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BROWNIAN MOTION OF SPHERICAL PARTICLES NEAR A DEFORMING INTERFACE

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Abstract—In this paper Brownian diffusion of spherical particles near a deformable fluid interface was examined by considering interface deformations that were caused by impulsive motions of the Brownian particles. First, the velocity fields were constructed in terms of eigenfunctions on the bipolar coordinate system which facilitated the separation of variables. Then, the rate of interface deformation was determined to calculate the force acting on a Brownian sphere due to the interface relaxation back toward a flat configuration. In addition, the covariance function of velocity correlation was determined by solving the Langevin equation which included the effects of the interface relaxation. Finally, the diffusion coefficient of spherical particles was evaluated by utilizing the Einstein-Smoluchowski relation in conjunction with the particle mobility calculated in the presence of a deforming interface.

Key words: *Brownian Motion, Brownian Diffusivity, Interface Deformation, Velocity Autocorrelation, Particle Mobility, Bipolar Coordinates*

INTRODUCTION

In this paper, Brownian motion of spherical particles near a deformable fluid-fluid interface is examined. Nearly all previous attempts to incorporate hydrodynamic interaction into Brownian motion or diffusion near a fluid interface have relied on solutions for a flat nondeforming interface [Brenner and Leal, 1982; Gotoh and Kaneda, 1982]. However, even in the absence of Brownian particles, the interface will fluctuate spontaneously around a flat configuration due to the thermal agitation of the surrounding fluids, and these random changes in the interface shape will produce random motions of Brownian particles in the vicinity of the interface [Teletzke et al., 1982; Buff et al., 1965]. Further, the motions induced in the two fluids by the impulsive motion of a Brownian particle will generally lead to a normal stress difference across the interface which can only be balanced by capillary forces if the interface deforms. In general, then, the interface will exhibit a continously changing shape which depends on its shape at earlier times [Lee and Leal, 1982; Berdan and Leal, 1982; Geller et al., 1986; Stoos and Leal, 1989]. This means that an accurate theoretical description of the mechanism would have to take into account the prior history of the particle motion as it approaches the interface.

Although the magnitude of interface deformations will be small compared to the particle size, corresponding to infinitesmal displacements of the Brownian particle on the inertial time scale, the displacement induced in the particle by the interface relaxation back toward equilibrium (i.e., the flat configuration) may be of the same order of magnitude as that caused initially by the random impulse and this 'rebound' effect may have an appreciable effect on the mean-square displacement (or the Brownian diffusivity) of the particle [Yang, 1995]. Thus, the interface effects on the motion of Brownian particles are of two distinct types; first, mechanical effects due to the spatially modified hydrodynamic mobility and the interface relaxation back toward a flat configuration from the deformed shapes caused by the particle motion and second, nonequilibrium thermodynamic effects due to the fluctuating velocity fields caused by the random changes in the interface shape.

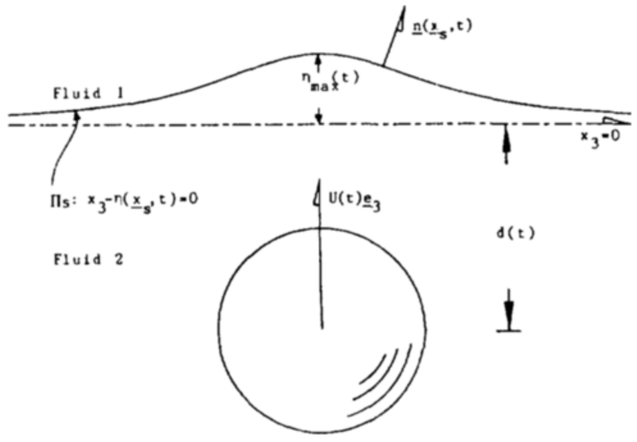

Fig. 1. Schematic sketch of the geometry of the problem when a sphere approaches a deforming interface.

In the present work, we examine the effect of interface deformation; namely, the modification in mean square displacement due to the 'elastic rebound' associated with the motion that is induced in the particle as the interface relaxation back toward equilibrium. In the analysis which follows the two bulk phase fluids are assumed to occupy the domain $x_3>0$ (fluid 1) and $x_3<0$ (fluid 2) as depicted in Figure 1. A uniform bulk concentration (i.e., number density) gradient is presumed to be maintained at the constant value parallel to the bounding interface and to be characterized by a macroscopic length scale L which is much larger than the radius of a Brownian sphere a (i.e., $L \gg a$). This gives rise to a steady flux of Brownian particles in a direction normal to the interface; one-dimensional description is therefore appropriate. Analysis of this normal mode of diffusion transport has been motivated both by potential important applications in the fields of aerosol and hydrosol deposition, and also as models for transient, nonequilibrium adsorption processes [O'Neill and Ranger, 1983]. We consider here both the spatial modification of the hydrodynamic mobility due to hydrodynamic interaction effects, and the effect of interface relaxation process on the Brownian diffusion of the particle.

DISTURBANCE FLOW BY BROWNIAN MOTION OF A SPHERE

We begin by considering a system which consists of two immiscible Newtonian fluids 1 and 2 that are separated by an interface, as depicted in Figure 1. The surface of the interface is denoted as Π_S defined by

$$\Pi_S = x_3 - \eta(\mathbf{x}_s, t) = 0 \quad (1)$$

where $\mathbf{x}_s$ is a position vector representing points lying in a plane parallel to the undeformed, flat interface located at $x_3=0$. Thus, $\eta(\mathbf{x}_s, t)$ in (2) denotes the interface displacement from the undefromed, flat configuration. The motion of particles in the presence of a fluid interface is, in general, nonlinear and depends on the prior history of the particle motion and of the interface deformation. This nonlinear interface deformation problem cannot be solved exactly (except by numerical methods) but can be solved approximately by linearizing the boundary conditions at the interface in the case of sufficiently small deformations. It is obvious that the difficulty arising from the time-dependence of the interface shape can be resolved by considering limiting cases corresponding to either very slow or very rapid particle motion. In particular, if the process of interface deformation is very slow relative to the time scale characteristic of particle motion, then the interface will not be able to deform significantly and remains arbitrarily close to flat at all times. At the other end of the spectrum, if the time scale for particle motion is very long compared to an intrinsic time scale for interface deformation, the interface shape at any instant will be the steady equilibrium form, in which the normal component of velocities are always zero at the interface [Lee and Leal, 1982; Berdan and Leal, 1982; Geller et al., 1986].

Let us consider the consequences of small deformations caused by *rapid* random motions of Brownian sphere *normal* to the interface, since the random Brownian displacement, $\sqrt{<|\Delta \mathbf{x}|^2>}$, of a sphere is only about 10^{-2} a-10^{-3} a in the very short fluctuation time τ_p of the particle velocities. Here, the time scale τ_p is defined by

$$\tau_p = \frac{m}{6\pi\mu_2 a} \quad (2)$$

in which m is the mass of the particle and μ_2 denotes the viscosity of fluid 2, and τ_p is O(10^{-9} sec) for a Brownian particle in aqueous medium at room temperature [Russel, 1981]. In view of the infinitesimal displacement corresponding to an impulse on the inertial time scale τ_p characteristic of the motions of a Brownian particle, it can be assumed that the relevant hydrodynamic mobility is that associated with a flat, but deforming interface. In this limiting case, the equations governing the motion in each fluid j (=1, 2) are then the quasi-steady creeping motion equation and the equation of continuity.

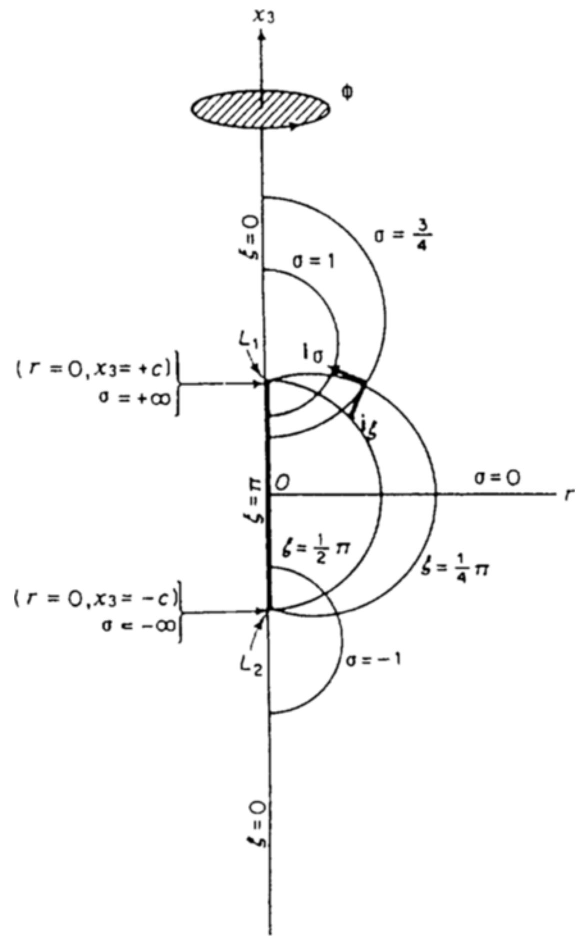

Fig. 2. Bipolar coordinates (ξ, ϕ, σ) versus cylindrical coordinates (r, ϕ, x_3).

$$\nabla p^{(j)} = \mu_j \nabla^2 \mathbf{u}^{(j)} \quad (3)$$

$$\nabla \cdot \mathbf{u}^{(j)} = 0 \quad (4)$$

Here, μ_j is the viscosity of fluid j. The boundary conditions to be satisfied in dimensional form are the following:

$$\mathbf{u}^{(j)} \rightarrow 0 \text{ as } x_3 \rightarrow \pm\infty \quad (5)$$

Since the deformation is sufficiently small, the boundary conditions at the interface can be linearized as

$$u_i^{(1)} = u_i^{(2)} \quad (6)$$

$$n_i u_i^{(1)} = n_i u_i^{(2)} = \frac{\partial \eta}{\partial t} \quad (7)$$

$$n_i T_{il}^{(1)} = n_i T_{il}^{(2)} \quad (8)$$

where $\mathbf{n}$ is the unit outward pointing normal vector from fluid 2 (i.e. $\mathbf{n} = \nabla\Pi_S/|\nabla\Pi_S|$) and $T_{il}^{(j)}$ is the stress tensor in fluid j.

Since the equations of motion are linear and the pressure in each fluid is harmonic, it is straightforward to derive a general solution of Stokes' equation, plus the continuity equation. Further, due to the presence of an interface, it is convenient to utilize a bipolar coordinate system (ξ, ϕ, σ) depicted in Figure 2. In application of the general solution to the present problem in which a rigid sphere normally approaches an interface between two immiscible viscous fluids, we shall identify the interface with the coordinate surface $\sigma=0$ and the sphere surface with the coordinate surface

$$\sigma=\sigma_0=-\cosh^{-1}(d/a) \tag{9}$$

Although the velocity components could be obtained in this bipolar system directly, it is more convenient for the present purposes to use the bipolar eigenfunctions to evaluate the velocity components in the related cylindrical coordinates (r, ϕ, x_3), which is sketched together with (ξ, ϕ, σ) in Figure 2. The bipolar and cylindrical coordinates are related via the transformation:

$$x_3=\frac{c\sinh\xi}{\cosh\sigma-\cos\xi} \text{ and } r=\frac{c\sin\xi}{\cosh\sigma-\cos\xi} \tag{10}$$

in which c is a constant which can be determined by the relative location of the boundaries $\sigma=0$ and $\sigma=\sigma_0$ [Happel and Brenner, 1983]. Each coefficient of the eigenfunction has been determined by satisfying the boundary condition at the sphere surface [i.e., the condition of vanishing velocity at infinity, (5), together with the conditions (7) and (8) at the interface]. Thus, the solution pertains to the limiting case, in which the interface remains arbitrarily close to flat at all times albeit with $u_in_i\neq0$ due to the particle motion, and can be applied to the present study. It can be easily shown that the stream function ψ for fluid 2 can be determined by eigenfunction expansions in bipolar coordinates and can be expressed as

$$\psi=c^2(\cosh\sigma-\cos\xi)^{-3/2}\sum_{n=1}^{\infty}W_n(\sigma)Q_{n+1}(\cos\xi) \tag{11}$$

Here, $Q_{n+1}(\cos\xi)$ is the Gegenbauer polynomial of order $(n+1)$ and degree $-1/2$ and $W_n(\sigma)$ is determined from the no-slip boundary conditions on the sphere surface specified by (9). The no-slip boundary condition can be expressed in terms of stream function ψ, i.e., on $\sigma=\sigma_0$ [$=-\cosh^{-1}(d/a)$]

$$\psi=\frac{r^2}{2},\ \frac{\partial\psi}{\partial\sigma}=r\frac{\partial r}{\partial\sigma} \tag{12}$$

Substituting (11) into the condition (12), we get the boundary values of the function $W_n(\sigma)$ as:

$$W_n(\sigma_0)=\sqrt{2}n(n+1)\left[\frac{e^{-(n-1/2)\sigma_0}}{2n-1}-\frac{e^{-(n+3/2)\sigma_0}}{2n+3}\right] \tag{13}$$

$$W_n'(\sigma_0)=-\frac{\sqrt{2}}{2}n(n+1)[e^{-(n-1/2)\sigma_0}-e^{-(n+3/2)\sigma_0}] \tag{14}$$

From this solution (11) in conjunction with (13) and (14), the normal component of velocity at the surface of interface can be found which is the rate at which the surface is *deforming*. It follows that the nonzero deformation rate can then be obtained by integrating the kinematic condition (7).

We now consider the interface shape by calculating the velocity at the interface from the solution of (11). The velocity component

$$w=\frac{U}{r}\frac{\partial\psi_2}{\partial r} \tag{15}$$

can be evaluated readily, and utilizing the transformation rule

$$c\frac{\partial}{\partial r}=-\left\{\sin\xi\sinh\sigma\frac{\partial}{\partial\sigma}+(1-\cos\xi\cosh\sigma)\frac{\partial}{\partial\xi}\right\} \tag{16}$$

$$c\frac{\partial}{\partial x_3}=\left\{(1-\cos\xi\cosh\sigma)\frac{\partial}{\partial\sigma}-\sin\xi\sinh\sigma\frac{\partial}{\partial\xi}\right\} \tag{17}$$

we have the maximum velocity component w_{max} corresponding to the largest displacement η_{max} of the interface, as shown in Figure 1:

$$w_{max}=\frac{\partial\eta_{max}}{\partial t}=-2\sqrt{2}U\sum_{n=1}^{\infty}(-1)^nH_n(d) \tag{18}$$

Here U is the magnitude of the particle velocity and H_n is defined by

$$\frac{(2n-1)(2n+3)}{\sqrt{2}n(n+1)}H_n(\sigma_0)=$$
$$\frac{(1+\lambda)\{(2n+1)^2\sinh^2\sigma_0-(2n+1)\sinh2\sigma_0+2\}+2(1-\lambda)e^{-(2n+1)\sigma_0}}{4\{\cosh(n+1/2)\sigma_0-\lambda\sinh(n+1/2)\sigma_0\}^2+(1-\lambda^2)(2n+1)^2\sinh^2\sigma_0} \tag{19}$$

in which $\lambda(=\mu_1/\mu_2)$ is the viscosity ratio of the two fluids 1 and 2. The effects of hydrodynamic interaction between the particle and the interface are contained in the complicated function $H_n(d)$ (i.e., $H_n\rightarrow0$ as $d\rightarrow\infty$) in (19). Thus, in order to proceed analytically to illustrate the qualitative nature of these effects, we will expand H_n in terms of the small $\varepsilon(=a/d\ll1)$ assuming that the particle is not closer than a few radii from the interface. The result is

$$w_{max}=\frac{\partial\eta_{max}}{\partial t}=$$
$$\frac{3}{1+\lambda}U\varepsilon\left[1-\frac{9}{8}\frac{1-\lambda}{1+\lambda}\varepsilon-\frac{1}{3}\varepsilon^2+\left(\frac{9}{8}\frac{1-\lambda}{1+\lambda}\right)^2\varepsilon^2\right]+O(\varepsilon^4) \tag{20}$$

The kinematic condition (20) provides a relationship between the particle velocity and the maximum deformation rate, w_{max}, of the interface. The maximum displacement η_{max} caused by a thermal impulse can then be obtained by integrating (20).

$$\eta_{max}=\frac{3}{(1+\lambda)}\sqrt{\frac{k_BT}{m}}\beta\varepsilon\left[1-\frac{9}{8}\frac{1-\lambda}{1+\lambda}\varepsilon-\frac{1}{3}\varepsilon^2+\left(\frac{9}{8}\frac{1-\lambda}{1+\lambda}\right)^2\varepsilon^2\right]$$
$$+O(\varepsilon^4) \tag{21}$$

In (21), the viscous relaxation time

$$\beta\equiv\frac{m}{6\pi\mu_2aC_D} \tag{22}$$

is a function of the distance d between the sphere center and the interface, and the drag ratio C_D (the drag divided by the Stokes drag $6\pi\mu_2Ua$) in this case is given by

$$C_D=\frac{\sqrt{2}}{3}(1+\lambda)\sinh\sigma_0\sum_{n=1}^{\infty}H_n \tag{23}$$

Again, utilizing an asymptotic expansion for H_n in terms of small ε and

$$\sinh\sigma_0=-\frac{1}{\varepsilon}+\frac{1}{2}\varepsilon+0(\varepsilon^2) \tag{24}$$

it can be shown that

$$C_D=1-\frac{9}{8}\frac{1-\lambda}{1+\lambda}\varepsilon+\left(\frac{9}{8}\frac{1-\lambda}{1+\lambda}\right)^2\varepsilon^2+O(\varepsilon^3) \tag{25}$$

The effect of the viscosity ratio, λ, on the drag ratio in the presence of a deforming interface is clearly evident in (25) for the limiting case in which the interface is instantaneously flat. In Figure 3, the drag ratio C_D is plotted as a function of the dimension-

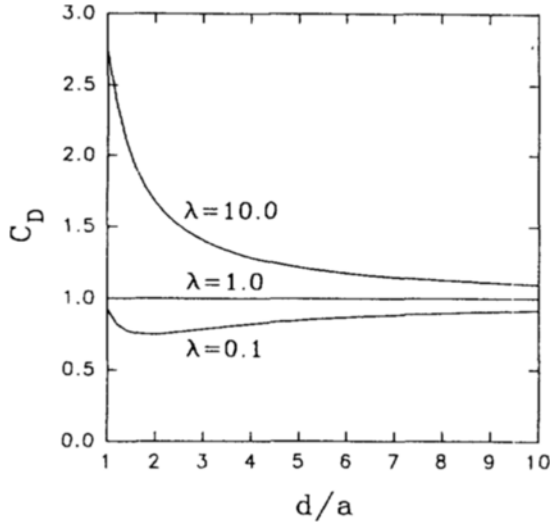

Fig. 3. Drag ratio C_D as a function of the dimensionless separation distance d/a in the presence of a deforming interface.

less separation distance d/a for three values of $\lambda=0.1$, 1.0 and 10. In particular, for $\lambda=1$ the instantaneous values of the normal component of velocity $(u_i n_i)$ along the interface are identical to the values which would exist along the same plane for sphere motion in a single unbounded fluid domain. As a consequence, the instantaneous fluid motion is unaffected by the interface and the drag ratio is identically equal to Stokes' drag, i.e., $C_D=1$. For values of $\lambda<1$, on the other hand, the drag for a sphere near a flat, deforming interface is decreased as the sphere moves closer to the interface, while for $\lambda>1$ the drag is increased under the same conditions. These results are all a consequence of the fact that the normal velocity given by (21) at the interface is smaller for $\lambda>1$ and larger for $\lambda<1$ than it would be on the same plane if the sphere were moving through single unbounded fluid. Thus, the drag for a flat, but deforming interface is highly sensitive to the viscosity ratio λ between two fluids. The drag ratio of a sphere particle moving toward a flat, non-deforming fluid interface has been determined by Yang and Leal [1984], Fuentes et al. [1988], and Yang and Leal [1990]. The result is

$$C_D=1+\frac{9}{8}\,\frac{2/3+\lambda}{1+\lambda}\varepsilon+\left(\frac{9}{8}\,\frac{2/3+\lambda}{1+\lambda}\right)^2\varepsilon^2+O(\varepsilon^3) \quad (26)$$

Thus, the drag in the presence of a non-deforming interface is always larger than that in the absence of an interface, which is independent of the viscosity ratio. This is due to the fact that for a nondeforming interface the normal component of velocity on the interface remains always zero, i.e., $u_i n_i=0$

EFFECT OF INTERFACE RELAXATION

Since the energy imparted by the thermal noise is dissipated very rapidly with respect to the averaging time scale Δt, the particle motion due to thermal agitation can be regarded as an impulsive fluctuation source for interface displacements. Recently, Yang [1995] developed a general solution for the attenuation of capillary waves on an interface. From his solution, the time variation of wave amplitude can be written as

$$\eta(\tau)=\eta_{max}e^{-\zeta\tau}\left[\cos\sqrt{1-\zeta^2}\tau+\frac{\zeta}{\sqrt{1-\zeta^2}}\sin\sqrt{1-\zeta^2}\tau\right] \quad (27)$$

Here, the time variable τ is nondimensionalized with the time scale τ_R

$$\tau_R=\frac{\rho_1+\rho_2}{k^2(\mu_1+\mu_2)} \quad (28)$$

where the interface displacement decays exponentially. The other dimensionless variable ζ is defined as

$$\zeta\equiv\frac{\tau_I}{\tau_R},\ \tau_I=\omega_0^{-1}=\sqrt{\frac{\rho_1+\rho_2}{(\Delta\rho)gk+\gamma k^3}} \quad (29)$$

in which ρ_j denotes the density of fluid j, g the gravity, γ the interfacial tension and k the wave number. Thus, $\omega_0(=\tau_I^{-1})$ is the natural frequency of capillary fluctuations and the dimensionless parameter ζ represents the ratio of viscous forces to capillary elastic response forces. Further, the hydrodynamic force on a Brownian sphere immersed in the capillary wave can be determined from the generalized Faxen's law [Yang, 1987]. The resulting force acting on the sphere can be written as

$$F_3=-6\pi\mu_2 a\omega_0\eta_{max}{}^{-kd}\frac{e^{-\zeta\tau}}{\sqrt{1-\zeta^2}}\sin\sqrt{1-\zeta^2}\tau \quad (30)$$

which clearly indicates that the force associated with the interface oscillations decays also exponentially on the time same scale τ_R as the amplitude of capillary wave.

Now, we consider the motions of a nearby Brownian particle which occur as a consequence of the force (30) generated by interface relaxation back toward a flat configuration. Since the external forces and the macroscopic time-evolution of particle momentum have to obey a linear law or a macroscopic rate equation of the Langevin type, i.e.,

$$\frac{dU}{dt}+\beta^{-1}U=\frac{F_3}{m} \quad (31)$$

Solving the Langevin equation for motion of the particle under the action of fluctuating force F_3 given by (30), we can readily evaluate the velocity correlation function of the particle as

$$R_U(d;\ \tau)=\langle U(t)\ U(t+\tau)\rangle=-\frac{\beta\eta_{max}\omega_0^2e^{-2kd}}{(\zeta\omega_0-\beta)^2+(1-\zeta^2)\omega_0^2}\cdot\sqrt{\frac{k_BT}{m}}\left[e^{-\lambda_{a\omega}|\tau|}-e^{-\zeta|\tau|}\left\{\cos\sqrt{1-\zeta^2}\tau+\frac{\zeta\omega_0-\beta}{\sqrt{1-\zeta^2}\omega_0}\sin\sqrt{1-\zeta^2}|\tau|\right\}\right] \quad (32)$$

in which

$$\lambda_{a\omega}\equiv\frac{\tau_I}{\beta} \quad (33)$$

is the ratio of the time scale for the interface oscillation (i.e., ω_0^{-1}) to that of the viscous relaxation of the particle velocity. Thus, the energy of the Brownian particle will be dissipated by the irreversible frictional processes of both the exponential viscous relaxation of the particle velocity on the time scale $\beta(=m/6\pi\mu_2 aC_D)$ which would be $\tau_p=m/(6\pi\mu_2 a)$ in an unbounded single fluid and of the interface relaxation on the time scale τ_R. In Figure 4, the velocity correlation function $R_U(d;\ \tau)$ is plotted as a function of the dimensionless time difference τ for $\zeta=0.2$, 0.6, 1.0 and 1.4, $\lambda=1$ and $d/a=3$. Yang [1995] demonstrated that the viscous relaxation of the particle velocity exhibits the three typical modes depending on the values of ζ (i.e., oscillatory damping for $\zeta<1$, critical damping for $\zeta=1$, and underdamping for $\zeta>1$). It is obvious from (21) that the interface displacement due to the impul-

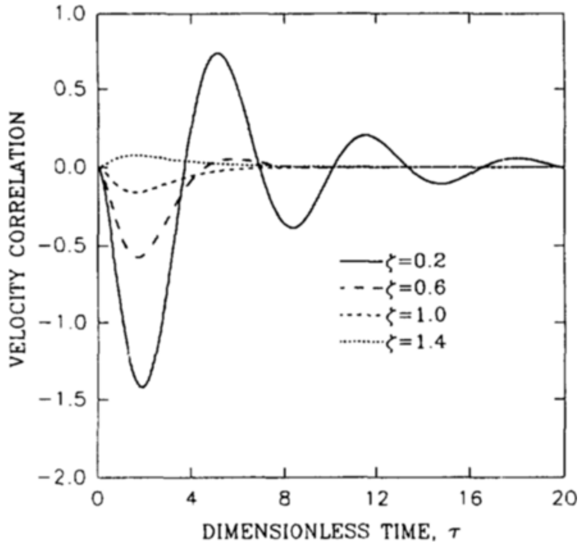

Fig. 4. Dimensionless correlation function

$$\frac{<U(t)\ U(t+\tau)>}{\beta\eta_{max}\omega_0^2 e^{-2kd}\sqrt{k_BT/m}/\{(\zeta\omega_0-\beta)^2+(1-\zeta^2)\omega_0^2\}}$$

as a function of the dimensionless time difference τ for $\tau_l/\tau_p=$ 2.0.

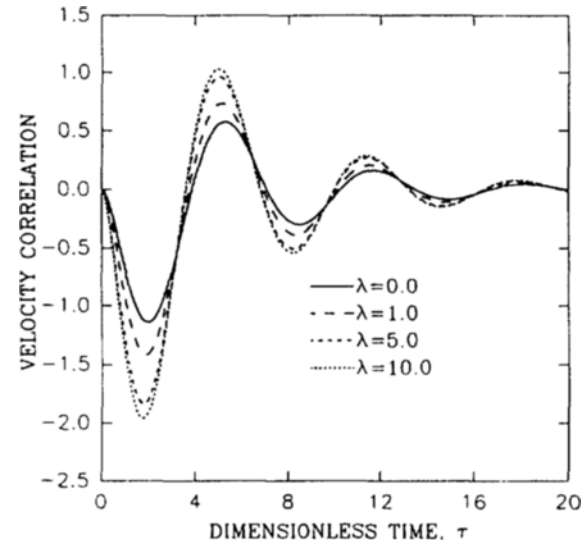

Fig. 5. Dimensionless correlation function

$$\frac{<U(t)\ U(t+\tau)>}{\beta\eta_{max}\omega_0^2 e^{-2kd}\sqrt{k_BT/m}/\{(\zeta\omega_0-\beta)^2+(1-\zeta^2)\omega_0^2\}}$$

as a function of the dimensionless time difference τ for $\tau_l/\tau_p=$ 2.0.

sive motion of a Brownian particle is decreased as the viscosity ratio λ becomes higher since the normal velocity at the interface is smaller. As a consequence, the magnitude of the particle velocity induced by the interface relaxation back to the flat configuration is decreased for the higher viscosity ratio λ, which is illustrated in Figure 5 for $\zeta=0.2$ and $d/a=3.0$. But, the particle mobility is also decreased so that the initial impulsive displacement will also be smaller. Perhaps the *relative* importance of the relaxation process is not so highly decreased in the limit of high viscosity ratio.

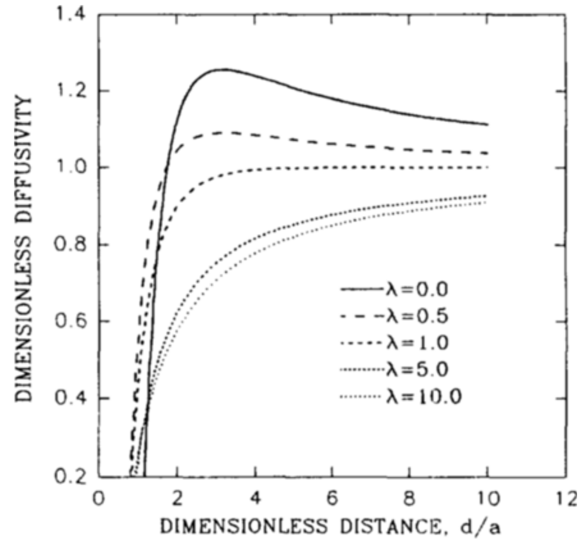

Fig. 6. Dimensionless diffusion coefficient, $D/\{k_BT/(6\pi\mu_2 a)\}$, as a function of the separation distance for $ka=0.5$.

It is important to realize that the solution of (32) contains the Einstein-Smoluchowski theory for the Brownian diffusion process as a limiting case when $\Delta t \gg \tau_{vp}$ and τ_R, so that the non-Markovian effects can be negligible in the averaging time Δt [Hauge and Martin-Löf, 1973]. Under these circumstances, the Einstein-Smoluchoswki diffusion coefficient can be readily evaluated from the definition

$$D=\int_0^\infty <U(t)\ U(t+t^0)>dt^0 \tag{34}$$

in which the integrand is the velocity correlation function given by (32). Thus, the diffusivity is immediately

$$D=\frac{k_BT}{6\pi\mu_2 aC_D}\left[1-\frac{3}{1+\lambda}e^{-kd}\varepsilon\left\{1-\frac{9}{8}\frac{1-\lambda}{1+\lambda}\varepsilon-\frac{1}{3}\varepsilon^2 +\left(\frac{9}{8}\frac{1-\lambda}{1+\lambda}\right)^2\varepsilon^2\right\}\right]+O(\varepsilon^4) \tag{35}$$

where the drag ratio C_D is given by (25). We now consider, in detail, the condition $\Delta t \gg \beta$ and τ_R for validity of the Einstein-Smoluchowski relation with the diffusion coefficient D of (35). The time scales β and τ_R, on which the particle velocity and the interface displacement relax exponentially, are approximately determined as

$$\beta=O(\tau_p)=O\left(\frac{m}{6\pi\mu_2 a}\right) \tag{36}$$

$$\tau_R=O\left(\frac{\rho_1+\rho_2}{\mu_1+\mu_2}a^2\right) \tag{37}$$

Thus, we can certainly choose an averaging time scale Δt which is much smaller than the observation time interval [$\approx O(1\ sec)$] but still very large compared to β and τ_R which are $O(\sim 10^{-8}$ sec) in usual systems of Brownian particles in water.

In Figure 6, the diffusion coefficient D given in (35) is illustrated as a function of the separation distance d between the interface and the sphere center for viscosity ratios $\lambda=0.0$, 0.5, 1.0, 5.0 and 10.0. As is obvious from (35), the diffusion coefficient is either increased or decreased by the presence of an interface depending on the viscosity ratio λ and the particle position relative to the interface. For $\lambda=1$, although drag ratio C_D is unchanged by the nearly flat, deforming interface, the *displacement* induced in the particle by the interface relaxation back toward equilibrium is increased as the particle moves closer to the interface. As a consequence, the diffusion coefficient, which approaches $k_BT/(6\pi\mu_2 a)$ as $d\to\infty$, is decreased as the separation distance becomes smaller. For values of $\lambda<1$, on the other hand, the diffusion coefficient is greater than it would be in a single unbounded fluid for larger separation distances due to the spatially modified drag ratio. However, for smaller separation distances, the dominant effect of the interface relaxation again causes the diffusivity to decrease. When the viscosity ratio is greater than one, the presence of an interface yields very low mobility (i.e., higher drag) for the particle motion and thus the diffusion coefficient is alwэys less than $k_BT/(6\pi\mu_2 a)$.

CONCLUSIONS

The motions of a Brownian sphere near a deformable interface have been examined by considering the 'rebound effects' arising from the interface relaxation back toward a flat configuration. The analysis leads to the following conclusions.

The effect of the viscosity ratio, λ, on the drag ratio in the presence of a deforming interface is quite different from that in the presence of a non-deforming interface. For values of $\lambda<1$, the drag for a sphere near a deforming interface is decreased as the sphere moves closer to the interface, while for $\lambda>1$ the drag is increased under the same conditions. On the other hand, the drag in the presence of a non-deforming interface is always larger than that in the absence of an interface, which is independent of the viscosity ratio.

The time variation of amplitude of the interface relaxation is characterized on the time scale τ_R on which the force associated with the interface oscillations decays exponentially. However, the energy of the Brownian particle is dissipated by the irreversible frictional processes of both the exponential viscous relaxation of the particle velocity on the time scale β and of the interface relaxation on the time scale τ_R.

The diffusion coefficient is decreased as the separation distance between the sphere center and the interface becomes smaller. For values of $\lambda<1$, the diffusion coefficient is greater than it would be in a single unbounded fluid for larger separation distances due to the spatially modified drag. However, for smaller separation distances, the dominant effect of the interface relaxation again causes the diffusivity to decrease. For $\lambda>1$, a deforming interface reduces the particle mobility and thus the diffusion coefficient is always less than that in the absence of an interface.

NOMENCLATURE

a : particle radius
c : constant defined by (10)
C_D : drag ratio given by (23)
d : separation distance between the particle and the plane interface
D : Brownian diffusivity
F_3 : force induced by the interface fluctuations on the particle
g : gravity
$H_n(\sigma)$: function defined by (19)
k : magnitudes of the wave vector **k** for the capillary wave fluctuations
k_B : Boltzmann constant
m : particle mass
n : unit normal vector on the interface
$p^{(j)}$: pressure of fluid j
Q_{n+1}: Gegenbauer polynomial of order n+1 and degree −1/2
R_U : velocity autocorrelation function
t : time
t^0 : time at reference state
$\mathbf{T}^{(j)}$, $T_{ik}^{(j)}$: stress tensor of fluid j
T : absolute temperature
$\mathbf{u}^{(j)}$: velocity of fluid j
U : Brownian particle velocity
w : velocity component along the x_3-axis
w_{max} : maximum velocity component along the x_3-axis on the interface, $\partial\eta_{max}/\partial t$
$W_n(\sigma)$: function defined by (13)
$\mathbf{x}_s$: position vector of a point placed on the interface
x_3 : coordinate perpendicular to the plane interface
β : viscous relaxation time for the particle motion defined by (22)
γ : interfacial tension
ε : small parameter, a/d
ζ : τ_I/τ_R
η : interface displacement from the plane of $x_3=0$
η_{max} : maximum interface displacement
λ : viscosity ratio, μ_1/μ_2
λ_{ω_0} : τ_I/β
μ_j : viscosity of fluid j
Π_S : shape function for the interface
ρ_j : density of fluid j
τ : dimensionless time difference
τ_I : reciprocal of the natural frequency of the interface oscillation, ω_0^{-1}
τ_p : viscous relaxation time for the particle motion with Stokes' law
τ_R : viscous relaxation time scale for the interface fluctuation
ψ_2 : stream function of fluid 2 defined by (11)
ω_0 : natural frequency of the interface oscillation

Symbols

$\Delta\rho$: density difference
$|\Delta\mathbf{x}|$: particle displacement

Coordinates

(r, ϕ, x_3) : cylindrical coordinates defined in Fig. 2
(ξ, ϕ, σ) : bipolar coordinates defined in Fig. 2

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