

BROWNIAN DIFFUSION NEAR A PLANE FLUID INTERFACE

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Abstract—The motion of Brownian particles in the vicinity of a fluid interface is studied by considering the spatial modification of the hydrodynamic mobility due to the direct hydrodynamic interactions between the particles and the interface. The analysis determines, for a simple model system, the conditions under which the simple Fickian form of the diffusion equation can be obtained in the presence of an interface. In addition, the theory shows that the diffusivity tensor can be evaluated from a knowledge of the mobility tensor for steady motion of a particle in Stokes flow.

INTRODUCTION

The irregular random motion of small particles suspended in liquids, known as 'Brownian motion', was first described by the English botanist, Robert Brown in 1828. Contraversy concerning the origin of the Brownian motion persisted for many decades and it was not until 1905 that Albert Einstein [1] first advanced a satisfactory theory, and eventually confirmed the molecular nature of matter by relating the Brownian motion to the thermal fluctuations of molecules in the surrounding fluid.

Recent years have witnessed an increasing amount of interest in the description of Brownian diffusion near a rigid wall or a fluid-fluid interface [2-5]. Treatments of this kind are designed to provide a theoretical basis in terms of molecular properties, for understanding and predicting the various transport coefficients that enter into the description of the same processes from a macroscopic point of view. Of considerable importance is prediction and interpretation of interphase mass-transfer rates in liquid-liquid systems, which are usual in many industrial operations, liquid-liquid extraction being a primary example. However, little is known about the effects of a fluid *interface* on the motion of Brownian particles. Indeed, our objective in the present study is to investigate the effect of the presence of an interface on the motion of Brownian particles by employing the general methods of statistical physics in conjunction with fundamental fluid mechanics. It is, of course, obvious from the point of view of nonequilibrium thermodynamics that the interface will fluctuate around equilibrium due to the thermal agitations of surrounding fluid molecules, and these random changes in the interface shape produce random mo-

tions of Brownian particles in the vicinity of the interface. Further, due to the impulsive motion of a Brownian particle the interface exhibits also a continuously changing shape which depends on the prior history of the particle motion and the interface shape at earlier times. Although the interface deformation is small, resulting from infinitesimal displacement of the Brownian particle, the displacement of the particle by interface relaxation back toward equilibrium may be of the same order of magnitude as that initially caused by the random impulse [6].

In the present study, we consider a relatively simple model system in which the interface remains *flat* non-deforming in spite of the arbitrary motion of particle in order to explore the validity of Einstein's diffusion theory for Brownian particles near an interface. The 'statistical-mechanical' model underlying the theoretical development consists of either spherical or elongated slender particles wholly immersed in one of the two contiguous fluids. The model is based upon the assumption of short-range attractive or repulsive forces exerted by the interface on a Brownian particle proximate to it. The analysis is carried out using a Langevin-type stochastic equation for the Brownian particles, and determines the conditions under which the normal macroscopic interfacial transport theory is valid for the model system, wherein a complete description of solute mass-transfer is possible down to the fine scale of hydrodynamic and physicochemical interactions between the solute (i.e., Brownian particles) and the solvent-solvent interface. We begin, however, with the theoretical framework which has been previously proposed for analysis of Brownian motion in an unbounded single-fluid domain. Following that we proceed to a detailed analysis of Brownian motion in

the presence of a fluid interface.

THEORY OF BROWNIAN MOTION IN AN UNBOUNDED DOMAIN

In his pioneering paper, Einstein [1] showed that the irregular motion of uncharged noninteracting particles can be modeled as a *diffusion* and thus the probability distribution $P(\mathbf{x})$ of Brownian particles in the configuration space \mathbf{x} must be governed by the so-called Einstein-Smoluchowski diffusion equation

$$\frac{\partial P(\mathbf{x})}{\partial t} = \nabla \cdot [\mathbf{D} \cdot \nabla P(\mathbf{x})] \quad (1)$$

in which \mathbf{D} denotes the diffusion coefficient tensor, and t is the time variable. In deriving (1), Einstein assumed that the movements of a Brownian particle could be idealized as a Markoff process, in the sense that the course which a Brownian particle will take depends only on the instantaneous values of its physical parameters and is entirely independent of its whole previous history. Utilizing the solution of the diffusion equation (1) with appropriate initial and boundary conditions, Einstein also derived the relationship between the diffusion coefficient D and the mean square displacement $\langle |\Delta \mathbf{x}|^2 \rangle$ of a Brownian *sphere*:

$$\langle |\Delta \mathbf{x}|^2 \rangle = 6D\Delta t \quad (2)$$

The mean square displacement is therefore proportional to the time interval Δt . This general relationship, (2), in combination with the velocity correlation function plays an important role in determining the diffusion coefficient.

The diffusion coefficient in (1) and (2), according to Einstein's theory, can be determined from the molecular-kinetic theory of heat, employing only thermodynamic concepts and the properties of systems in dynamic equilibrium. For a suspension of uncharged, noninteracting particles with spatial number-density gradient, the translational diffusion flux at equilibrium is evidently the same as the convective flux resulting from the application to each particle of a steady thermodynamic force which is due solely to the existence of osmotic pressure. As far as osmotic pressure is concerned, solute molecules and suspending Brownian particles are identical in their behavior at great dilution. According to the van't Hoff's law, the osmotic pressure p^{os} in dilute solution obeys the relationship, $p^{os} = c\kappa_B T$, in which c denotes the number-density of solute particles that may be regarded as the probability density $P(\mathbf{x})$ in the configuration space of a dilute suspension. Here, κ_B is the Boltzmann constant and T is the absolute temperature. Then, the thermodynamic force, \mathbf{F}^{os} , as a consequence of the concentration gradient of Brownian particles, can be derived from the

osmotic pressure and is given by

$$\mathbf{F}^{os} = -\kappa_B T \nabla \ln \{P(\mathbf{x})\} \quad (3)$$

Thus, the corresponding convective flux is equal to $-P(\mathbf{x}) \mathbf{M} [\kappa_B T \nabla \ln \{P(\mathbf{x})\}]$. This convective flux is balanced by the diffusion flux

$$\mathbf{j}_D = -\mathbf{D} \cdot \nabla P(\mathbf{x}) \quad (4)$$

with the diffusivity tensor \mathbf{D} related to the hydrodynamic mobility tensor \mathbf{M} for a particle by the Nernst-Planck-Einstein relation:

$$\mathbf{D} = \kappa_B T \mathbf{M}. \quad (5)$$

This classical expression for diffusivity of uncharged particles has been verified experimentally in many types of diffusion. It is noteworthy that Einstein's approach employs only the concept of a *thermodynamic* driving force on the particle as representation of the diffusive effect of Brownian motion without taking into account the dynamics of the particle motion in the suspending fluid.

Brownian motion of individual particles in a single unbounded fluid domain can also be modeled as a diffusion process in a dilute suspension by a 'rigorous' generalization of the Liouville equation [7] of classical dynamics to include Brownian motion. This approach to Brownian motion begins with a consideration of the equation of motion for a suspended particle, i.e., the Langevin equation [8]:

$$\frac{d\mathbf{U}}{dt} = -\boldsymbol{\beta} \cdot \mathbf{U} + \mathbf{A}(t) \quad (6)$$

where \mathbf{U} denotes the particle velocity, $\boldsymbol{\beta}$ is the hydrodynamic resistance tensor and $\mathbf{A}(t)$ the random force on the particle arising from the thermal agitations of surrounding fluid molecules. According to the Langevin equation, the influence of the surrounding medium on the motion of Brownian particle can be split into two parts: first, a very rapidly fluctuating part $\mathbf{A}(t)$ with a molecular motion time scale, $\tau_f (\approx 10^{-13} \text{ sec for water})$; and, second, a systematic hydrodynamic friction part $-\boldsymbol{\beta} \cdot \mathbf{U}$ associated with a characteristic time scale $\tau_{vp} \equiv \boldsymbol{\beta}^{-1} (\approx 10^{-9} \text{ sec for a free sphere in water})$. Assuming that $\tau_f \ll \tau_{vp} \ll O(1)$, as is characteristic of Brownian motion, we can introduce time intervals Δt in which the physical parameters such as position, orientation and velocity of the Brownian particle change by *infinitesimal* amounts, while the number of fluctuations arising from collisions with surrounding fluid molecules remains extremely large:

$$\tau_f \ll \tau_{vp} \ll \Delta t \ll O(1). \quad (7)$$

That a transformation of Liouville equation into the famous Fokker-Planck equation should be possible under these circumstances is apparent when we recall that the Brownian movements in a time interval Δt satisfying (7) can be regarded as a Markoff process so that

the probability distribution $P(\mathbf{U} + \Delta\mathbf{U}, \mathbf{x} + \Delta\mathbf{x}, t + \Delta t)$ in the phase space governing the probability of occurrence of $\mathbf{U} + \Delta\mathbf{U}$ at time $t + \Delta t$ can be derived from the distribution $P(\mathbf{U}, \mathbf{x}, t)$ at the present time and a knowledge of the transition probability $\Gamma(\mathbf{U}, \Delta\mathbf{U})$ that \mathbf{U} suffers an increment $\Delta\mathbf{U}$ in the time interval Δt . According to the Langevin equation (6)

$$\Delta\mathbf{U} = -\boldsymbol{\beta} \cdot \mathbf{U} \Delta t + \int_t^{t+\Delta t} \mathbf{A}(s) ds, \Delta\mathbf{x} = \mathbf{U} \cdot \Delta t \quad (8)$$

in which the integral denotes the net acceleration arising from fluctuations that a Brownian particle suffers in the time interval Δt . From the molecular-kinetic theory, the probability distribution of the integral must be Maxwellian and thus it follows at once that the transition probability has the Maxwellian distribution in terms of $\Delta\mathbf{U} + \boldsymbol{\beta} \cdot \mathbf{U} \Delta t$. With condition (7), it can also be expected that a Maxwell-Boltzmann distribution of the velocity will be established at all points after time intervals Δt as the result of superposition of a large number of random accelerations caused by collisions with surrounding molecules [9,10]. Thus, the Fokker-Planck equation in the phase space (\mathbf{U}, \mathbf{x}) can be applied to the configuration space, \mathbf{x} , independently of the velocity space, \mathbf{U} , provided that we are interested only in the time intervals Δt . Then, integration of the Fokker-Planck equation over the velocity space \mathbf{U} provides us the Einstein-Smoluchowski equation (1), i.e., differential equation for the probability distribution, $P(\mathbf{x})$, of Brownian particles in the configuration space, \mathbf{x} , and yields the *same* diffusivity coefficient tensor of (5) as Einstein's thermodynamic approach.

It will be evident, however, that the Langevin equation (6) with the instantaneous friction law determined from the steady Stokes equation gives only a partial picture of the effect of thermal fluctuations in the system and predicts a rapid exponential decay on the time scale β^{-1} in the velocity correlation function. The first indication of a deficiency in the Langevin equation came in numerical simulations of the molecular motions in liquids which produced velocity correlations of spherical particles with a long 'tail' decaying as $t^{-3/2}$ rather than an exponential decaying as predicted by (6) [11, 12]. Recently, several analyses [13, 14], which allow for the distribution of thermal fluctuations throughout the fluid, have predicted correctly the full velocity correlation as well as the diffusion coefficient tensor of (5). Linearity is, however, preserved in the governing differential equations for the fluid motion, because the velocities remain small enough to render the convective terms negligible. It is important to realize that both the classical Langevin method with $\boldsymbol{\beta}$ determined from the steady Stokes equation and the above corrected approaches lead to exactly the Einstein-

in-Smoluchowski diffusion equation (1) with the *same* diffusion coefficient tensor (5), provided the condition (7) is satisfied.

BROWNIAN MOTION NEAR A PLANE FLUID INTERFACE

Let us begin by considering a model system consisting of Brownian particles dispersed in a viscous incompressible Newtonian fluid in the semi-infinite domain $-\infty < x_3 < 0$, bounded by a plane fluid interface at $x_3 = 0$ (cf. Fig. 1). In the region $x_3 > 0$, we suppose that there is a second unbounded fluid. The viscosity ratio $\lambda = \frac{\mu_1}{\mu_2}$ between the two fluids is assumed to be arbitrary. In addition, we assume that the interface remains flat and non-deforming.

The difference between the problem discussed in this section and the classical problem of Brownian motion in an unbounded domain is the possible existence of a short-range force of interaction (attractive or repulsive), $\mathbf{F}_{ex}(\mathbf{x})$ which we assume acts between the particles and the interface, and the dependence of the hydrodynamic mobility \mathbf{M} [i.e. $(m\boldsymbol{\beta})^{-1}$; m is the particle mass] on the configuration of the particle relative to the interface (i.e., its position, and if the particle is non-spherical, its orientation), as a consequence of hydrodynamic interactions.

Application of the so-called 'thermodynamic approach' that was outlined in the preceding section shows that the same relationship holds between the mobility and the diffusion tensors as in (5) even in the presence of a flat interface in the absence of a physicochemical interaction force. Further, this approach shows that the relevant hydrodynamic mobility is still that for steady creeping motions.

The presence of a short-range physicochemical attraction (or repulsion) between the particles and the interface will generate steep spatial gradients in the particle number density, $P(\mathbf{x})$. The resulting nonuniform hydrodynamic interactions between particles will also lead to nonisotropic and spatially dependent mobility. These *indirect* interface effects owing to particle-particle hydrodynamic interactions will contribute to nonisotropy and spatial dependence of the diffusivity. Furthermore, although successful in determining the relevant diffusion coefficient of Brownian particles near an interface in the absence of a physicochemical interaction, the thermodynamic approach cannot provide any conditions for validity of the normal diffusion theory in the presence of the physicochemical attraction (or repulsion).

Let us thus turn to the fundamental statistical approach in which the governing differential equation for the probability density in the phase space (\mathbf{U}, \mathbf{x}) is

the Liouville equation, in order to explore the conditions for validity of the diffusion process defined by (4) and (5) in the presence of a flat fluid-fluid interface. Compared to the case of a single unbounded fluid domain, the Langevin equation is modified by the interface in that the hydrodynamic mobility is dependent upon proximity to the interface (and is anisotropic even for spherical particles) due to the direct and indirect hydrodynamic interaction effects that were described above, and by the existence in some cases of an interface-induced physicochemical force field $\mathbf{F}_{ex}(\mathbf{x})$:

$$\frac{d\mathbf{U}}{dt} = -\beta(\mathbf{x}) \cdot \mathbf{U} + \mathbf{F}_{ex}(\mathbf{x}) + \mathbf{A}(t) \quad (9)$$

When one observes the process of Brownian motion in the averaging time intervals Δt satisfying the condition (7), the stochastic movements of a Brownian particle can be regarded as a Markoff process. Further, if the length scales characteristic of variations in $\beta(\mathbf{x})$ and $\mathbf{F}_{ex}(\mathbf{x})$ are sufficiently large relative to the mean displacement $\sqrt{\langle \Delta \mathbf{x}^2 \rangle}$ of a Brownian particle in the time interval Δt , the physical parameters $\beta(\mathbf{x})$ and $\mathbf{F}_{ex}(\mathbf{x})$ can be approximated as constant during Δt . In effect, there is the condition of a fixed 'configuration' over the averaging period, Δt , in which the increments $\Delta \mathbf{x}$ and $\Delta \mathbf{U}$ in position and velocity of a typical particle are given by

$$\Delta \mathbf{U} = -[\beta(\mathbf{x}) \cdot \mathbf{U} - \mathbf{F}_{ex}(\mathbf{x})] \Delta t + \int_t^{t+\Delta t} \mathbf{A}(s) ds \quad (10)$$

with $\Delta \mathbf{x} = \mathbf{U} \Delta t$. The integral in (10) represents the net acceleration that a Brownian particle may suffer during Δt due to the thermal agitations of surrounding molecules. We now assert that the invariance of the Maxwell-Boltzmann distribution requires that the probability of occurrence of different values for the net acceleration be governed by the Maxwell distribution function, and it allows that the transition-probability distribution $\Gamma(\mathbf{U}, \Delta \mathbf{U})$ is Maxwellian in terms of $\Delta \mathbf{U} + [\beta(\mathbf{x}) \cdot \mathbf{U} - \mathbf{F}_{ex}(\mathbf{x})] \Delta t$.

A conservative estimate of the length scales of variations in $\beta(\mathbf{x})$ and $\mathbf{F}_{ex}(\mathbf{x})$, i.e., l_β and l_f , respectively, which are allowable for (9) and (10) to be valid, can be obtained by using the Stokes resistance for a particle at large distances from the interface, β . The resulting condition for the fixed configuration is

$$l_\beta, l_f \gg \frac{\sqrt{\frac{\kappa_B T}{m}}}{\beta} \approx O(\sqrt{\langle \Delta \mathbf{x}^2 \rangle}). \quad (11)$$

For an extremely short-range interaction force $\mathbf{F}_{ex}(\mathbf{x})$, the condition (11) may not always be satisfied for the very small Brownian particles (i.e., large solute molecules), for which the mean-square displacements in the averaging time interval Δt can be quite large. If we adopt (10) and (11) a generalized Einstein-Smol-

uchowski equation governing the time evolution of the local number density $P(\mathbf{x})$ in the configuration space can be derived from the Liouville equation via the Fokker-Planck equation by averaging the probability distribution $P(\mathbf{U}, \mathbf{x})$ in the phase space over the time interval Δt satisfying the condition (7):

$$\frac{\partial P(\mathbf{x})}{\partial t} = \nabla \cdot [\mathbf{D}(\mathbf{x}) \cdot \nabla P(\mathbf{x}) - \mathbf{M}(\mathbf{x}) \cdot \mathbf{F}_{ex}(\mathbf{x}) P(\mathbf{x})] \quad (12)$$

in which the mobility and diffusivity tensors $\mathbf{M}(\mathbf{x})$ and $\mathbf{D}(\mathbf{x})$ refer to a torque-free particle and are related by (5). Thus, the simple Fickian form of the diffusion equation is obtained in the presence of a flat fluid-fluid interface under the conditions (7) and (11), and the diffusivity tensor can be calculated from a knowledge of the mobility tensor for steady motion of a freely rotating particle in the vicinity of a plane interface. In the next section, for an illustrative purpose, we evaluate the diffusion tensor for either spherical or elongated slender particles near a plane interface.

DISCUSSIONS

Equations of motion for a rigid particle of arbitrary shape in creeping flow can be expressed in general terms, provided the interface remains flat, by defining the so-called translational resistance tensor \mathbf{K}_T , the rotational resistance tensor \mathbf{K}_R , and the coupling tensor \mathbf{K}_C [15]. Two fundamental relations exist between the translational and rotational velocities and the force and torque in terms of these tensors:

$$\mathbf{F} = \mathbf{K}_T \cdot \mathbf{U} + \mathbf{K}_C^T \cdot \boldsymbol{\Omega} \quad (13a)$$

$$\mathbf{T} = \mathbf{K}_C \cdot \mathbf{U} + \mathbf{K}_R \cdot \boldsymbol{\Omega} \quad (13b)$$

where \mathbf{F} and \mathbf{T} are the total hydrodynamic force and torque, and \mathbf{U} and $\boldsymbol{\Omega}$ are the translational and rotational velocities, respectively. The various components of these tensors are intrinsic geometric properties of the particle and have already been determined for both a spherical and a slender rod-like particles [16, 17].

In accordance with the usual definition of mobility as the 'velocity' imparted to the particle per unit 'force', we are led to define a mobility tensor \mathbf{M} by means of the expression:

$$\mathbf{U} = \mathbf{M} \cdot \mathbf{F} \quad (14a)$$

where \mathbf{M} is given explicitly by

$$\mathbf{M} = [\mathbf{K}_T - \mathbf{K}_C^T \cdot \mathbf{K}_R^{-1} \cdot \mathbf{K}_C]^{-1} \quad (14b)$$

for a freely rotating torque-free particle.

On the basis of the Nernst-Planck-Einstein equation, it is natural to define a diffusivity tensor by the relation (5).

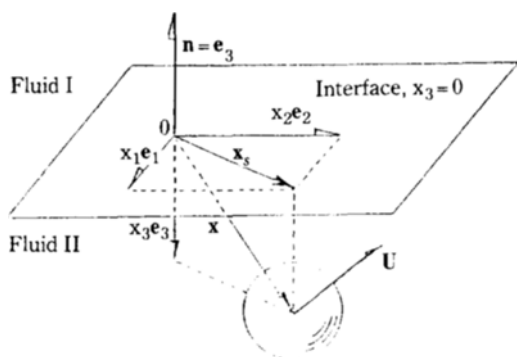


Fig. 1. Definition sketch for a planar interface. The instantaneous coordinates of the center of the Brownian sphere are $\mathbf{x}=(x_1, x_2, x_3)$ and the points lying in a plane parallel to the interface are conveniently represented by the planar position vector $\mathbf{x}_s = x_1\mathbf{e}_1 + x_2\mathbf{e}_2$.

$$\mathbf{D} = \kappa_B T \mathbf{M} = \kappa_B T [\mathbf{K}_T - \mathbf{K}_C^t \cdot \mathbf{K}_R^{-1} \cdot \mathbf{K}_C]^{-1} \quad (15)$$

For spherical particles, each component of the mobility tensor \mathbf{M} can be determined from the solution of Yang and Leal [17] and the diffusion tensor is thus given by

$$D = \begin{bmatrix} D_{11} & 0 & 0 \\ 0 & D_{22} & 0 \\ 0 & 0 & D_{33} \end{bmatrix} \quad (16a)$$

For a given coordinate system as in Figure 1, it is obvious that

$$D_{11} = D_{22} \quad (16b)$$

The components D_{ij} are functions of the particle position relative to the interface as a consequence of spatially modified mobility. In the case of spherically isotropic particles in an unbounded single-fluid domain, $\mathbf{K}_C = \mathbf{O}$, the present result (16) reduces to the conventional diffusivity tensor

$$\mathbf{D} = \frac{\kappa_B T}{6\pi\mu a} \mathbf{I} \quad (17)$$

where μ is the viscosity of the surrounding fluid, a is the sphere radius and \mathbf{I} denotes the identity factor. The diffusion tensor (17) has been shown to have the physical significance of real diffusivities.

In order to illustrate the qualitative nature of the hydrodynamic interaction effect, the components D_{11} and D_{33} based on the approximate singularity-method solution of Yang and Leal [17] are plotted in Figure 2 as a function of the distance d from the interface for $\lambda=0, 1$ and ∞ . The magnitude of diffusion coefficient, D_{11} , is either increased or decreased depending on the viscosity ratio λ owing to the presence of an interface.

It will be noted from Figure 2 that the effect is a strong function of the position relative to the interface arising from the spatial modification of hydrodynamic mobility. The decrease in the diffusivity coefficient D_{11} (or D_{22}) is established primarily as a consequence of the fact that a much more viscous fluid above the interface yields a small slip velocity on the interface and thus higher velocity gradient above the sphere than below it. The 'reversal' in the diffusivity coefficient when the upper fluid is much less viscous than the lower fluid results primarily from the existence of a substantial slip velocity on the interface, and a resultant velocity gradient above the sphere which is smaller than below. However, the diffusivity coefficient D_{33} is decreased relative to the unbounded case, even for $\lambda \rightarrow 0$ (i.e., free-surface boundary case), and this effect is due essentially to the kinematic condition (i.e., zero-normal velocity) at the interface.

For anisotropic particles (e.g., elongated slender particles), the mobility is, in general, dependent on the particle orientation relative to the interface in addition to the separation distance d between the particle center and the interface. The diffusivity tensor for elongated slender particles can be evaluated from the solution of Yang and Leal [16] who determined the hydrodynamic resistance tensors by means of the slender-body theory. In Figure 3, as an example of this orientation dependence, the diffusivity coefficient D_{11} of a slender rod-like particle with the length of axis $2l$, is illustrated as a function of the oblique angle θ between the body axis and the interface for two values of particle position $\frac{d}{l} = 1.01$ and 2. For each value of $\frac{d}{l}$, we

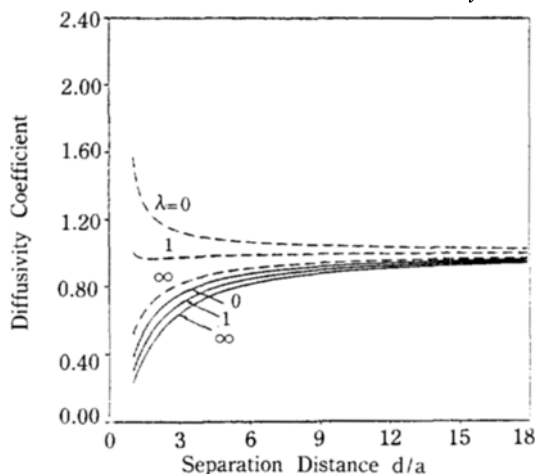


Fig. 2. Dimensionless diffusion coefficients, $\frac{D_{11}}{\kappa_B T / (6\pi\mu_2 a)}$ (or $\frac{D_{22}}{\kappa_B T / (6\pi\mu_2 a)}$) and $\frac{D_{33}}{\kappa_B T / (6\pi\mu_2 a)}$, as a function of the separation distance d/a ; ---, for D_{11} (or D_{22}); —, for D_{33} .

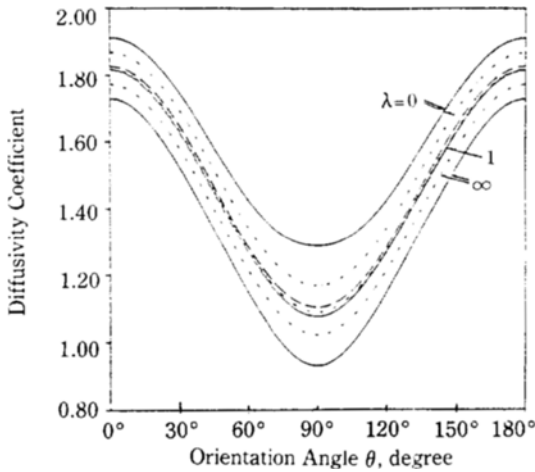


Fig. 3. Dimensionless diffusion coefficients, $\frac{D_{11}}{k_B T / (4\pi\mu l \epsilon)}$, as a function of the orientation angle θ ; the aspect ratio of the circular cylindrical slender body $\kappa = 100$ (i.e., $\epsilon = 0.1887$); —, for $d/l = 1.01$; ---, for $d/l = 2.0$; - · -, for an unbounded single fluid case.

include three values of the viscosity ratio, $\lambda = 0, 1$ and ∞ . Also shown is the corresponding result for diffusion in an unbounded single-fluid domain. The quantitative dependence of the diffusivity on the particle configuration (i.e., d and θ) relative to the interface is a consequence of the spatially modified and orientation-dependent hydrodynamic mobility due to the *direct* hydrodynamic interactions between the particle and the interface.

The instantaneous configuration of an anisotropic particle can be parametrized by six independent coordinates. Three of these are required to specify the position of the particle in physical space. The remaining three are needed to describe the orientation of the body relative to the interface. Accordingly, one must describe the diffusion phenomena in a six-dimensional space composed of these two distinct subspaces. In particular, for a slender rod-like particle, the rotational Brownian diffusion tensor can also be evaluated from the result of Yang and Leal [16] and is equal to

$$\mathbf{D}_R = \kappa_B T [\mathbf{K}_R - \mathbf{K}_C \cdot \mathbf{K}_T^{-1} \cdot \mathbf{K}_C^T]^{-1}. \quad (18)$$

Thus one could treat the Brownian diffusion of elongated slender particles by considering both the translational and the rotational Brownian motions which are coupled with each other.

This completes illustrative calculations of Brownian diffusion tensor in the vicinity of a flat interface utilizing the hydrodynamic solutions for Stokes flow. It is worth commenting that the scope of the present

analysis can be readily extended to investigate the effect of Brownian motion on the rheology of a dilute suspension of rigid particles in a linear shear or a pure straining flow.

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NOMENCLATURE

a	: sphere radius
\mathbf{A}	: random-fluctuation force
c	: number density of Brownian particles
\mathbf{D}	: translational diffusion tensor
\mathbf{D}_R	: rotational diffusion tensor
$\mathbf{F}_{ex}(\mathbf{x})$: physicochemical interaction force
$\mathbf{F}^{os}(\mathbf{x})$: thermodynamic force due to osmotic pressure
\mathbf{I}	: idemfactor
\mathbf{j}_D	: diffusion flux
\mathbf{K}_C	: coupling tensor
\mathbf{K}_R	: rotational resistance tensor
\mathbf{K}_T	: translational resistance tensor
l	: half-length of slender-body axis
l_b, l_f	: length scales of variations in $\beta(\mathbf{x})$ and $\mathbf{F}_{ex}(\mathbf{x})$
m	: particle mass
\mathbf{M}	: mobility tensor
P^{os}	: osmotic pressure
P	: probability distribution function
r_o	: radius of slender-body cross-section
t	: time variable
Δt	: averaging time interval
T	: absolute temperature
\mathbf{U}	: translational velocity
\mathbf{x}	: position vector
x_1, x_2, x_3	: Cartesian coordinate system
β	: hydrodynamic resistance tensor
$\bar{\beta}$: characteristic value of β
ϵ	: slenderness ration $[\ln 2\kappa]^{-1}$
Γ	: transition probability function
κ	: aspect ratio of slender particle $\frac{l}{r_o}$
κ_B	: Boltzmann constant
λ	: viscosity ratio of two fluids $\frac{\eta_1}{\eta_2}$
μ	: viscosity of fluid
Ω	: rotational velocity
τ_f	: molecular motion time scale
τ_{vp}	: viscous relaxation time scale
$\langle \rangle$: ensemble average

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