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Drag of a Solid Particle Trapped in a Thin Film or at an Interface: Influence of Surface Viscosity and Elasticity

Rumiana Dimova,[1],*,† Krassimir Danov,* Bernard Pouligny,† and Ivan B. Ivanov*

* *Laboratory of Thermodynamics and Physicochemical Hydrodynamics, Faculty of Chemistry, Sofia University, 1 J. Bouchier Avenue, 1126 Sofia, Bulgaria; and †Centre de recherche Paul-Pascal, CNRS, Avenue A. Schweitzer, 33600 Pessac, France*

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We propose a theoretical model for the motion of a spherical particle entrapped in a thin liquid film or in a monolayer of insoluble surfactant at the air/water interface. Both surface shear and dilational viscosity, surface diffusion, and elasticity of the film are taken into consideration. The drag force acting on the particle is analytically calculated and asymptotic expressions of the problem are provided. The relevance of the model is discussed by comparing the calculated "viscoelastic" drag, γ_{vel}, to the one predicted by Saffman's theory, γ_{S}, for cylindrical inclusions in membranes. Numerical analyses are performed to evaluate the contributions of the surface viscosity and the diffusion coefficient of the layer on the hydrodynamical resistance experienced by the particle. © 2000 Academic Press

Key Words: **particle motion; thin film; drag force; hydrodynamical resistance; surface viscosity; Gibbs elasticity; surface diffusivity.**

1. INTRODUCTION

The problem of the motion of a solid particle in a viscous elastic layer pertains to a large variety of systems such as biological membranes, foam and emulsion films, and monolayers of surface-active components. For instance, a protein in a membrane can be roughly modeled as a cylindrical inclusion in a continuous film. A theory for the motion of this body in a biological membrane was proposed by Saffman and Delbrück (1) and by Saffman (2). The theory was later generalized by Hughes *et al.* (3), Evans and Sackmann (4), and recently by Stone and Ajdari (5). Basically, Saffman computed the drag on a cylindrical particle undergoing translational and rotational motion in a model lipid bilayer. He showed that the viscosity, η, of the medium surrounding the particle had to be taken into account for the particle drag coefficient to be finite in the low Reynolds number regime (the convective term in the Navier–Stokes equation may be neglected). Applying a singular perturbation technique, Saffman (2) found an asymptotic solution of the problem in the limit of large membrane viscosity leading to an inverse logarithmic dependence of the resistance coefficient on the radius of the cylinder:

$$\zeta_{\mathrm{S}} \cong 4\pi\eta_{\mathrm{S}}\frac{1}{\ln(l_{\mathrm{S}}/a) - C}. \qquad [1]$$

In Eq. [1], η_{S} is the membrane shear surface viscosity (note that surface viscosity has units of [bulk viscosity × length] or surface poises, sP) and $l_{\mathrm{S}} = \eta_{\mathrm{S}}/\eta$ is a characteristic length which we will refer to as the "Saffman length". $C = 0.5772257$ is the Euler–Masceroni constant. Equation [1] is valid when a, the radius of the disk (the cylindrical inclusion), is definitely smaller than l_{S}. Subsequently, Hughes *et al.* (3) enlarged the region of validity of the solution up to large particle sizes.

Interestingly, the theory was experimentally tested from the observation of the Brownian motion of proteins in model membranes (6) and of circular solid lipid domains in a layer of fluid lipid (7, 8). Results were found to be in line with the theory of Hughes *et al.* (3).

In Saffmann's and related theories, the membrane is supposed to be an incompressible two-dimensional (2-d) fluid. This assumption is acceptable for artificial lipid membranes and biological membranes. Conversely, thin liquid films and, in general, monolayers of surface-active compounds differ from membranes in that they may be highly compressible. When a particle moves along the film, this provokes a compression and an expansion of the film ahead of and behind the particle, respectively. A surface tension gradient results, which creates a force acting against the particle motion. This force has its origin in the layer elasticity and may be termed "Marangoni". This process is counteracted by the surface diffusion of surfactant molecules, which tends to make the surface concentration uniform. Clearly, the elastic contribution to the particle friction will be small whenever the layer compressibility is small or when the surfactant diffusion is fast.

To summarize, we expect the particle drag coefficient to depend not only on the layer shear viscosity (η_{S}), but also on the dilational viscosity (η_{D}), the Gibbs elasticity (E), and the surfactant diffusion coefficient (D_{s}). Only η_{S} was taken into consideration in Refs. (1–5).

The physical systems of interest in this paper are dilute monolayers of surfactant molecules, or films made of two such

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[1] To whom correspondence should be addressed. Current address: Max-Planck-Institute for Colloids and Interfaces, Am Muehlenberg 2, 14476 Golm, Germany. Fax: 49-331-567-9612.

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monolayers separated by a slot of bulk fluid. As for the diffusion process, we will consider only surface diffusion, not the bulk diffusion (9). Strictly speaking, this restriction makes our model applicable only to films of insoluble surfactants. However, it may be extended to soluble surfactants, provided that the concentration is below the critical micellar concentration (10). The model is not applicable to membranes made of a pure lipid: in this case it is impossible to define a Marangoni effect and a collective diffusive mode of the surface-active molecules.

Danov *et al.* (11) addressed the problem of a sphere floating on a surfactant monolayer at the air/water interface, and numerically computed the particle drag coefficient with both η_S and η_D taken into account. The theory (which we will refer to as DADL) was designed to interpret data from experiments aimed at measuring film viscosities with spherical probes (12). DADL is relevant to systems with low surface viscosity. The surfactant diffusion has to be fast enough to suppress the effect of the gradient in the surface tension. Thus the main contribution to the friction is the surface viscosity.

A common and essential feature of Saffman's theory and of DADL is the role played by the 3-d fluid surrounding the film: the particle drag coefficient (either a cylinder or a sphere) explicitly depends on the 3-d fluid viscosity. In this article, we consider a film in contact with a medium of negligible viscosity, e.g., a vacuum, and a particle trapped across this film. Our model may be relevant, for instance, to explain the motion of spots in vertical foam films (13). As we will see, the particle drag coefficient (ζ) does take on a finite value in the general case when film elasticity, viscosity, and surface diffusion are taken into account. In other words, taking into consideration the above-mentioned Marangoni process leads to a finite drag force in the Stokes regime, though there is no dissipation in the surrounding bulk phases.

The paper is organized as follows. In Section 2, we set up the basic equations of our problem. The film/layer is modeled as a 2-d compressible fluid, whose density obeys a diffusion equation. We arrive at a set of equations for the vorticity and the divergence of the flow field, which are analytically solved in Section 3. We then compute the force acting on the particle, which is the sum of viscous and elastic parts. In Section 4, we thoroughly discuss the influences of the different film parameters on the particle drag. Particularly, we examine the relevance of our theory by comparing ζ to ζ_S, the drag coefficient in Saffman's theory for a cylinder of the same size. We find different regimes, which we tentatively relate to different examples of real systems. Section 5 is a conclusion.

2. MATHEMATICAL FORMULATION

The problem of an infinitely long cylinder moving inside an incompressible 3-d fluid leads to the well-known Oseen's paradox. The paradox comes from neglecting the convective term in the Navier–Stokes (NS) equation, an approximation that one might expect to be valid in the low velocity limit. One finds that a steady force applied to the cylinder gives an infinite velocity; no solution for the flow field is found that can satisfy the Stokes equation and the boundary conditions simultaneously (no-slip condition at the cylinder surface and zero flow velocity at infinity). To find a physically acceptable solution, it is necessary to solve the full NS equation, which is nonlinear. Lamb's approximation (14) for the convective term makes the problem tractable, and yields the following result:

$$F_O \cong 4\pi\eta V \frac{1}{\ln(l_O/a) + \frac{1}{2} - C}. \qquad [2]$$

In the above equation, F_O is the friction force per unit length of the cylinder. V is the cylinder velocity inside the 3-d fluid, and a is the cylinder radius. l_O, the Oseen length, is defined as $l_O = 4\eta/\rho V$. Here, ρ is the fluid mass density and η is its viscosity.

Saffman's and subsequent theories (1–5) address the problem of a disk moving in a film made of an incompressible fluid, e.g., a membrane. If the film is in vacuum, the problem is exactly the same as that of the cylinder in the (3-d) fluid. The analogy breaks down if the membrane is in contact with a viscous 3-d fluid. In this case, the motion of the disk can be described by the Stokes equation, taking into account the coupling to the surrounding fluid. This approach, developed by Saffman (2), yields Eq. [1] for the disk drag coefficient, ζ_S. Note that Saffman's equation has the same structure as the above Oseen's equation, but with a different characteristic length, l_S.

Since both inertia and coupling to an external viscous phase are present in real systems, it is important to guess which one influences most the particle drag. The question amounts to comparing l_O and l_S. The l_S/l_O ratio is simply equal to V/V^*, with $V^* = 4\sqrt{e}\eta/\rho_s$, $e = 2.718$. Here ρ_s is the film surface mass density. In the case of a lipid membrane in water, V^* is on the order of 10^5 cm/s, which is huge compared to practical particle velocities. This means that inertia has a negligible influence on the disk friction, and then that Saffman's result, Eq. [1], is the relevant one.

We now come to our problem. We consider a spherical particle, of radius a, which is trapped across a film (Fig. 1). By "film", we mean a slab of a viscoelastic fluid whose thickness is very small compared to a. In practice, the film can be a foam film (see Fig. 1a) or a surfactant monolayer at the water/air interface (see Fig. 1b). (The numerical results in Section 4 demonstrate that for reasonable values of the bulk phase viscosity, the bulk friction is negligible; thus the problem is pertinent as well for a particle moving along a water/air interface.) The portion of the particle in the plane of the film is a disk of radius a^*. The particle moves along the film in the y-direction, with velocity V. We suppose that the film is in a vacuum, which amounts to neglecting couplings of the flow field in the film with surrounding 3-d fluids. In this context, the portions of the particle on both sides of the film play no role; only the disk is important. For this reason, we will refer to the particle as a disk, whose radius will be denoted a, without loss of generality.

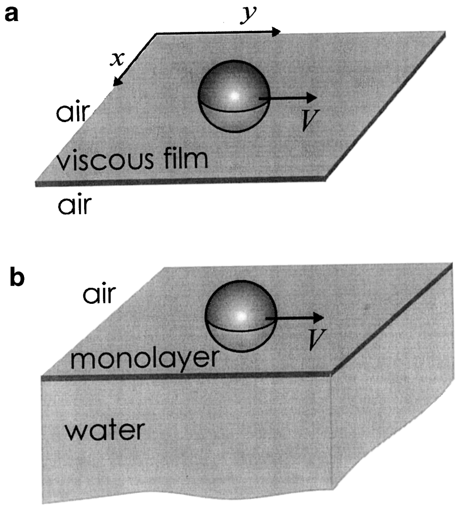

FIG. 1. Geometry of the system: (a) particle trapped in a viscous film; (b) particle floating on a monolayer at the air/water interface.

Since the thickness of the film is negligible, we apply a 2-d (membrane) approach. Our model is based on Scriven's equations for interfacial hydrodynamics (15). The equations govern the space–time evolution of surface–excess fields. For a stationary motion, the mass conservation equation and the interfacial NS equation read (16)

$$\nabla_{\mathrm{s}} \cdot (\rho_{\mathrm{s}} \mathbf{u}) = 0 \qquad [3]$$

$$\nabla_{\mathrm{s}} \cdot (\rho_{\mathrm{s}} \mathbf{u}\mathbf{u}) = \nabla_{\mathrm{s}} \sigma + \nabla_{\mathrm{s}} \cdot \mathbf{T}. \qquad [4]$$

In Eqs. [3] and [4] ∇_{s} denotes the surface gradient, ρ_{s} is the total surface–excess mass density, $\mathbf{u}$ is the average mass velocity at the surface, σ is the thermodynamic surface tension, and $\mathbf{T}$ is the surface viscosity tensor. In Eq. [4] we omit a term which is related to the pressure jump occurring when crossing an interface between two continuous phases. In Appendix A we justify this approximation.

We suppose that the film fluid is Newtonian and that the surface viscosity tensor is related to the flow by the Boussinesq–Scriven constitutive law (15):

$$\mathbf{T} = (\eta_{\mathrm{D}} - \eta_{\mathrm{S}})(\nabla_{\mathrm{s}} \cdot \mathbf{u})\mathbf{I} + \eta_{\mathrm{S}} \left\lfloor (\nabla_{\mathrm{s}} \mathbf{u}) \cdot \mathbf{I} + \mathbf{I} \cdot (\nabla_{\mathrm{s}} \mathbf{u})^{\mathrm{T}} \right\rfloor. \qquad [5]$$

Here, η_{D} and η_{S} are the interfacial dilational and shear surface viscosities, respectively. They are supposed to be constant. $\mathbf{I}$ is the unit surface idemfactor and $(\nabla_{\mathrm{s}} \mathbf{u})^{\mathrm{T}}$ is the conjugate of the $\nabla_{\mathrm{s}} \mathbf{u}$ tensor.

We are interested in interfacial films, i.e., systems involving a liquid whose interfacial tension is modified by the adsorption of surface-active molecules. This is the source of the Marangoni effect. We simply suppose that the gradient in σ is proportional to the gradient in Γ, the surface–excess mass density of the surfactant:

$$\nabla_{\mathrm{s}} \sigma = -\left(\frac{E}{\Gamma_0}\right) \nabla_{\mathrm{s}} \Gamma. \qquad [6]$$

$E = -\partial\sigma/\partial \ln \Gamma$ is the film Gibbs elasticity, which will be supposed to be constant. Γ_0 is the unperturbed (equilibrium) surface concentration.

The above system of equations is closed by the mass balance equation for the surface-active compound:

$$\nabla_{\mathrm{s}} \cdot (\Gamma \mathbf{u} - D_{\mathrm{s}} \nabla_{\mathrm{s}} \Gamma) = 0. \qquad [7]$$

D_{s}, which we suppose to be constant, is the surfactant surface diffusion coefficient. Note that Eq. [7] is valid only for small perturbations, i.e., when Γ remains close to Γ_0. As we comment in Appendix B, this condition is fulfilled only when the particle velocity is small enough. Quantitatively, this implies that the surface Peclet number, $Pe = Va/D_{\mathrm{s}}$, is $\ll 1$.

We define polar coordinates, (r, ϕ), in the plane of the layer, with the origin set at the center of the particle and $\phi = 0$ taken along the x axis. The polar components of the velocity vector are u_r and u_ϕ.

If we take into account the inertia term in Oseen's manner, the substitution of the surface viscosity tensor, $\mathbf{T}$, from Eq. [5] into Eq. [4] yields the following system of second-order differential equations:

$$\begin{aligned}
&(\eta_{\mathrm{D}} + \eta_{\mathrm{S}}) \frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}(r u_r) + \frac{1}{r}\frac{\partial u_\phi}{\partial \phi}\right] \\
&\quad - \frac{\eta_{\mathrm{S}}}{r}\frac{\partial}{\partial \phi}\left[\frac{1}{r}\frac{\partial}{\partial r}(r u_\phi) - \frac{1}{r}\frac{\partial u_r}{\partial \phi}\right] + \frac{\partial \sigma}{\partial r} \\
&\quad - \rho_{\mathrm{s}} V \left(\sin\phi \frac{\partial u_r}{\partial r} + \frac{\cos\phi}{r}\frac{\partial u_r}{\partial \phi} - \frac{\cos\phi}{r} u_\phi\right) = 0 \\
&(\eta_{\mathrm{D}} + \eta_{\mathrm{S}}) \frac{1}{r}\frac{\partial}{\partial \phi}\left[\frac{1}{r}\frac{\partial}{\partial r}(r u_r) + \frac{1}{r}\frac{\partial u_\phi}{\partial \phi}\right] \\
&\quad + \eta_{\mathrm{S}} \frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}(r u_\phi) - \frac{1}{r}\frac{\partial u_r}{\partial \phi}\right] + \frac{1}{r}\frac{\partial \sigma}{\partial \phi} \\
&\quad - \rho_{\mathrm{s}} V \left(\sin\phi \frac{\partial u_\phi}{\partial r} + \frac{\cos\phi}{r}\frac{\partial u_\phi}{\partial \phi} + \frac{\cos\phi}{r} u_r\right) = 0.
\end{aligned} \qquad [8]$$

We suppose that the fluid does not slip along the particle surface and that the particle does not perturb the flow field at infinity. Then, for a snapshot of the velocity profile:

$$u_r = V \sin\phi, \quad u_\phi = V \cos\phi \quad \text{at } r = a \qquad [9]$$

$$u_r \xrightarrow[r \to \infty]{} 0, \quad u_\phi \xrightarrow[r \to \infty]{} 0. \qquad [10]$$

Below we apply methods developed for 2-d flow problems (17).

We introduce the vorticity and stream functions, defined as

$$w = \frac{1}{r}\frac{\partial(ru_\phi)}{\partial r} - \frac{1}{r}\frac{\partial u_r}{\partial \phi}, \quad \alpha = \frac{1}{r}\frac{\partial(ru_r)}{\partial r} + \frac{1}{r}\frac{\partial u_\phi}{\partial \phi}. \qquad [11]$$

It is convenient to define dimensionless fields,

$$\begin{gathered} u_r = V\tilde{u}_r, \quad u_\phi = V\tilde{u}_\phi, \\ w = \frac{V}{a}\tilde{w}, \quad \alpha = \frac{V}{a}\tilde{\alpha}, \quad \sigma = \frac{\eta_D + \eta_S}{a}V\tilde{\sigma}, \end{gathered} \qquad [12]$$

and dimensionless parameters,

$$p \equiv \frac{\eta_S}{\eta_D + \eta_S}, \quad m \equiv \frac{\rho_s V a}{\eta_D + \eta_S}, \quad q \equiv \frac{Ea^2}{D_s(\eta_D + \eta_S)}. \qquad [13]$$

p represents the importance of shear viscosity relative to the total viscosity. m is the surface Reynolds number. q may be viewed as the ratio of elastic to viscous forces. Note that $1/\sqrt{q} = l_{\text{vel}}/a$, where l_{vel} is a new characteristic length, namely the "visco-elastic" length, defined by

$$l_{\text{vel}}^2 = \frac{D_s(\eta_D + \eta_S)}{E}. \qquad [14]$$

Let us define $z \equiv r/a$. Substitution of Eqs. [12] and [13] in Eq. [8] brings forth

$$\begin{aligned} &\frac{\partial\tilde{\alpha}}{\partial z} - \frac{p}{z}\frac{\partial\tilde{w}}{\partial\phi} + \frac{\partial\tilde{\sigma}}{\partial z} \\ &\quad - m\left(\sin\phi\frac{\partial\tilde{u}_r}{\partial z} + \frac{\cos\phi}{z}\frac{\partial\tilde{u}_r}{\partial\phi} - \frac{\cos\phi}{z}\tilde{u}_\phi\right) = 0 \\ &\frac{1}{z}\frac{\partial\tilde{\alpha}}{\partial\phi} + p\frac{\partial\tilde{w}}{\partial z} + \frac{1}{z}\frac{\partial\tilde{\sigma}}{\partial\phi} \\ &\quad - m\left(\sin\phi\frac{\partial\tilde{u}_\phi}{\partial z} + \frac{\cos\phi}{z}\frac{\partial\tilde{u}_\phi}{\partial\phi} + \frac{\cos\phi}{z}\tilde{u}_r\right) = 0. \end{aligned} \qquad [15]$$

Equation [15] is the scaled NS equation in Oseen's approximation. The scaled mass balance equation (Eq. [7]) reads

$$\tilde{\alpha} - \frac{1}{q}\widetilde{\Delta_s\Gamma} = 0 \qquad [16]$$

In Eq. [16], Δ_s is the Laplace surface operator. $\widetilde{\Delta_s\Gamma}$ is defined through $\Delta_s\Gamma \equiv [(\eta_D + \eta_S)/a^3E]V\Gamma_0\widetilde{\Delta_s\Gamma}$.

3. SOLUTION TO THE PROBLEM

In real systems, m is usually very small compared to unity, which incites us to neglect the inertial term in the NS equation (Eq. [15]). In the case of an incompressible film (infinite E), this approximation results in Oseen's paradox, as we already mentioned. p is <1. If we assume that $\eta_D < \eta_S$, as reported experimental values suggest, p cannot be less than $1/2$. Consequently the vorticity term in Eq. [15] is always important. As we will see in the analysis of real systems, q can be either large or small, and then different limits must be discussed.

3.1. Incompressible Films

When q is very large ($q \gg 1$), the divergence α is zero: this is the limit of an incompressible fluid. From the definition, Eq. [13], large values of q are favored by large particle sizes, high film elasticities, small surface viscosities of the layer, and small diffusion coefficients.

The q-infinite limit brings us back to the Oseen problem and leads to Eq. [2] for the friction force. As we already commented, the Oseen result for the drag coefficient is not the physically relevant one in this case because the viscosity of the surrounding 3-d phase cannot be ignored. In other words, the real drag coefficient is that given by the Saffman–Hughes theory rather than by the Oseen equation.

3.2. Analytical Solution for a Film/Monolayer

In this section, we will concentrate on the situation in which q is not very large. Small q suggests low elasticity, high surface viscosity of the layer, fast diffusion, and/or small particle size. With foam films stabilized by different surface-active molecules (see Refs. 10 and 16 and references therein), E may vary from 0.005 to 0.02 N/m, D_s from 1×10^{-10} to 7×10^{-9} m^2/s, and the surface viscosity from about 10^{-8} to 10^{-3} N s/m (for films stabilized by proteins, surface viscosity may be up to 2 N s/m, see Refs. 18 and 19). Thus, l_{vel} varies between about 10 and 50 mm. One can then realize experimental conditions corresponding to $q \cong 1$ with particle sizes in this range.

As we recalled in the Introduction, in the case of an inclusion inside an incompressible film or membrane in a vacuum, the convective term in the NS equation cannot be neglected. When the film is compressible, as we will now see, the problem has an analytical solution even for $m = 0$, i.e., when the convective acceleration term in the NS equation vanishes. The system of differential equations to be solved is

$$\begin{gathered} \frac{\partial\tilde{\alpha}}{\partial z} - \frac{p}{z}\frac{\partial\tilde{w}}{\partial\phi} + \frac{\partial\tilde{\sigma}}{\partial z} = 0 \\ \frac{1}{z}\frac{\partial\tilde{\alpha}}{\partial\phi} + p\frac{\partial\tilde{w}}{\partial z} + \frac{1}{z}\frac{\partial\tilde{\sigma}}{\partial\phi} = 0. \end{gathered} \qquad [17]$$

Eliminating the divergence provides an equation for the vorticity,

$$\frac{1}{z}\frac{\partial}{\partial z}\left(z\frac{\partial\tilde{w}}{\partial z}\right) + \frac{1}{z^2}\frac{\partial^2\tilde{w}}{\partial\phi^2} = 0, \qquad [18]$$

whose solution is

$$\tilde{w} = \frac{A'}{z}\cos\phi, \qquad [19]$$

A' being an arbitrary constant. Correspondingly, the equation for the divergence is obtained from Eqs. [6], [16], and [17]:

$$z^2\frac{\partial^2\tilde{\alpha}}{\partial z^2}+z\frac{\partial\tilde{\alpha}}{\partial z}-(qz^2+1)\tilde{\alpha}=0. \qquad [20]$$

The solution of Eq. [20] can be put as

$$\tilde{\alpha}=BK_1(\sqrt{q}z)\sin\phi, \qquad [21]$$

where K_1 is the modified Bessel function of first order. B is a constant to be determined from the boundary conditions (Eq. [9]).

The geometry of the problem (see Eq. [8] and the linearized boundary conditions [9] and [10]) allows us to decouple the z and ϕ components in the velocity field according to

$$\tilde{u}_r=\sin\phi\, R(z), \quad \tilde{u}_\phi=\cos\phi\,\Phi(z). \qquad [22]$$

From Eqs. [11], [19], [21], and [22] we obtain

$$\begin{aligned} BK_1(\sqrt{q}z)&=\frac{1}{z}\frac{\partial}{\partial z}(zR)-\frac{\Phi}{z}\\ A'&=\frac{\partial}{\partial z}(z\Phi)-R. \end{aligned} \qquad [23]$$

In terms of the functions R and Φ, the boundary conditions become

$$R(1)=1, \quad \Phi(1)=1 \quad \text{at } z=1 \qquad [24]$$

$$R(z)\xrightarrow[z\to\infty]{}0, \quad \Phi(z)\xrightarrow[z\to\infty]{}0. \qquad [25]$$

The constant A' is determined from the condition for zero velocity at infinity: $A'=0$. This result, combined with Eq. [19], shows that the vorticity is zero ($w=0$), which implies that we have a nonrotational (potential) motion.

Elimination of R in Eq. [23] yields an equation for Φ:

$$z\frac{\partial^2\Phi}{\partial z^2}+3\frac{\partial\Phi}{\partial z}=BK_1(\sqrt{q}z). \qquad [26]$$

The solution for Φ is a superposition of the solution to the homogeneous equation, A/z^2, where A is an arbitrary constant, and any partial solution to Eq. [26], e.g. $(B/qz)K_1(\sqrt{q}z)$. Thus, the resulting expressions for $R(z)$ and $\Phi(z)$ are

$$R(z)=-\frac{A}{z^2}+\frac{B}{q}\frac{d}{dz}[K_1(\sqrt{q}z)] \qquad [27]$$

$$\Phi(z)=\frac{A}{z^2}+\frac{B}{qz}K_1(\sqrt{q}z). \qquad [28]$$

From the boundary conditions [24] and [25], the constants A and B are determined as

$$A=1+\frac{2K_1(\sqrt{q})}{\sqrt{q}K_0(\sqrt{q})}, \quad B=-\frac{2\sqrt{q}}{K_0(\sqrt{q})}. \qquad [29]$$

Here, K_0 is the modified Bessel function of zeroth order. Finally, the explicit expressions for $R(z)$ and $\Phi(z)$ are

$$\begin{aligned} R(z)=-\frac{1}{z^2}&+\frac{2}{\sqrt{q}K_0(\sqrt{q})}\\ &\times\left[\sqrt{q}K_0(\sqrt{q}z)+\frac{K_1(\sqrt{q}z)}{z}-\frac{K_1(\sqrt{q})}{z^2}\right] \end{aligned} \qquad [30]$$

$$\Phi(z)=\frac{1}{z^2}+\frac{2}{\sqrt{q}K_0(\sqrt{q})}\left[\frac{K_1(\sqrt{q})}{z^2}-\frac{K_1(\sqrt{q}z)}{z}\right]. \qquad [31]$$

This result, combined with Eq. [22], gives the flow field everywhere in the film.

The general form of the drag force exerted on the moving particle by the surrounding layer is a superposition of two terms, a viscous one and an elastic one: $F=F_{\text{visc}}+F_{\text{el}}$. The viscous contribution may be obtained by integration of the tangential part of the surface viscosity tensor, $\mathbf{T}$ (see Eq. [5]), along the friction contour. We find

$$F_{\text{visc}}=2\pi V(\eta_{\text{D}}+\eta_{\text{S}})\frac{\sqrt{q}K_1(\sqrt{q})}{K_0(\sqrt{q})}. \qquad [32]$$

The elastic or "Marangoni" part of the drag force is given by

$$F_{\text{el}}=-\int_0^{2\pi}(\sigma-\sigma_0)\sin\phi\, a\, d\phi\bigg|_{z=1}. \qquad [33]$$

In Eq. [33], σ_0 is the film surface tension at equilibrium ($V=0$). $\sigma-\sigma_0$ as a function of ϕ and z can be readily found from Eqs. [17], [21], and [29] (details are given in Appendix B). We find

$$F_{\text{el}}=2\pi\frac{Ea^2V}{D_{\text{s}}}. \qquad [34]$$

Thus, the final expression for the drag force for a particle floating across a viscous layer is

$$F=2\pi V(\eta_{\text{D}}+\eta_{\text{S}})\left[\frac{\sqrt{q}K_1(\sqrt{q})}{K_0(\sqrt{q})}+q\right]. \qquad [35]$$

Basically, this result holds for a particle across an interfacial viscoelastic layer characterized by, e.g., $\eta_{\text{D}}+\eta_{\text{S}}$ and q. In the case of a particle across a soap film, with two such layers, we expect the friction force to be just twice that given by Eq. [35] (see Appendix A for arguments).

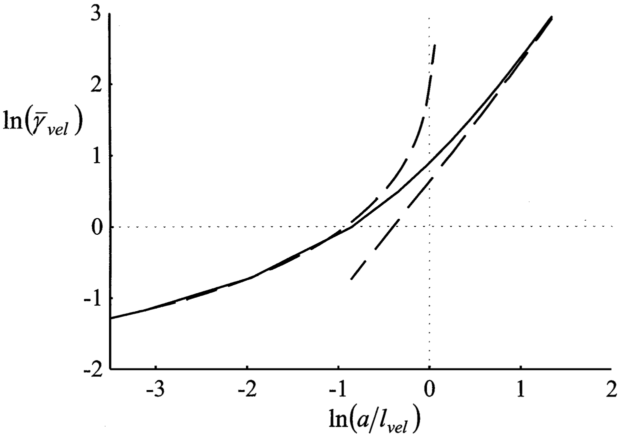

FIG. 2. Log–log plot of the reduced viscoelastic coefficient, $\bar{\gamma}_{\mathrm{vel}}$, as a function of a/l_{vel}. The solid line shows the exact solution, Eq. [35]. The dashed lines represent the asymptotic expressions for small (Eq. [36]) and large (Eq. [36]) values of a/l_{vel}.

The friction coefficients in Oseen's and Saffman's formulas are given as functions of the reduced lengths a/l_{O} and a/l_{S}, respectively. Similarly, our result, Eq. [35], can be expressed as a function of $\sqrt{q} = a/l_{\mathrm{vel}}$, where l_{vel} is the length defined by Eq. [14]. As examples of how either small or large values of q can be found with real systems, corresponding to either $a \ll l_{\mathrm{vel}}$ or $a \gg l_{\mathrm{vel}}$, it is useful to derive asymptotic forms of Eq. [35]. Using known asymptotic expansions of the K_0 and K_1 functions (20), we find

$$F = 2\pi V(\eta_{\mathrm{D}} + \eta_{\mathrm{S}})\left(q + \sqrt{q} - \frac{1}{8}\right) \qquad [36]$$

for “large” particles ($q \gg 1$), and

$$F = 2\pi V(\eta_{\mathrm{D}} + \eta_{\mathrm{S}})\left(\frac{q}{2} + \frac{C(q/2) - 1}{\ln(\sqrt{q}/2) + C}\right) \qquad [37]$$

for “small” particles ($q \ll 1$).

Let us define the particle drag coefficient, γ_{vel}, by $F = \gamma_{\mathrm{vel}} V$ and the dimensionless coefficient $\bar{\gamma}_{\mathrm{vel}} = \gamma_{\mathrm{vel}}/2\pi(\eta_{\mathrm{D}} + \eta_{\mathrm{S}})$. Figure 2 shows $\bar{\gamma}_{\mathrm{vel}}$ versus $\sqrt{q} = a/l_{\mathrm{vel}}$ in log–log representation. The solid line corresponds to Eq. [35], while the right and left dotted lines correspond to Eqs. [36] and [37], respectively. For $a/l_{\mathrm{vel}} \geq 2.9$, Eq. [36] is valid to within 5%. This is so with Eq. [37] whenever $a/l_{\mathrm{vel}} \leq 0.4$.

4. NUMERICAL ANALYSIS AND DISCUSSION

We start the discussion with a criticism about the relevance of our model. We supposed that our film was in a “vacuum”, while real systems are obviously in contact with 3-d fluids. It is essential to determine whether neglecting the coupling to the 3-d fluids is legitimate or not. This question can be answered in the most general way only from the general theory, where both film elasticity and coupling to outer fluids are taken into account. As this theory is not available, all what we can do is to compare the friction force given by Eq. [35] to that of Saffman, Eq. [1]. If we find that the former is much larger than the latter, that means that the membrane elasticity is more important than the viscosity of the bulk fluids in determining the particle friction. If this is so, our model is relevant.

γ has a Saffman limit, γ_{S} (given by Eq. [1]), and a viscoelastic limit, γ_{vel} (given by Eq. [35]). We slightly simplify the discussion by supposing $\eta_{\mathrm{D}} = \eta_{\mathrm{S}}$; then the reduced coefficient reads $\bar{\gamma} = \gamma/(4\pi\eta_{\mathrm{S}})$. The reduced Saffman coefficient, $\bar{\gamma}_{\mathrm{S}}$, is a function of a/l_{S}. Similarly, $\bar{\gamma}_{\mathrm{vel}}$ is a function of a/l_{vel}, where l_{vel}, the viscoelastic length, is given by Eq. [14]. Both functions are shown in Fig. 3, in log–log representation. The graph in Fig. 3a is based on the theory of Hughes *et al.* (3), in order to include both the $a < l_{\mathrm{S}}$ regime (Eq. [1]) and the large size regime ($a \gg l_{\mathrm{S}}$). Comparing $\bar{\gamma}_{\mathrm{S}}$ and $\bar{\gamma}_{\mathrm{vel}}$ is just a matter of superposing the two graphs. In the superposition, the graph of Fig. 3a has to be moved to the left if $l_{\mathrm{vel}} > l_{\mathrm{S}}$, and to the right in the opposite case. With this procedure, we immediately see that $\gamma_{\mathrm{vel}} > \gamma_{\mathrm{S}}$ when $l_{\mathrm{vel}} < l_{\mathrm{S}}$, whatever the particle size. In this situation, the particle friction is primarily influenced by the membrane viscoelasticity. Conversely, when $l_{\mathrm{vel}} > l_{\mathrm{S}}$, we find two regimes, separated by

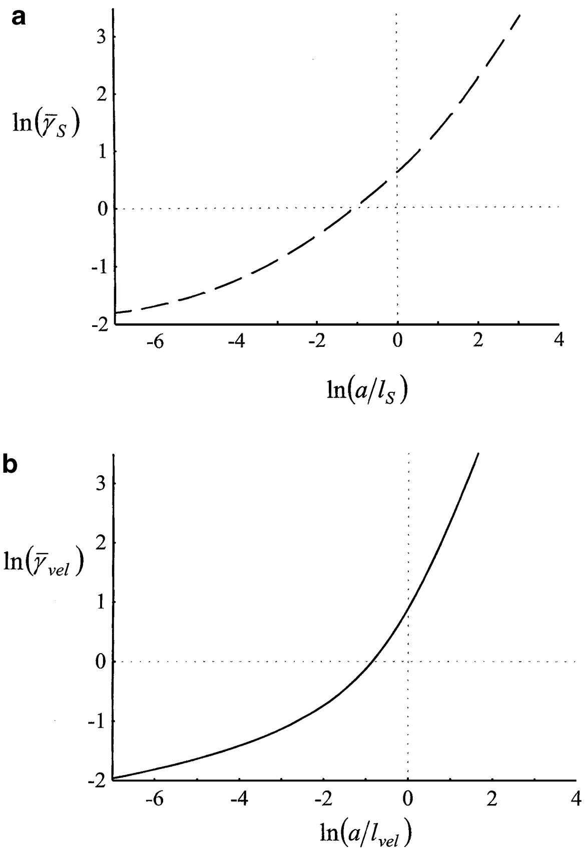

FIG. 3. (a) Log–log plot of the reduced Saffman coefficient, $\bar{\gamma}_{\mathrm{S}}$, as a function of a/l_{S}; calculations are based on the theory of Hughes *et al.* (3). (b) Log–log plot of the reduced viscoelastic coefficient, $\bar{\gamma}_{\mathrm{vel}}$, as a function of a/l_{vel}.

a crossover particle size, $a_{\mathrm{co}} \cong l_{\mathrm{vel}}^2 / l_{\mathrm{S}}$. If the particle is "small", $a < a_{\mathrm{co}}$, the friction is of the Saffman type, i.e., mostly due to the coupling to the 3-d fluids. If $a > a_{\mathrm{co}}$, the viscoelasticity mechanism dominates (provided that the surface Peclet number remains small, as we explained).

Let us now illustrate these considerations on examples of real systems. Literature data on foam films (or monolayers) (18, 19, 21) give $10^{-8} < \eta_{\mathrm{S}} < 10^{-3}$ N s/m, $5 \times 10^{-3} < E < 2 \times 10^{-2}$ N/m, $1 \times 10^{-10} < D_{\mathrm{s}} < 7 \times 10^{-9}\mathrm{m}^2/\mathrm{s}$. These films usually are in air, the viscosity of which is about 2×10^{-5} N s/m^{-2}. We thus find $10^{-8} < l_{\mathrm{vel}} < 10^{-4}$ m and $10^{-3} < l_{\mathrm{S}} < 10^2$ m, roughly. It is then clear that $l_{\mathrm{vel}} < l_{\mathrm{S}}$, which means that our description, based on viscoelasticity, is relevant for foam films.

Henceforth, we investigated the influence of the different factors governing the hydrodynamical resistance experienced by the particle. The range of values for the parameters in the model is wide depending on the type of the surfactant stabilizing the film, its chemical structure, and its concentration (18, 19, 21, 22) (see also (16)). The shear and the dilational viscosities enter the expression for the drag force as a sum. Thus, the effects of each of them cannot be discussed separately. For many systems, the data reported in the literature demonstrate that the two parameters are of the same order of magnitude. Only for biological membranes may they exhibit a difference of several orders of magnitude (usually the shear viscosity is the larger one). The effect of the layer viscosity on γ is presented in Fig. 4, where γ is displayed as a function of the particle radius, a, for different surface viscosities. As one can expect, the larger the viscosity, the higher the drag coefficient.

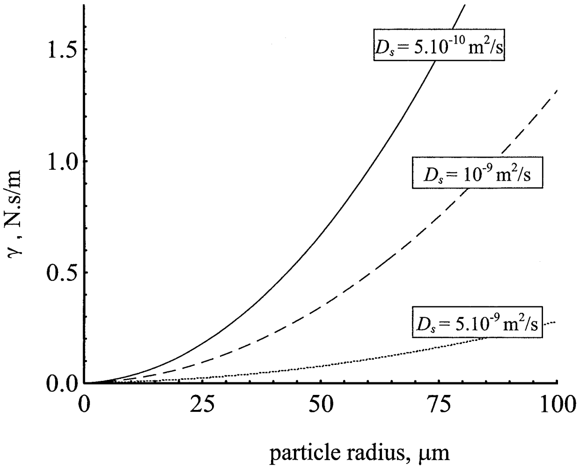

FIG. 5. Effect of surface diffusion on hydrodynamical resistance. Calculations are performed for $E = 0.02$ N/m, $\eta_{\mathrm{D}} = \eta_{\mathrm{S}} = 2 \times 10^{-4}$ N s/m. The solid line corresponds to the calculated value of γ for $D_{\mathrm{s}} = 5 \times 10^{-10}$ m^2/s; the dashed line is for $D_{\mathrm{s}} = 1 \times 10^{-9}$ m^2/s; the dotted line is for $D_{\mathrm{s}} = 5 \times 10^{-9}$ m^2/s.

The effect of the surface diffusion coefficient is illustrated in Fig. 5. Indirect experimental approaches provide estimates for D_{s} on the order of 10^{-9} m^2/s and even 10^{-8} m^2/s for films stabilized by fatty acids (10). Low values for D_{s} are found with films stabilized by mixtures of surfactant and proteins as reported in (18). For layers of phospholipids, D_{s} can be on the order of 10^{-12} m^2/s as indicated in (22–24). In Fig. 5, D_{s} is varied between 5×10^{-10} and 5×10^{-9} m^2/s. Obviously, for low values of D_{s}, the motion of the particle will be hindered by the low mobility of the molecules composing the layer, as Fig. 5 demonstrates.

Figures 4 and 5 showed the influences of the viscosity and surface diffusivity, considered as independent parameters. In real systems, η_{D}, η_{S}, D_{s} and E do not vary independently. The usual experimental variable is the surface area per surfactant molecule, $A = 1/\Gamma$. We do not know of experimental data simultaneously giving the values of η_{D}, η_{S}, D_{s}, and E as a function of A.

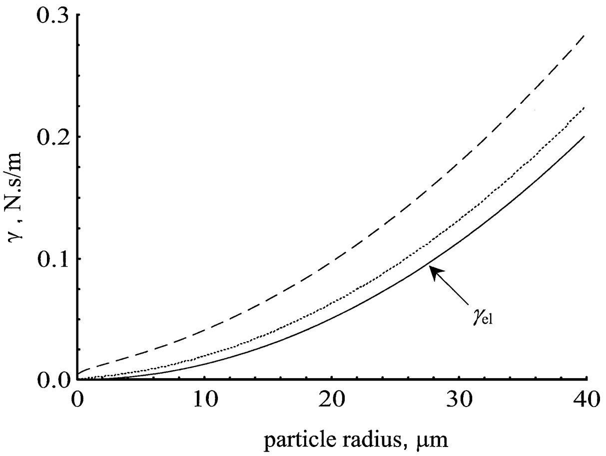

FIG. 4. Effect of surface viscosity on hydrodynamical resistance. Calculations are done for $D_{\mathrm{s}} = 10^{-9}$ m^2/s and $E = 0.02$ N/m. The dashed line represents the drag coefficient, γ, for $\eta_{\mathrm{D}} = \eta_{\mathrm{S}} = 2 \times 10^{-3}$ N s/m; the dotted line is for 2×10^{-4} N s/m. The lowest curve (solid line) corresponds to the results for the elastic or "Marangoni" part of the drag coefficient, γ_{el} ($F_{\mathrm{el}} = \gamma_{\mathrm{el}} V$).

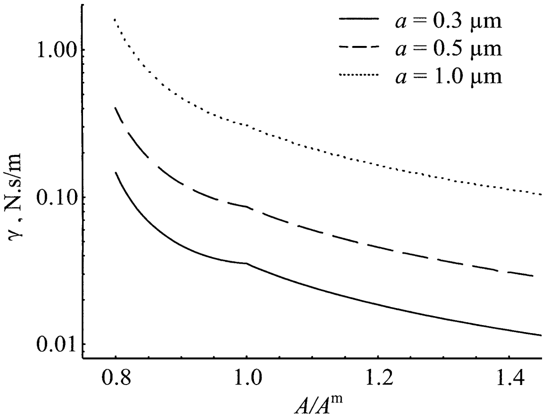

FIG. 6. Dependence of the resistance coefficient on the scaled surface area per molecule, A/A^{m}, for different particle sizes, a. The solid line corresponds to $a = 0.3$ μm, the dashed line to $a = 0.5$ μm, and the dotted line to $a = 1$ μm. The surface viscosity dependence on adsorption is taken from experimental data reported in (25). Elasticity is estimated according to the Langmuir isotherm. Calculations are done for $D_{\mathrm{s}} = 1 \times 10^{-9}$ m^2/s.

Nevertheless, we tentatively estimated the variation of γ versus A in the case of arachidic acid films, for which an ($\eta_D + \eta_S$, A) graph is available (25). We supposed that E followed the Langmuir equation, $E = k_B T \Gamma/(1 - \Gamma/\Gamma_\infty)$, where $k_B T$ is the thermal energy and Γ_∞ is the surface concentration corresponding to full packing ($A^m = 1/\Gamma_\infty = 20$ Å^2/molecule). D_s does not vary very much with A. We took D_s to be constant, with no better reason than simplicity. Doing so, we arrived at the curves displayed in Fig. 6 for three different particle sizes. As one might expect, γ monotonically decreases when A increases. Nevertheless, the curves slightly bend up around an intermediate value of A. This feature is caused by an anomaly in the total viscosity (η_{tot}), which, according to Ref. (25), reaches a maximum not at full packing but at $A^m \cong 25$ Å^2/molecule. Note that the anomaly is more visible with small particles than with large ones.

5. CONCLUSIONS

We compute the drag force felt by a particle moving along a surfactant film. We considered compressible films, in which the surfactant surface concentration is locally modified by the particle motion. In our model, the film properties were defined by a compression modulus, E, surface viscosities η_D and η_S, and a surfactant difusion coefficient, D_s. We calculated the particle drag coefficient, γ, in the limit when coupling to the bulk fluids on both sides on the film is negligible. We found that γ would take on finite values, provided that E is finite.

This result is in contrast with that given by Saffman's theory (1–3) for incompressible films, in which coupling to the bulk fluids is essential.

We discussed the relevance of our model in the general situation, in which both surface elasticity and coupling to the outer fluids are present. We found that elasticity was essential whenever the viscoelastic length, defined by Eq. [14], was smaller than Saffman's viscous length. In practice, this kind of situation might exist, for instance, with foam films in air. Thus, the theory is open to experimental check with real systems.

APPENDIX A: DISCUSSION ON THE MODEL EQUATIONS

At any interface between two contiguous bulk phases, one always has a "jump" in the generic tensor fields. The pressure jump which is to appear when crossing, for example, an air/water interface would bring in the equation for the momentum transport (Eq. [4]) an additional term, i.e., $\langle \mathbf{P} \rangle \cdot \mathbf{n}$, where $\mathbf{P}$ is the pressure tensor and $\mathbf{n}$ is the unit normal to the surface (on each surface of the film, Fig. 1a, or at the monolayer surface, Fig. 1b, $\mathbf{n}$ is pointing out to the air phase). The general approach to estimate this term for a thin liquid film is to employ the lubrication approximation, provided that the film thickness is much smaller than the particle size and that the motion is characterized by a low Reynolds number. This implies that the normal pressure derivative is zero, and one may write

$$-\nabla_\parallel P + \eta \frac{d^2 \mathbf{v}_\parallel}{d\zeta^2} = 0, \qquad \text{[A1]}$$

where $\nabla_\parallel P$ is the lateral local pressure gradient, η is the bulk viscosity of the fluid, $\mathbf{v}_\parallel$ is the lateral component of the fluid velocity, and ζ is the normal coordinate. Solving Eq. [A1] provides

$$\mathbf{v}_\parallel = \frac{1}{2\eta} \nabla_\parallel P \left[\zeta^2 - \left(\frac{h}{2} \right)^2 \right] + \mathbf{u}, \qquad \text{[A2]}$$

where h is the film thickness and $\mathbf{u}$ is the surface velocity as defined in Eq. [4]. Correspondingly, for the pressure jump term one finds

$$\langle \mathbf{P} \rangle \cdot \mathbf{n} = \frac{h}{2} \nabla_\parallel P. \qquad \text{[A3]}$$

On the other hand, for a flat surface we have a constant pressure, $P = \text{const}$. Therefore, we find $\langle \mathbf{P} \rangle \cdot \mathbf{n} = 0$, and using Eq. [4] is appropriate. At the same time, for small *Pe* numbers, the surfactant concentration profile in the bulk phase may be regarded as independent of ζ , the coordinate normal to the interface (see, e.g., Ref. 10). The latter assumption implies that the contribution to the diffusion flux of surfactant from the bulk phase may also be neglected. The only difference to be accounted for, when a particle trapped in a film is discussed, compared to the system of a particle floating on a monolayer at the air/water interface, is that the value obtained for the drag force and, correspondingly, the friction coefficient is to be doubled, thus introducing the contributions from the two surfaces of the film.

APPENDIX B: INFLUENCE OF THE GIBBS ELASTICITY ON THE DRAG FORCE

The elastic component of the drag force can be expressed as

$$F_{el} = - \int_0^{2\pi} (\sigma - \sigma_0) \sin\phi \, a \, d\phi \bigg|_{z=1}. \qquad \text{[B1]}$$

Here, σ_0 is the surface tension of the unperturbed surface and satisfies the expansion

$$\sigma = \sigma_0 + \left(\frac{\partial \sigma}{\partial \Gamma} \right) (\Gamma - \Gamma_0). \qquad \text{[B2]}$$

Therefore, to obtain an explicit expression for F_{el}, one needs to solve the equation for the surface mass density [7]. For simplicity, with Γ' we will denote the perturbation to the layer surface density ($\Gamma' \equiv \Gamma_0 - \Gamma$) caused by the particle motion. Introducing it into Eq. [7] and substituting the expression found for $\tilde{\alpha}$ from Eqs. [21] and [29] yields

$$\frac{1}{z}\frac{\partial}{\partial z}\left(z\frac{\partial\Gamma'}{\partial z}\right)+\frac{1}{z^2}\frac{\partial^2\Gamma'}{\partial\phi^2}+\frac{2\Gamma_0 Va}{D_\mathrm{s}}\frac{\sqrt{q}K_1(\sqrt{q}z)}{K_0(\sqrt{q})}\sin\phi=0. \qquad \text{[B3]}$$

The solution for Eq. [B3] is a superposition of the general solution of the homogeneous equation and the partial solution of the inhomogeneous equation:

$$\Gamma'=M\frac{\sin\phi}{z}-\frac{2\Gamma_0 Va}{D_\mathrm{s}}\frac{K_1(\sqrt{q}z)}{\sqrt{q}K_0(\sqrt{q})}\sin\phi, \qquad \text{[B4]}$$

M being an arbitrary constant. It can be determined by imposing a boundary condition requiring the mass transfer at the particle surface to be zero:

$$\left.\frac{\partial\Gamma}{\partial z}\right|_{z=1}=0. \qquad \text{[B5]}$$

Thus M is found to be

$$M=\frac{2\Gamma_0 Va}{D_\mathrm{s}}\left(1+\frac{K_1(\sqrt{q})}{\sqrt{q}K_0(\sqrt{q})}\right). \qquad \text{[B6]}$$

Finally, for the elastic component of the force, Eqs. [B1], [B2], [B4], and [B6] provide

$$F_\mathrm{el}=2\pi\frac{Ea^2V}{D_\mathrm{s}}. \qquad \text{[B7]}$$

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