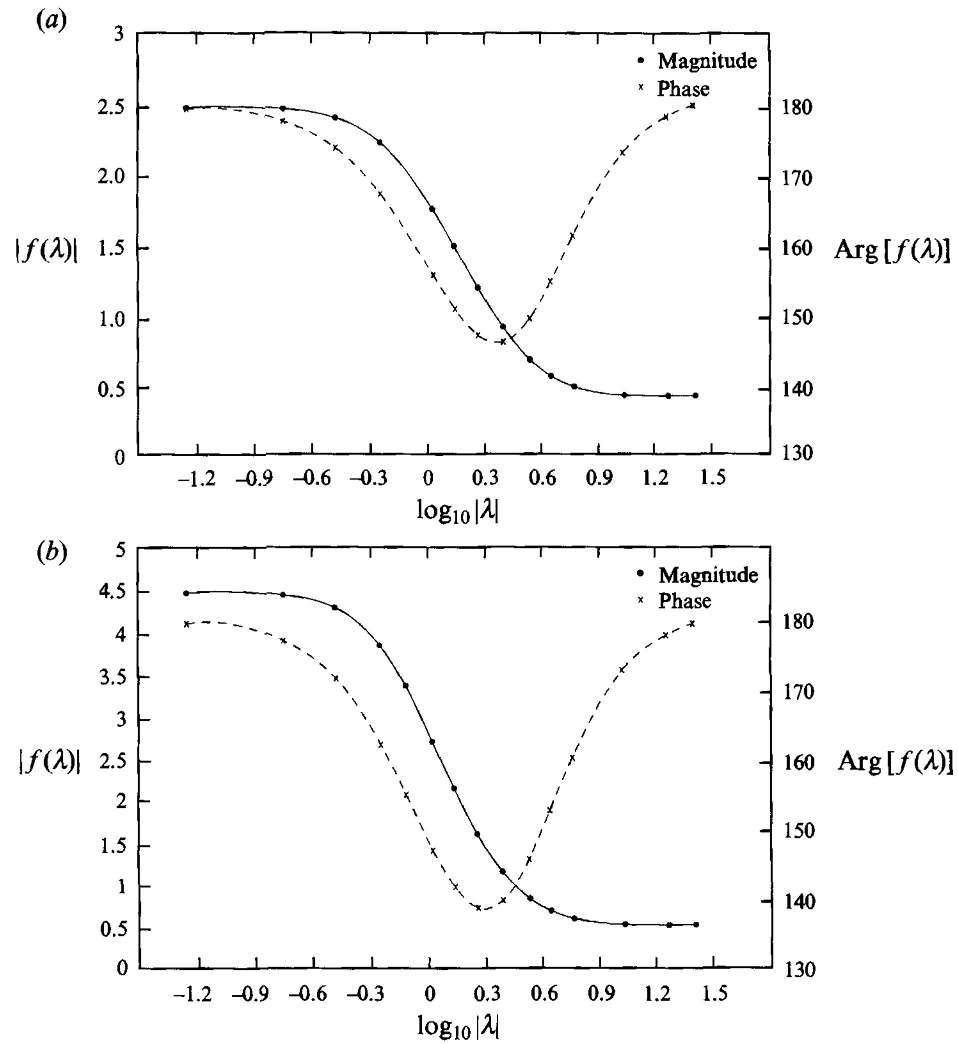

FIGURE 5. The magnitude and phase angle (in degrees) of the $O(\phi)$ coefficient f as a function of the non-dimensional frequency parameter λ, for (a) $\rho_p/\rho = 2$ and (b) $\rho_p/\rho = 4$.

although the difference $\mu_0 - \mu_s$ in the numerator approaches zero as $\lambda \to 0$, the lengthscale of the interactions increases, and this offsets the decrease in magnitude when we integrate over all separations.

To illustrate the effect of particle concentration on the dynamic mobility we have used these $f(\lambda)$ values to calculate μ_D/μ_0 for a suspension with a volume fraction of 5%. This quantity is plotted in figure 6. The symbol $\mu_D(\lambda;\phi)$ in this figure is the dynamic mobility of a suspension of volume fraction ϕ, at dimensionless frequency λ, divided by the mobility of an isolated sphere. As would be expected from the plots of $f(\lambda)$ in figure 5, the changes in the average mobility are greater in a suspension with particles of relative density 4, than when the relative density is 2.

The particle interactions have the effect of decreasing the magnitude and the phase lag of the mobility. Thus the mobility spectrum changes in a way that would indicate smaller particles and smaller ζ potential if the dilute theory was used to interpret the spectra.

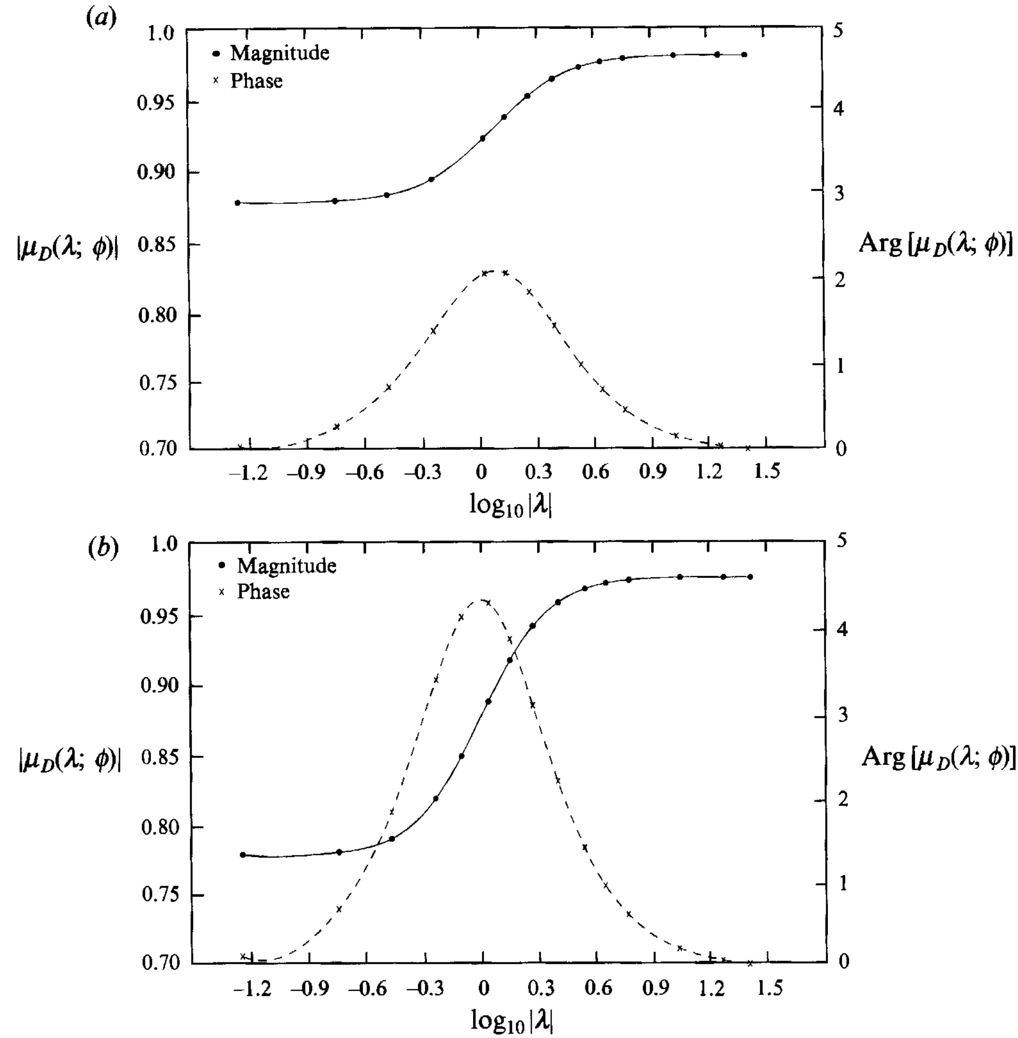

FIGURE 6. The dynamic mobility μ_D for a suspension with a 5% volume fraction normalized by the mobility of an isolated sphere, for (a) $\rho_p/\rho = 2$ and (b) $\rho_p/\rho = 4$.

In practice most colloidal particles have densities in the range

$$2 < \frac{\rho_p}{\rho} < 4.$$

The $O(\phi)$ correction to the dynamic mobility for such suspensions can be obtained by interpolating between the f values in figure 5.

As a check on our formula (6.5) for the dynamic mobility to $O(\phi)$ we have also evaluated the $O(\phi)$ correction using Batchelor's renormalization method (1974). Although this method yields an apparently different formula, the maximum discrepancy between the two results was only 3%, and this is probably due to the numerical integration procedure.

In this calculation we have assumed a uniform pair distribution. In practice, there are a number of effects which may limit the validity of this assumption. The dipole–dipole interactions between the particles owing to the applied field will create a steady attractive force between the particles and this will lead to a non-uniform pair distribution if the field is applied for too long. The particle dipole strength is of $O(\epsilon a^3\langle E\rangle)$, and so the force between a pair of spheres separated by a distance of order the particle radius is $O(\epsilon a^2\langle E\rangle^2)$. This force will cause the particles to move with a steady velocity of $O(\epsilon a\langle E\rangle^2/\eta)$. For 1 μm particles in a field of 1000 V/m this velocity is 1 μm/s. Thus the electric field should be applied for much less than a second if this effect is to be unimportant.

Most suspensions need to be stirred in order to prevent particle settling, and this stirring might also alter the pair distribution. The calculation of this effect is likely to be very complicated for the stirring motion is usually turbulent. The size of the effect can, however, be estimated in practice by measuring the dynamic mobility at a number of stirrer speeds.

Although there have been a number of studies of the ESA effect in non-dilute suspensions in the literature (see for example James, Texter & Scales 1991) none of these are suitable for comparison with our theory. This is because the ESA signal depends on the acoustic properties of the suspension as well as the dynamic mobility. These acoustic properties vary with particle concentration, and there is no formula available for predicting this variation. Thus it is not possible at present to extract the $O(\phi)$ correction to μ_D from the measured ESA signal. We are, however, in the process of developing a device which will enable the direct determination of μ_D in suspensions of arbitrary concentration. When the prototype version is available we plan to test our predictions for the $O(\phi)$ correction to μ_D.

The work presented here was made possible by the support of the Australian Government, through a Senior Research Fellowship for R.W.O.B. and an Australian Postgraduate Research Award for P.F.R. We also wish to thank the CSIRO for the provision of a postgraduate studentship for P.F.R. during this period, and for the use of their computing facilities.

Appendix. Calculation of the resistance coefficients and the Basset force for a pair of spheres

A.1. *The collocation procedure*

To solve the axisymmetric problem (hereinafter referred to as problem 1) we used the stream function in the form given by Lawrence & Weinbaum (1986). Problems involving translation perpendicular to the line of centres, and rotation about an axis perpendicular to the line of centres (to be referred to as problems 2 and 3, respectively) were solved using the approach of Kim & Russel (1985). Both problems were solved using the collocation procedure. We will discuss the procedure here for the case of problem 2.

Following Kim & Russel we write the collocation velocity field as

$$v(r) = \sum_{i=1}^{2}\sum_{n=1}^{\infty}\bigg(-\frac{1}{\lambda^2}\nabla\left[\frac{a_{ni}}{r_i^{n+1}}P_n^1(\mu_i)\sin\phi\right] + \nabla\times\nabla\times[r_i b_{ni}k_n(\lambda r_i)P_n^1(\mu_i)\sin\phi] + \nabla\times[r_i c_{ni}k_n(\lambda r_i)P_n^1(\mu_i)\cos\phi]\bigg), \quad (A\ 1)$$

ϕ, θ_i and r_i are spherical polar coordinates with the origin at the centre of sphere i. The

$\theta = 0$ line passes through the sphere centres. $k_n(z)$ is the nth order modified Bessel function of the third kind (Abramowitz & Stegun 1992); $z_i = \lambda r_i$, and $P_n^1(\mu)$ is the associated Legendre function of the first kind, with $\mu_i = \cos\theta_i$.

From the symmetry of the problem we can derive simple relations between the $i = 1$ and $i = 2$ coefficients (see Kim & Russel 1985).

It is assumed that the flow can be well represented by truncating the series after $3M$ terms, where M will depend on both the centre to centre separation and the frequency parameter λ. No-slip boundary conditions for the components of the velocity field are enforced at M collocation points on the surface of one of the spheres. This gives us $3M$ equations which determine the coefficients of the truncated series. These coefficients are then used to calculate the hydrodynamic torques and forces on either sphere with the aid of the following formulae.

The hydrodynamic force on particle 1 is related to the coefficients in the expansion (A 1) by the formula

$$F = \tfrac{4}{3}\pi(3a_{11} + \lambda^2). \tag{A 2}$$

This is valid for problems 2 and 3. A similar expression can be derived for the resistance coefficient $F_{\parallel}^{U}$ in problem 1.

The torque on sphere 1 is determined by the c_{11} coefficient in (A 1) and is given by

$$\left.\begin{aligned} T &= \tfrac{8}{3}\pi\, c_{11} f_1(\lambda) + \tfrac{8}{3}\pi\, F_1(\lambda)\,[k_1(\lambda)\, c_{11} + 1], \\ f_1(\lambda) &= \tfrac{1}{2}\pi \frac{e^{-\lambda}}{\lambda^2}(3 + 3\lambda + \lambda^2); \quad k_1(\lambda) = \frac{\pi}{2\lambda} e^{-\lambda}\left(1 + \frac{1}{\lambda}\right), \\ F_1(\lambda) &= \frac{\lambda^2 \sinh\lambda - 2\lambda\cosh\lambda + 2\sinh\lambda}{\lambda\cosh\lambda - \sinh\lambda}. \end{aligned}\right\} \tag{A 3}$$

Again this is valid for problems 2 and 3. The derivation of this expression is more complicated than in the Stokes flow case because the stress tensor is no longer divergence free. In the derivation we used the Lorentz reciprocal theorem to rewrite the expression for the torque as an integral involving the stress over the interior surface of a hollow sphere executing rotary oscillations about a diameter.

As our collocation points we used the roots of the Chebyshev polynomials. For problem 1 we removed the two points nearest the equator, and replaced them with points 1.5° either side of the equator. For problem 2 we made no change to the Chebyshev points. The use of these points gave better program performance than various linear distributions (cf. Kim & Russel 1985).

Gluckman *et al.* (1971) looked at the convergence of the ratio of the hydrodynamic force on either sphere of the pair to that of an isolated sphere to determine when sufficient terms had been retained in the truncated stream function. In our case the hydrodynamic force is a complex quantity, and we use the magnitude of the ratio

$$\frac{F}{-6\pi\eta a(1 + \lambda + \frac{1}{9}\lambda^2)} \tag{A 4}$$

to determine when convergence has occurred. Here F is the hydrodynamic force per unit velocity on either sphere of the pair, and the denominator is the hydrodynamic force per unit velocity on an isolated sphere. The ratio is between 0.6 and 1.3 for all the translational motions considered in this paper. We use the magnitude of analogous ratios to determine convergence when looking at T^U, F^{Ω}, and T^{Ω}. Convergence of these ratios was sought to four significant figures.

A.2. *Tests of numerical results*

Limits of calculations

All programs were written in single precision and used the IMSL subroutine LSLCG to solve the linear systems generated by the collocation technique.

For axisymmetric motion the hydrodynamic force was calculated for all separations, and frequencies of oscillations satisfying $3.5 \times 10^{-2} < \lambda < 7.9 \times 10^3$. In the transverse and rotational problems the various resistance coefficients were calculated for $D \geqslant 2.05$ and $5.7 \times 10^{-2} < \lambda < 7.9 \times 10^3$.

The low-frequency asymptotic test

From the asymptotic formula (8.1) it can be seen that plots of $\mathrm{Re}(-F^U)$ against $\mathrm{Re}(\lambda)$, and $\mathrm{Im}(-F^U)$ against $\mathrm{Im}(\lambda)$ should yield straight lines of known slope and intercept. The quantity D_0, that determines the slopes and intercepts, can be calculated exactly using the results of Stimson & Jeffery (1926) and Goldman *et al.* (1966) for problems 1 and 2, respectively. We found that the calculated points did lie along a straight line. The errors obtained were between 0.04% and 2.4%.

For both problems 1 and 2 the agreement of the slope and intercept for the real part were in better agreement with the exact values than the results from the imaginary plots. This is to be expected as at low frequencies the real part of the calculated force dominates the magnitude of the ratio (A 4), and the convergence criterion can be satisfied without the imaginary part of the force converging. As the frequency of oscillation increases, however, the imaginary part of the force increases relative to the real part and so the relative error in the imaginary part should decrease.

High-frequency asymptotic test

From the high-frequency form (8.2) we expect that a plot of both the real and imaginary parts of the force against $\mathrm{Re}(1/\lambda)$ and $\mathrm{Im}(1/\lambda)$, respectively, should yield straight lines with known slopes and intercepts. This turns out to be the case, and the agreement between the measured and exact slopes and intercepts is even better than in the low-frequency comparisons, for the maximum error is only 0.2%.

The force-torque ratio

Using the Lorentz reciprocal relations it can be shown that the force per unit rotational velocity, F^{Ω}, is equal to the torque per unit translational velocity, T^U. This relation was used by Goldman *et al.* (1966) as a check on their results for resistance coefficients at zero frequencies. We also used this as a check on the consistency of our numerical results for problems 2 and 3, and found that for a given sphere separation, agreement was excellent for frequencies below an upper limit, λ_{max} say, where λ_{max} depends on the separation between the spheres. The exponential decay of the viscous interactions with increasing frequency, and increasing separation means that it is unreasonable to expect the ratio to agree with the reciprocal relation over the full range of the frequency parameters described above, as it is these viscous terms which are the origin of the induced torques and forces.

A.3. *Calculated resistance coefficients*

The forces presented in this section are normalized by the force on an isolated sphere (5.7). We will only present the results for $F^U_{\parallel}$ and $F^U_{\perp}$ as all the resistance quantities needed for our work have previously been calculated by Clercx (1991). Rotational motions have little effect on the transverse dynamic mobility (§8), and $F^U_{\perp}$ is the most

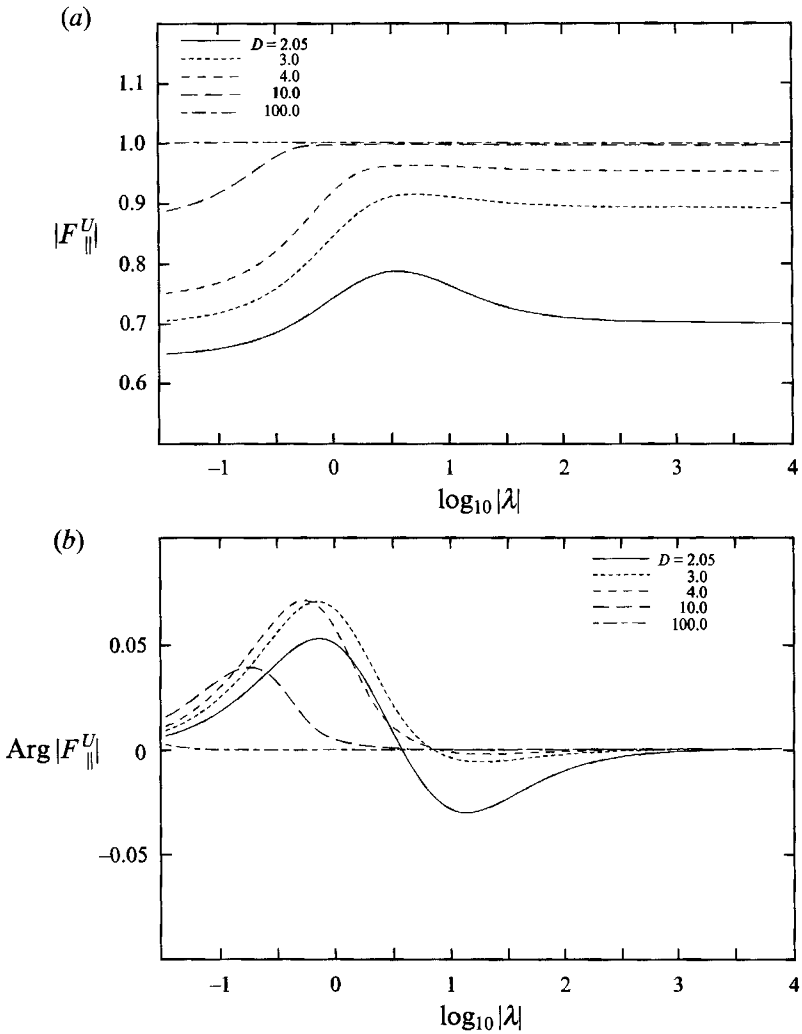

FIGURE 7. The hydrodynamic resistance coefficient $F_{\parallel}^{U}$ as a function of frequency, at various centre to centre separations.

important resistance coefficient in (7.14). $F_{\parallel}^{U}$ is the only quantity needed for the axisymmetric dynamic mobility.

Axisymmetric motion

The magnitude and phase of the resistance coefficient $F_{\parallel}^{U}$ in (7.7) is presented in figure 7. The very rapid approach of the high-frequency ratio to unity as D varies from 2 to 10 is due to the short range r^{-3} interactions characteristic of potential flow. At low frequencies the interaction drops off like r^{-1} and so the drag coefficient approaches unity much more slowly as D increases.

In axisymmetric motion the fluid velocity at points on the axis is always in the direction of the motion of the sphere generating the flow. Hence the spheres convect each other in the direction of motion, and the hydrodynamic drag ratio is always less than one.

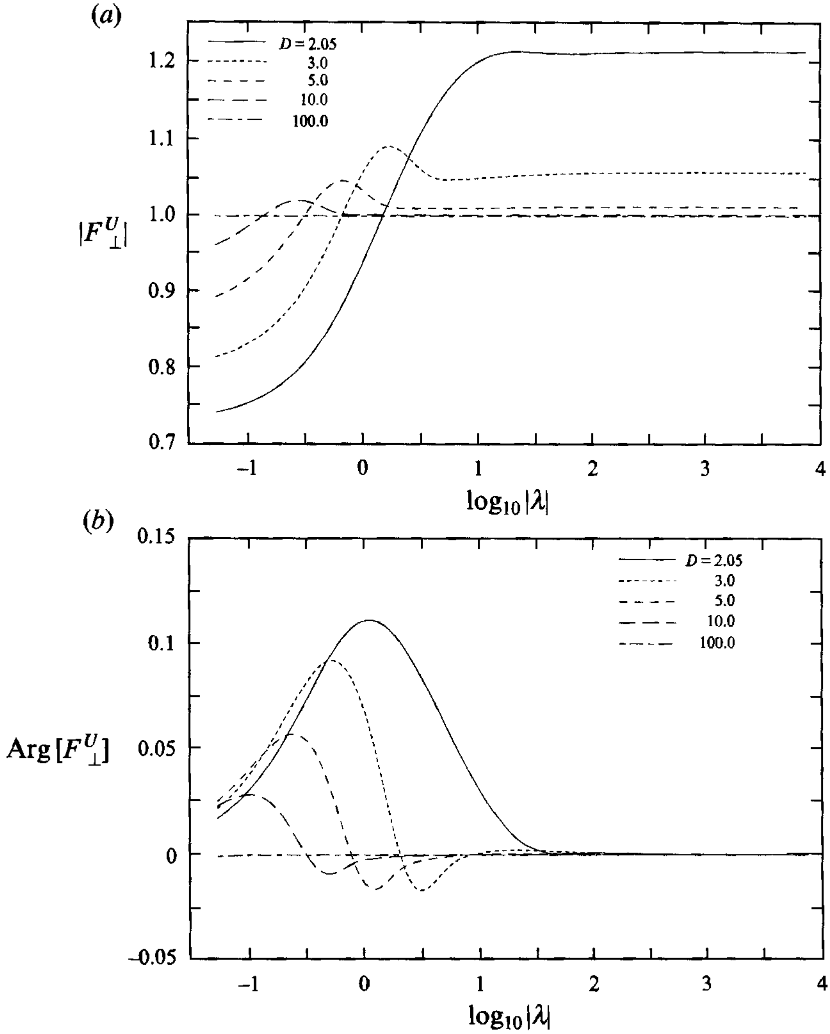

FIGURE 8. The hydrodynamic resistance coefficient $F^U_\perp$ as a function of frequency, at various centre to centre separations.

Transverse motion

The resistance coefficient $F^U_\perp$ in (7.7) is shown in figure 8.

Again the drag ratio is less than one at low frequencies, as the flow generated by each sphere convects the other in the direction of motion. At high frequencies flow directly above a sphere is in the opposite direction to the velocity of the sphere, and the drag is greater for either sphere of a pair than for an isolated sphere.

A.4. *Basset force calculation*

The Basset force of a sphere pair has not been discussed in the literature before. We calculated the Basset force coefficient B using the formula (8.3). The calculation involves the determination of the surface velocity U_s for irrotational flow around the sphere-pair. For the transverse case we determined B using the form of the velocity potential given by Reed & Morrison (1976) in their work on electrophoresis. For the axisymmetric case we used the stream function formulation derived by Jeffery (1912).

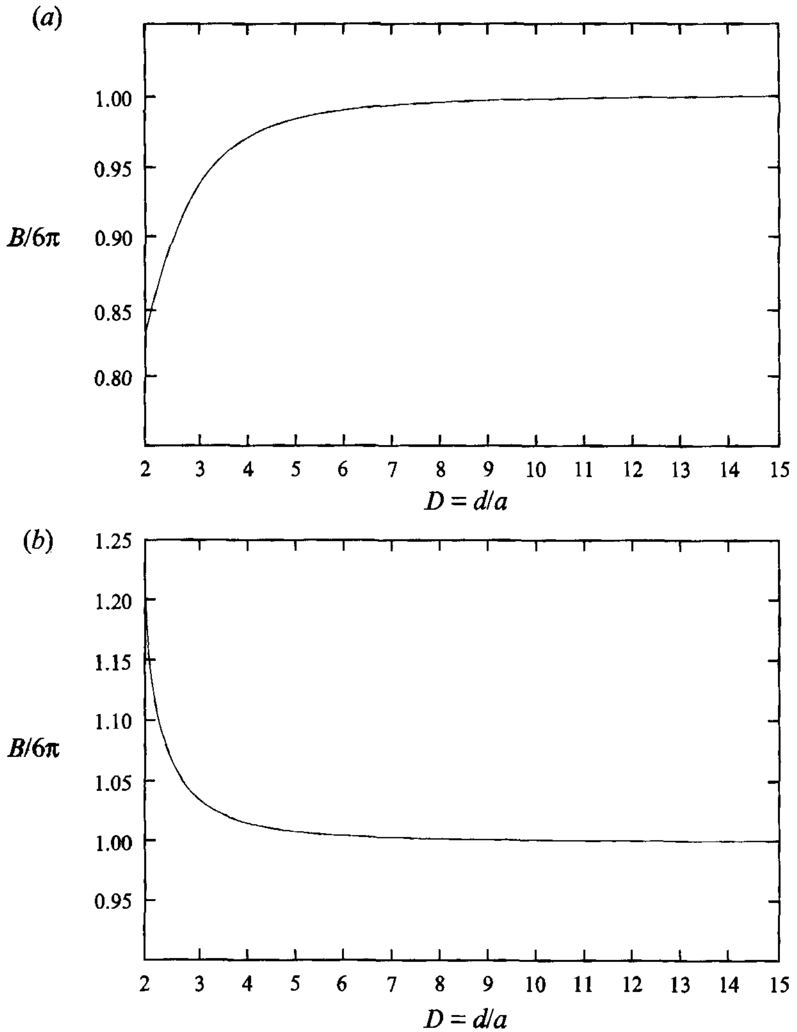

FIGURE 9. The Basset force for equal spheres moving with equal velocities as a function of centre to centre separation for (*a*) axisymmetric motion, and (*b*) transverse motion.

As we mentioned at the start of §8, it is possible to determine analytically the stream function for the potential flow field for the axisymmetric problem. As this result has not been reported before, we present it here.

Jeffery (1912) gives the following form for the stream function in bipolar coordinates

$$\psi(\xi,\mu) = (\cosh\xi-\mu)^{-\frac{1}{2}}\sum_{n=0}^{\infty} a_n \cosh((n+\tfrac{1}{2})\xi)\,V_n(\mu)-\tfrac{1}{2}U\alpha^2\frac{1-\mu^2}{(\cosh\xi-\mu)^2}, \qquad \text{(A 5)}$$

ξ and θ are the bipolar coordinates. $\mu=\cos\theta$, $\alpha = a\sinh\xi_0$, and $\coth\xi_0 = d/2a$.

This stream function is appropriate in a frame in which the spheres are at rest. The functions $V_n(\mu)$ are defined by (Stimson & Jeffery 1926)

$$V_n(\mu) = P_{n-1}(\mu)-P_{n+1}(\mu).$$

Using the boundary conditions appropriate for potential flow we find the coefficients a_n to be

$$a_n = \frac{\sqrt{2}U\alpha^2 n(n+1)\exp[-(n+\tfrac{1}{2})\xi_0]}{(2n+1)\cosh((n+\tfrac{1}{2})\xi_0)}$$

It is necessary to evaluate the integral in (8.3) numerically. In figure 9 we plot $B/6\pi$ as a function of sphere separation for both axisymmetric and transverse motions. (6π is the Basset force coefficient for an isolated sphere.) It can be seen that the interactions in the Basset force are short-ranged. The origin of this is the r^{-3} decay of the velocity field for an isolated sphere in potential flow.

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