Hindered mobility of a particle near a soft interface

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The translational motion of a solid sphere near a deformable fluid interface is studied in the low Reynolds number regime. In this problem, the fluid flow driven by the sphere is dynamically coupled the instantaneous conformation of the interface. Using a two-dimensional Fourier transform technique, we are able to account for the multiple backflows scattered from the interface. The mobility tensor is then obtained from the matrix elements of the relevant Green function. This analysis allows us to express the explicit position and frequency dependence of the mobility. We recover in the steady limit the result for a sphere near a perfectly flat interface. At intermediate time scales, the mobility exhibits an imaginary part, which is a signature of the elastic response of the interface. In the short time limit, we find the intriguing feature that the perpendicular mobility may, under some circumstances, become lower than the bulk value. All those results can be explained from the definition of the relaxation time of the soft interface.

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I. INTRODUCTION

The motion of a particle in the vicinity of a bounding surface is a long standing problem in colloidal science. When a colloidal sphere suspended in a quiescent fluid approaches a wall, the drag force acting on it increases with respect to the drag force when far from the wall. This property is attributed to hydrodynamic interactions that develop because of the boundary conditions imposed by the wall on the fluid flow. In addition, the motion of the particle becomes anisotropic since the mobility is higher in the direction parallel to the wall than in the perpendicular direction.

Although the first investigations on the influence of a bounding wall date back to the early work of Lorentz, this field has known a certain revival during the past two decades. The main reason for this is certainly the achievement of technical progress, in particular in the field of single-molecule techniques, that allows nowadays to measure the position-dependent mobility of individual micron-size particles with a great accuracy. Among the most efficient tools, one can quote evanescent waves techniques, single particle tracking by video-microscopy, particle handling with optical tweezers, AFM noise analysis, or fluorescence correlation spectroscopy. Those various methods share the common feature of probing the random motion of Brownian objects near one or two solid wall, and the the mobility coefficients deduced from the experimental data agree remarkably well with the theoretical predictions.

The renewal of interest for this question is also due to the development of microfluidics. Indeed, by reducing the size of the systems, the influence of surface effects are inevitably enhanced with respect to the bulk properties. Consequently, most of the physical phenomena take place near the boundaries. A fundamental understanding on how surface properties might affect the overall flow field has therefore become crucial in order to propose new solutions that would take advantage of this predominance. Lastly, it has been suggested recently to use colloidal particles as local probes of the flow properties near surfaces. This idea has been introduced in the context of the no-slip boundary condition, where the motion of the particles is expected to contain a signature of the slip length. More generally, one can think of a Brownian particle as a probe of the viscoelastic properties of the bounding surface.

From a theoretical viewpoint, the motion of a solid particle in the presence of a nearby, plane interface has been extensively studied in the past. During the last few years, calculations of mobility coefficients have been extended to particles near surfactant-covered interfaces, in a liquid film between two fluids, or in a Poiseuille flow between planar walls. The effect of fluid inertia has also been accounted for, as well as the possibility of liquid slippage at the wall. Here, we re-examine this question for a particle near a fluid-fluid interface. Results are available for the drag force acting on a sphere of radius moving at a distance of a perfectly flat interface, up to second order in the ratio. While this problem is of some intrinsic interest, and is a logical starting point in the limit of very high surface tension, it is obvious that a real interface will generally deform owing to the motion of the particle. For finite surface tension, the motion of the particle is expected to be dynamically coupled to the conformations of the interface. Indeed, the fluid flow caused by the displacement of the particle exerts stresses that deform the interface. Relaxing back to its equilibrium position, the interface creates a backflow that in turn perturbs the motion of the particle, and so on. The delay in the response of the soft surface to hydrodynamic stresses is therefore expected to induce memory effects in the motion of the particle.

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In general, the problem of the motion near a soft surface is highly non-linear due to the fact that the shape of the interface is unknown. Although it cannot be solved exactly, iterative solutions have been derived when the deformation of the interface is asymptotically small \[20, 21\]. The idea is to first solve the motion of a spherical bead near a flat surface. As the resulting velocity produces an imbalance of normal stress at the interface, it is then possible to determine a first nonzero approximation for the deformation \[20\]. This strategy is however limited as it only describes the first “image” correction to hydrodynamic interactions. Also, it assumes a quasi-steady deformation profile and does not allow for a possible delay inherent in the response of an elastic interface.

In this article, we present an analytical method that rigorously accounts for the infinite series of hydrodynamic reflections on the soft interface. This scheme is achieved within the only assumption that interface deformations remain moderate. The rest of the paper is organized as follows. In Section II, we specify the system and introduce the general set of equations that govern the problem. We reformulate in Section III the small deformation problem in terms of equivalent boundary conditions at the undisplaced interface. Results for the Oseen problem are then discussed in Section IV. In particular, we find that the frequency-dependent mobility switches between two regimes over a time scale corresponding to the relaxation time of the interface. Finally, we come back to the relationship with experiments and draw some concluding remarks in Section V.

II. FORMULATION OF THE PROBLEM

A. Linear hydrodynamics

We consider a spherical particle of radius \(a\) moving near a fluid interface in the low Reynolds number regime. The interface separates two viscous, incompressible and immiscible fluids. Its average position is chosen to coincide with the \(x - y\) plane, with the \(z\)-coordinate directed perpendicular to it. The two fluids are labelled with indices 1 and 2, fluid 1 lying above fluid 2. Furthermore, we denote \(\eta_1\) and \(\eta_2\) the shear viscosities, \(\rho_1\) and \(\rho_2\) the mass densities, and \(\Delta \rho = \rho_2 - \rho_1 > 0\) the mass density difference. In order to get the mobility tensor of the particle, we shall first evaluate the appropriate Green function — called the Oseen tensor in this context — and investigate the effect of a time-dependent point force \(\mathbf{F}(t)\) acting at position \(\mathbf{r}_0 = (x_0, y_0, z_0)\) on the flow field \[22\]. Without loss of generality, we can assume that the sphere is fully immersed in fluid 1. For small-amplitude and low-frequency motion, the flow velocity \(\mathbf{v}(\mathbf{r}, t)\) and the pressure \(p(\mathbf{r}, t)\) are governed by the Stokes equations

\[
\eta_\alpha \nabla^2 \mathbf{v} - \nabla p + \mathbf{F}(\mathbf{r}, t) = 0, \tag{1}
\]

\[
\nabla \cdot \mathbf{v} = 0, \tag{2}
\]

with \(\alpha = 1\) or 2, depending on whether the point \(\mathbf{r}\) is located above or below the interface. In Eq. (1), \(\delta\) stands for the Dirac delta-function. The two fluids are assumed to be quiescent except for the disturbance flow caused by the motion of the sphere.

B. Physics of interfaces

The Stokes equations have to be solved together with the usual boundary conditions at the interface, namely the velocity and the tangential constraints must be continuous. The normal-normal component of the stress tensor presents a discontinuity which is balanced by the restoring force exerted by the deformed interface on the fluid. This question is quite involved since, in principle, the tangential and normal directions depend on the local and instantaneous configuration of the interface. However, an approximate solution can be found for moderate deformations. In this case, the position of the almost flat interface can be described by a single-valued function \(h(\mathbf{r}, t)\), with \(\mathbf{r} = (x, y)\). For our purpose, it is more convenient to use the two-dimensional Fourier representation

\[
h(\mathbf{q}, t) = \int d^2 \rho \exp[-i\mathbf{q} \cdot \mathbf{r}] h(\mathbf{r}, t), \tag{3}
\]

with \(\mathbf{q} = (q_x, q_y)\). The elastic properties of the interface are then described by the Hamiltonian \[23\]

\[
\mathcal{H} = \frac{\gamma}{2} \int d^2 \mathbf{q} \left( q_x^2 + q_y^2 \right) |h(\mathbf{q}, t)|^2, \tag{4}
\]

where \(\gamma\) is the surface tension and \(l_c = \sqrt{\gamma/(g\Delta \rho)}\) the capillary length, \(g\) being the gravitational acceleration. The capillary length scale typically lies in the millimeter range for \(\gamma \approx 100\, \text{mN/m}\), but can be as low as a few microns for ultra-soft interfaces with \(\gamma \approx 0.1\, \mu\text{N/m} \[24\]. We then proceed in the same manner as for linearized theory of capillary waves and express all the boundary conditions at the undisplaced interface \(z = 0\). This hypothesis of smooth deformation is valid up to linear order in the deformation field \(h\), so that our approach is fully consistent with the harmonic description of the interface energy Eq. (4).

C. Method of solution

In spite of these classical simplifications, the coupling between the motion of the particle and the capillary waves leads to a rich behaviour. Before solving the Stokes equations, we first remark that the shape of the interface
depends on the detailed history of the motion of the particle as well as on the shape at some earlier times. We are then naturally lead to perform a Fourier mode analysis in time, the Fourier transform \( \tilde{f}(\omega) \) of an arbitrary function \( f(t) \) being defined as

\[
\tilde{f}(\omega) = \int_{-\infty}^{+\infty} dt \exp[-i\omega t] f(t) .
\]

(5)

Besides, one can note that the problem is translationally invariant along the direction parallel to the surface. It is thus helpful to use the two-dimensional Fourier representation introduced above in Eq. (3). It also appears judicious for this study to decompose the vector fields into their longitudinal, transverse and normal components \( \tilde{ \mathbf{q}} \). This defines a new set of orthogonal unit vectors \( (\tilde{ \mathbf{q}}, \tilde{ \mathbf{t}}, \tilde{ \mathbf{n}}) \), where \( \tilde{ \mathbf{q}} \) is the unit vector parallel to \( \mathbf{q} \), \( \tilde{ \mathbf{n}} \) the unit vector in the \( z \)-direction, and \( \tilde{ \mathbf{t}} \) the in-plane vector perpendicular to \( \tilde{ \mathbf{q}} \) and \( \tilde{ \mathbf{n}} \). These vectors are connected to the cartesian basis \( ( \mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z ) \) through

\[
\tilde{ \mathbf{q}} = \frac{q_0}{q} \mathbf{e}_x + \frac{q_y}{q} \mathbf{e}_y ,
\]

\[
\tilde{ \mathbf{t}} = \frac{q_0}{q} \mathbf{e}_x - \frac{q_y}{q} \mathbf{e}_y ,
\]

\[
\tilde{ \mathbf{n}} = \mathbf{e}_z .
\]

(6)

The velocity and the force are written \( \mathbf{v} = v_\mathbf{q} \tilde{ \mathbf{q}} + v_\mathbf{t} \tilde{ \mathbf{t}} + v_\mathbf{z} \tilde{ \mathbf{n}} \) and \( \mathbf{F} = F_\mathbf{q} \tilde{ \mathbf{q}} + F_\mathbf{t} \tilde{ \mathbf{t}} + F_\mathbf{z} \tilde{ \mathbf{n}} \), respectively. Inserting these representations into the Stokes equations (13 - 14) finally leads to a system of ordinary differential equations for the Fourier-transformed quantities

\[
- \eta_0 q^2 v_\mathbf{q} + \eta_0 \frac{\partial^2 v_\mathbf{q}}{\partial z^2} - i q v_e \tilde{F}_e \delta(z - z_0) = 0
\]

(7)

\[
- \eta_0 q^2 v_\mathbf{t} + \eta_0 \frac{\partial^2 v_\mathbf{t}}{\partial z^2} + \tilde{F}_t \delta(z - z_0) = 0
\]

(8)

\[
- \eta_0 q^2 v_\mathbf{z} + \eta_0 \frac{\partial^2 v_\mathbf{z}}{\partial z^2} - \frac{\partial v_e}{\partial z} + \tilde{F}_z \delta(z - z_0) = 0
\]

(9)

with the divergenceless condition

\[
iv_\mathbf{q} + \frac{\partial v_\mathbf{z}}{\partial z} = 0.
\]

(10)

Interestingly, the condition (12) for the longitudinal coordinate together with the incompressibility condition (10) implies an additional boundary condition for the normal coordinate of the velocity, namely

\[
\left. \frac{\partial v_\mathbf{z}}{\partial z} \right|_{0^+} = \left. \frac{\partial v_\mathbf{z}}{\partial z} \right|_{0^-} .
\]

(15)

### III. BOUNDARY CONDITIONS

To describe the flow in the presence of an interface, we must consider the flow on each side separately, and then require proper matching conditions for the velocity and surface forces. As stated above, the hypothesis of smooth deformations around the planar configuration enables us to express the boundary conditions at the undisplaced interface \( z = 0 \). Because our representation of the velocity in terms of longitudinal and transverse coordinates is not commonly used in the literature, we find it worthwhile to give some details regarding the derivation of the boundary values.

#### A. Continuity of the velocity

First of all, we have to ensure that the velocity is continuous at the interface. Explicitly, this requirement reads

\[
\tilde{v}_\mathbf{q}(\mathbf{q}, 0^+, \omega) = \tilde{v}_\mathbf{q}(\mathbf{q}, 0^-, \omega) ,
\]

(12)

\[
\tilde{v}_\mathbf{t}(\mathbf{q}, 0^+, \omega) = \tilde{v}_\mathbf{t}(\mathbf{q}, 0^-, \omega) ,
\]

(13)

\[
\tilde{v}_\mathbf{z}(\mathbf{q}, 0^+, \omega) = \tilde{v}_\mathbf{z}(\mathbf{q}, 0^-, \omega) .
\]

(14)

#### B. Balance of tangential forces

Secondly, tangential stresses have to be balanced at the interface. In real space, the continuity condition for the normal-tangential components of the stress tensor reads \( \sigma_{xx,0^+} = \sigma_{xx,0^-} \) and \( \sigma_{xy,0^+} = \sigma_{xy,0^-} \), with \( \sigma_{jk} = -\rho \delta_{jk} + \eta_0 (\partial v_j / \partial x_k + \partial v_k / \partial x_j) \) the stress tensor in cartesian coordinates. Switching to \( \{ \mathbf{q}, z, \omega \} \) variables, both requirements reduce to

\[
\eta_1 \left. \frac{\partial v_\mathbf{q}}{\partial z} \right|_{0^+} + i \eta_0 \tilde{v}_\mathbf{q} = \eta_2 \left. \frac{\partial v_\mathbf{q}}{\partial z} \right|_{0^-} ,
\]

where the two-dimensional vector \( \tilde{v}_\mathbf{q} = (\tilde{v}_\mathbf{q}, \tilde{v}_\mathbf{t}) \) is the parallel velocity. Projecting this equation onto the transverse direction leads to the condition

\[
\eta_1 \left. \frac{\partial v_\mathbf{q}}{\partial z} \right|_{0^+} = \eta_2 \left. \frac{\partial v_\mathbf{q}}{\partial z} \right|_{0^-} ,
\]

(16)

whereas projection onto the longitudinal coordinate gives another condition which still involves both \( \tilde{v}_\mathbf{q} \) and \( \tilde{v}_\mathbf{z} \). In order to obtain a boundary condition for the normal component only, the incompressibility condition (10) is once more invoked. We finally get

\[
\eta_1 \left. \frac{\partial^2 \tilde{v}_\mathbf{z}}{\partial z^2} + q^2 \tilde{v}_\mathbf{z} \right|_{0^+} = \eta_2 \left. \frac{\partial^2 \tilde{v}_\mathbf{z}}{\partial z^2} + q^2 \tilde{v}_\mathbf{z} \right|_{0^-} .
\]

(17)
Note that the balance of tangential stresses is also relevant with regard to the normal component of the velocity.

C. Discontinuity of normal stress

The next condition that has to be enforced concerns the normal-normal stress difference that comes into play whenever the interface is bent. Indeed, a deformation of the interface gives rise to normal restoring forces, expressed as the functional derivative of the Hamiltonian \( \mathcal{H} \). For small displacements, the forces are small and proportional to \( h \). The normal stress condition reads, in real space, \( \sigma_{zz}|_{0-} - \sigma_{zz}|_{0+} = -\delta \mathcal{H}/\delta h \). In terms of the variables \( \{q, z, \omega\} \), we have

\[
\tilde{p}(0^+) - \tilde{p}(0^-) - 2\eta_1 \left. \frac{\partial \tilde{v}_z}{\partial z} \right|_{0+} + 2\eta_2 \left. \frac{\partial \tilde{v}_z}{\partial z} \right|_{0-} = -E_q \tilde{h}(q, \omega),
\]

where we define the energy density \( E_q = \gamma(q^2 + \lambda^2) \). It can be seen that the normal stress difference at the interface is balanced by interfacial tension and buoyancy forces (due to the density difference between the two fluids). This condition still involves both the normal component of the velocity as well as the pressure field. To get a relation in terms of \( \tilde{v}_z \) only, we shall first use Eq. (4) to express the pressure difference (remember that \( z_0 > 0 \))

\[
i q (\tilde{p}(0^+) - \tilde{p}(0^-)) = \eta_1 \left. \left( \frac{\partial^2 \tilde{v}_z}{\partial z^2} - q^2 \tilde{v}_z \right) \right|_{0+} - \eta_2 \left. \left( \frac{\partial^2 \tilde{v}_z}{\partial z^2} - q^2 \tilde{v}_z \right) \right|_{0-}.
\]

Substitute \( \tilde{v}_z \) for \( \tilde{v}_z \) thanks to relation (4), we arrive at the condition on the third derivative of the velocity

\[
\eta_1 \left. \left( \frac{\partial^3 \tilde{v}_z}{\partial z^3} - 3q^2 \frac{\partial \tilde{v}_z}{\partial z} \right) \right|_{0+} = \eta_2 \left. \left( \frac{\partial^3 \tilde{v}_z}{\partial z^3} - 3q^2 \frac{\partial \tilde{v}_z}{\partial z} \right) \right|_{0-} - q^2 E_q \tilde{h}(q, \omega).
\]

D. Immiscibility of the two fluids

To make the calculations tractable, we suppose that the condition of immiscibility can be written at \( z = 0 \). This approximation is justified since the fact that it is in any rigor valid at \( z = h \) is an effect of higher order. Within this assumption, the time rate of change of the shape function is related to the normal velocity at the interface through

\[
\tilde{v}_z(q, 0, \omega) = i\omega \tilde{h}(q, \omega),
\]

up to linear order in the deformation field. This closure relation is especially relevant since, as shown in the following, it allows to work out the instantaneous deformation of the interface in response to hydrodynamic stresses.

IV. GREEN FUNCTION AND TRANSLATIONAL MOBILITY

A. Motion of the interface

We now have all the ingredients to solve the Stokes equations. Because our calculations are algebraically involved, we save the details for the appendices. An interesting results is that the local deformation of the interface is directly proportional to the amplitude of the point force applied at height \( z_0 \)

\[
\tilde{h}(q, \omega) = \tilde{R}(q, z_0, \omega) \tilde{F}(\omega),
\]

where the vector \( \tilde{R} \) is the response function obtained thanks to the closure relation (10). For a vertical force \( \tilde{F} = (0, 0, \tilde{F}_z) \), we find in Appendix B

\[
\tilde{R}_z(q, z_0, \omega) = \frac{1}{4\eta q (\omega_q + i\omega)}(1 + q z_0)e^{-q z_0}. \tag{21}
\]

As expected, the relaxation dynamics of the profile is governed by the mean viscosity \( \bar{\eta} = (\eta_1 + \eta_2)/2 \). The response of a deformation mode with wavevector \( q \) is characterized by its relaxation rate

\[
\omega_q = \frac{\gamma}{4\bar{\eta}} (q^2 + \lambda^2). \tag{22}
\]

Remark that different wavevectors are not damped in the same way. The amplitude of the response function is always maximum for \( q = 0 \), \( \tilde{h}(0, \omega) = \tilde{F}_z/(\Delta \rho g) \). It then vanishes with increasing \( q \), all the more rapidly as the frequency \( \omega \) or the distance \( z_0 \) are large. The result Eq. (21) can be interpreted as follows. The real part of \( \tilde{R}_z \), which is in phase with the strain, is the analogous of a storage modulus for a viscoelastic medium (20). This contribution corresponds to the elastic energy stored in the deformation of the interface. On the other hand, the imaginary part of \( \tilde{R}_z \) plays the role of a loss modulus and describes the viscous dissipation associated with the relaxation of individual deformation modes.

Coming back to the motion of the interface in real space, one can evaluate the inverse Fourier transform of the response function, though the calculations will not be performed here. A deformation may also be obtained as a result of a point force applied parallel to the interface. We find

\[
\tilde{R}_l(q, z_0, \omega) = \frac{1}{4\eta q (\omega - i\omega_q)}q z_0 e^{-q z_0}, \tag{23}
\]

\[
\tilde{R}_t(q, z_0, \omega) = 0, \tag{24}
\]

for the longitudinal and transverse coordinate, respectively. Note that the shape of the interface is not affected by the transverse component of the force.
B. Oseen tensor

The components of the Oseen tensor are then obtained by identification with the definition

\[ \bar{v}_i = \sum_j \tilde{G}_{ij} \tilde{F}_j, \]  

(25)

where \( i, j \in \{l, t, z\} \). For symmetry reasons, the Green function satisfies the general relation \( \tilde{G}_{ij}(r, r', t) = \tilde{G}_{ji}(r', r, t) \) for \( z \) and \( z' \) on the same side of the interface. This is re-expressed in terms of our particular choice of variables as \( \tilde{G}_{ij}(q, z, z', \omega) = \tilde{G}_{ji}(-q, z', z, -\omega) \), property that can be checked along the calculations. As shown in the appendices, the Green function can always be written as

\[ \tilde{G}(q, z, z_0, \omega) = \tilde{G}^{(0)}(q, z - z_0) + \Delta \tilde{G}(q, z, z_0, \omega) \]

\[ = \tilde{G}^{(0)}(q, z - z_0) + \Delta \tilde{G}^{(1)}(q, z, z_0) \]

\[ + \frac{\omega}{\omega - i\omega_q} \Delta \tilde{G}^{(2)}(q, z, z_0), \]  

(26)

see Appendix A for the exact expression of \( \tilde{G}_{ij} \), Appendix B for the components \( \tilde{G}_{zz} \), and Appendix C for the components \( \tilde{G}_{ij} \). The first term, which depends only on the relative distance \((z - z_0)\), would reduce to the usual free-space Green function if the viscosities were equal. The second term, \( \Delta \tilde{G}^{(1)} \), is the correction for an undistorted interface. Both contributions have already been obtained in previous work, though not in this particular choice of coordinates.\[ \] The original part of this study is the derivation the contribution coming from the deformation of the interface. The prefactor \((\omega - i\omega_q)^{-1}\) in Eq. 26 is a clear signature of hydrodynamic scattering effects on the soft surface. Indeed, the fluid flow resulting from a displacement of the particle exerts stresses that deform the interface. Relaxing back to its equilibrium position, \( \tilde{G}^{(1)} \) is then expanded from the deformation of the interface. The correction \( \Delta \tilde{G}^{(2)} \) is then expanded in powers of \( a/z_0 \). In the limit of small particles \( a \ll z_0 \), the correction to the mobility tensor is given, at leading order, by

\[ \Delta \tilde{G}^{(2)}(q, z, z_0) = \int \frac{d^2q}{(2\pi)^2} \Delta \tilde{G}^{(2)}(q, z, z_0). \]  

(27)

C. Translational mobility tensor

From the matrix elements of the Oseen tensor, we can obtain the mobility matrix for a sphere. To this aim, we still have to enforce the no-slip boundary condition for the fluid flow on the surface of the particle. In the following, we assume that the particle is a sphere of radius \( a \). If we note \( \mathbf{U}(r_0) \) and \( \mathbf{\Omega} \) respectively the translational and rotational velocity of the sphere, \( r_0 \) being the position of its center-of-mass, then the fluid velocity satisfies

\[ \mathbf{v}(\mathbf{r}_0 + \mathbf{a}) = \mathbf{U}(\mathbf{r}_0) + \mathbf{\Omega} \times \mathbf{a}, \]  

(29)

for any vector \( \mathbf{a} \) scanning the surface of the bead. Integrating this relation over the particle, one obtains a linear relation between the total friction force \( \mathbf{F}_H \) exerted by the liquid and velocity of the particle. This relation defines the (frequency-dependent) mobility tensor through \( \mathbf{U} = -\mathbf{F}_H/\mathbf{\Omega} \). It can be written as the sum of two terms, \( \mu_{kl}(z_0, \omega) = \mu_0 \delta_{kl} + \Delta \mu_{kl}(z_0, \omega) \), with \( \mu_0 = (6\pi \eta a)^{-1} \) the bulk value for a particle in fluid 1 but infinitely far from the interface. The correction \( \Delta \mu_{kl} \) is then expanded in powers of \( a/z_0 \). In the limit of small particles \( a \ll z_0 \), the correction to the mobility tensor is given, at leading order, by

\[ \Delta \mu_{kl}(z_0, \omega) = \int \frac{d^2q}{(2\pi)^2} \Delta \tilde{G}^{(2)}(q, z, z_0). \]  

(30)

As a matter of fact, it can be shown that all cross-contributions vanish, so that the correction to the mobility tensor is also diagonal with elements \( \Delta \mu_{xx} = \Delta \mu_{yy} = \Delta \mu_{\perp} \) and \( \Delta \mu_{zz} = \Delta \mu_{\parallel} \).

1. Perpendicular mobility

From the result Eq. 26 for the normal-normal component of the Oseen tensor, we find

\[ \Delta \mu_{\perp}(z_0, \omega) = -\frac{1}{16\pi \eta_1 z_0} \left( \frac{2\eta_1 + 3\eta_2}{\eta_1 + \eta_2} \right) \]

\[ + \frac{5}{32\pi \eta_1 z_0} F \left( \omega, \frac{z_0}{l_c} \right). \]  

(31)

In this expression, \( \tau = 4\pi \eta_c / \gamma \) corresponds to the longest time required for elastic stuctures in the fluid — in our case, the interface — to relax. For typical values \( \eta = 10^{-2} \text{ Pa.s} \) and \( \Delta \rho = 10^2 \text{ kg.m}^{-3} \), it ranges from \( \tau \approx 10^{-3} \text{ s} \) for usual interfaces with \( \gamma = 100 \text{ mN.m}^{-1} \) up to \( \tau \approx 1 \text{ s} \) for ultra-soft interfaces with \( \gamma = 0.1 \text{ \mu N.m}^{-1} \). The frequency-dependent contribution \( F \) arises from surface deformations and is therefore governed by the mean viscosity \( \eta \). It is given by

\[ F(s, k) = \frac{4}{5} \int_0^\infty dx \frac{ikxx}{1 + isx + x^2(1 + kx)^2} \exp[-2kx] \]

\[ = F'(s, k) + iF''(s, k). \]  

(32)
This integral actually corresponds to the sum over all deformation modes of the interface. For $\omega = 0$, one has $F(0, z_0/l_c) = 0$ and the authoritative reader will recognize on the right hand side of Eq. (31) the correction to the mobility of a sphere near a flat, liquid-liquid interface. One even recovers the result of Lorentz for a hard wall by taking the limit of $\omega \tau \ll 1$.

We find that the correction vanishes when $\omega = 0$. A similar reasoning applies to the other limit $\omega \tau \gg 1$, that would correspond to an interface with vanishing surface tension. Since no elastic energy can be stored anymore, $F''$ has to vanish when $\omega \to \infty$. Interestingly, the sign of the real part of $\Delta \mu_\perp$ may change depending on whether $\omega \tau \ll 1$ or $\omega \tau \gg 1$. Indeed, it is always negative at low frequencies, whereas it may be positive at high frequencies provided that $\eta_1 > \eta_2$. This surprising property, peculiar to soft interfaces, may strongly influence the statistical properties of Brownian particles since surface deformation may enhance diffusion – with regards to the bulk value – at short times.

2. Parallel mobility

Similar conclusions can be drawn for the mobility parallel to the surface. We find that

$$\Delta \mu_\parallel (z_0, \omega) = \frac{1}{32\pi \eta_1 z_0} \left( \frac{2\eta_1 - 3\eta_2}{\eta_1 + \eta_2} \right) + \frac{1}{64\pi \eta z_0} G \left( \omega \tau, \frac{z_0}{l_c} \right) ,$$

(34)

where the frequency-dependent contribution is given by

$$G(s, k) = 4 \int_0^\infty dx \frac{i k x}{1 + is x + x^2} k^2 x^2 \exp(-2kx) .$$

(35)

In particular, one recovers the mobility coefficient for a sphere near a rigid interface in the asymptotic limit $\omega \tau \ll 1$

$$\Delta \mu_\parallel (z_0, \omega = 0) = \frac{1}{32\pi \eta_1 z_0} \left( \frac{2\eta_1 - 3\eta_2}{\eta_1 + \eta_2} \right) ,$$

(36)

whereas one obtains in the other limit $\omega \tau \gg 1$

$$\Delta \mu_\parallel (z_0, \omega \to \infty) = \frac{3}{32\pi \eta_1 z_0} \left( \frac{\eta_1 - \eta_2}{\eta_1 + \eta_2} \right) .$$

(37)
V. DISCUSSION

To summarize, we have calculated the mobility tensor of a spherical particle moving close to a fluid-fluid interface. Several lengths are inherent in the system, namely the radius \( a \) of the particle, the distance from the wall \( z_0 \), and the capillary length \( l_c \). The results presented in this work concern the response to a point force and are valid for particles far from the interface \( a \ll z_0 \). Because a soft interface can deform and store elastic energy, the mobility tensor decomposes into a real and an imaginary part. In steady-state limit \( \omega \tau \ll 1 \), deformations are irrelevant and one recovers the classical result for a flat, fluid-fluid interface. On the other hand, the short-time limit \( \omega \tau \gg 1 \) presents the intriguing feature that the perpendicular mobility can be higher than the bulk mobility if \( \eta_1 > \eta_2 \). Yet this result does not break any fundamental law since it arises from the fact that the particle “feels” the other side of the interface, which has a lower shear viscosity. Finally coming back to time variable, the friction force experienced by the particle will be negligible the relaxation time of the interface. This corresponds to the relaxation time of the interface then induce memory effects in the motion of the particle.

The framework developed in this study may be adapted to various problems near soft interfaces. For instance, one might investigate surface-mediated contributions to the coupled diffusion of two particles. One can also consider more complex surfaces, such as surfactant-covered interfaces or fluid membranes. Predictions regarding the rotational mobility might be relevant for experiments as well, especially in the case of anisotropic particles. Remark that translational and rotational motions are not coupled for a sphere in the linearized theory. This might not be true anymore for large deformations, where non-linear effects come into play.

Another point that might be included in the theory is the effect of fluid inertia. This contribution has been neglected so far, though it becomes relevant at frequencies higher than \( \omega_c = \eta/( \rho a^2) \). For typical values \( \eta = 10^{-3} \) Pa.s, \( \rho = 10^3 \) kg.m\(^{-3} \) and \( a = 1 \) \( \mu \)m, we obtain \( \omega_c \approx 10^6 \) rad.s\(^{-1} \). Here however, we consider time scales comparable to the relaxation time of the interface. This corresponds to frequencies in the kHz range, so that our approximation is fully justified. At this point, it should be mentioned that a study similar to ours, including fluid inertia, has been published during the completion of this work. In the steady limit, the author obtains the result for a rigid wall with stick boundary conditions. This however cannot be correct since one expects to find in this limit the mobility of a sphere near a fluid-fluid interface. The results derived in Ref. [30] are therefore questionable, but a closer inspection would be required to identify the origin of the discrepancy.

Finally, let us comment on some possible comparisons with experiments. Recently, de Villeneuve et al. have considered the sedimentation of PMMA spheres towards an interface with ultra-low tension \( \gamma \approx 0.1 \) \( \mu \)N/m. In this regime, long-range hydrodynamic interactions are dominant and lubrication theory does not apply. The authors clearly observe strong deformations of the interface, of the order several micrometers for spheres with radius \( a = 15 \) \( \mu \)m. Moreover, they measure sedimentation velocities that do not follow the theoretical curves for an undistorted interface, the particles falling faster towards the soft interface. The interpretation of those results might be quite straightforward in the light of the present analysis, even though the non-linear equations of motion might be challenging to solve. Work on this question is currently under progress.

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APPENDIX A: TRANSVERSE COMPONENT OF THE VELOCITY

We begin with Eq. (8) for the transverse component, which is easier to solve since it does not couple with the longitudinal and vertical coordinates of the velocity. This equation can be rewritten as

\[
\frac{\partial^2 \tilde{v}_t}{\partial z^2} - q^2 \tilde{v}_t = -\frac{\tilde{F}_t}{\eta_1 q^2} \delta(z - z_0) .
\]  

(A1)

With the condition that the fluid is at rest at infinity, the solution is

\[
\tilde{v}_t(q, z, \omega) = A e^{-q z} \quad \text{for } 0 < z_0 < z ,
\]

\[
\tilde{v}_t(q, z, \omega) = B e^{q z} + C e^{-q z} \quad \text{for } 0 < z < z_0 ,
\]

\[
\tilde{v}_t(q, z, \omega) = D e^{q z} \quad \text{for } z < 0 < z_0 .
\]

We then need to specify the boundary conditions in order to determine the four integration constants. The continuity of the velocity and the balance of tangential stresses at height \( z = 0 \) give the conditions (13) and (16). We get another couple of conditions by invoking the standard continuity conditions for the Green function at the singularity \( z = z_0 \). Explicitly, these requirements read

\[
\tilde{v}_t(q, z_0^+, \omega) = \tilde{v}_t(q, z_0^-, \omega) ,
\]  

(A2)

\[
\frac{\partial \tilde{v}_t}{\partial z} \bigg|_{z_0^+} - \frac{\partial \tilde{v}_t}{\partial z} \bigg|_{z_0^-} = -\frac{\tilde{F}_t}{\eta_1 q^2} .
\]  

(A3)

Enforcing the boundary conditions (13), (16), and (A2), we find the following expression for \( z \geq 0 \)

\[
\tilde{v}_t(q, z, \omega) = \frac{\tilde{F}_t}{2 \eta_1 q} \left[ e^{-q|z-z_0|} - \left( \frac{1 - \lambda}{1 + \lambda} \right) e^{-q(z+z_0)} \right] ,
\]  

(A4)
and for \( z \leq 0 \)

\[
\tilde{v}_z(\mathbf{q}, z, \omega) = \frac{\tilde{F}_z}{2\eta q} \left( \frac{2}{1 + \lambda} \right) e^{-q|z-z_0|}. \tag{A5}
\]

The transverse components of the Green function are then obtained by comparison of equation (4) (for \( z \geq 0 \)) or (A5) (for \( z \leq 0 \)) with the definition of the Oseen tensor \( \tilde{v}_t = \tilde{G}_{tt} \tilde{F}_t + \tilde{G}_{zt} \tilde{F}_z \). Obviously, we get \( \tilde{G}_{tt} = \tilde{G}_{zt} = 0 \), the only non-zero component being \( \tilde{G}_{tt} \). Note that the transverse component of the velocity is not affected by the shape of the interface.

**APPENDIX B: NORMAL COMPONENT OF THE VELOCITY**

1. Differential equation and general solution

The solution of the fourth-order differential equation \( (11) \) satisfied by \( \tilde{v}_z \) is

\[
\tilde{v}_z(\mathbf{q}, z, \omega) = (A + Bz) e^{-qz} \quad \text{for } z > z_0
\]

\[
\tilde{v}_z(\mathbf{q}, z, \omega) = (C + Dz) e^{qz} + (E + Fz) e^{-qz} \quad \text{for } z < z_0
\]

\[
\tilde{v}_z(\mathbf{q}, z, \omega) = (G + Hz) e^{qz} \quad \text{for } z < 0
\]

For the sake of simplicity, we shall focus separately on the situations where \( (\tilde{F}_t = 0, \tilde{F}_z \neq 0) \) and \( (\tilde{F}_t \neq 0, \tilde{F}_z = 0) \). According to the superposition principle, each solution leads by identification to the components of the Green tensor \( \tilde{G}_{zz} \) and \( \tilde{G}_{zt} \), respectively. Obviously, the normal-transverse component is identically zero, \( \tilde{G}_{zl} = 0 \).

2. Normal-normal component

We first consider the case where \( \tilde{F}_t = 0 \) and \( \tilde{F}_z \neq 0 \). In addition to the boundary conditions (14), (15), (17) and (18), we have to enforce the usual conditions for the Green function at the singularity position \( z = z_0 \), namely the velocity, its first and its second derivative are continuous at \( z = z_0 \). The only discontinuity comes from the third derivative

\[
\frac{\partial^3 \tilde{v}_z}{\partial z^3} \bigg|_{z_0^+} - \frac{\partial^3 \tilde{v}_z}{\partial z^3} \bigg|_{z_0^-} = \frac{q^2 \tilde{F}_z}{\eta}, \tag{B1}
\]

The algebra involved to evaluate the height integration constants is rather lengthy but presents no difficulty. We simply get the resulting velocity field

\[
\tilde{v}_z(\mathbf{q}, z, \omega) = \frac{\tilde{F}_z}{4\eta q} \left[ (1 + q|z-z_0|)e^{-q|z-z_0|} - \left( \frac{1 - \lambda}{1 + \lambda} \right) (1 + q(z + z_0) + 2q^2 z_0 e^{-q(z+z_0)}) \right] - \omega \tilde{h}(\mathbf{q}, \omega)(1 + qz)e^{-qz}, \tag{B2}
\]

the velocity (B2) or (B3) at height \( z = 0 \) and comparing with (19) then leads to

\[
\tilde{h}(\mathbf{q}, \omega) = \frac{1}{\omega_q + i\omega} (1 + qz_0) e^{-qz_0} \tilde{F}_z \frac{1}{4\eta q}, \tag{B4}
\]

Bringing Eq. (B2) and (B3) together with (B4), we finally obtain the normal-normal component of the Green function

\[
\tilde{G}_{zz}(\mathbf{q}, z, z_0, \omega) = \frac{1}{4\eta q} \left[ (1 + q|z-z_0|)e^{-q|z-z_0|} - \left( \frac{2}{1 + \lambda} \right) \left( 1 + q(z + z_0) + \frac{2q^2 z_0}{1 + \lambda} \right) e^{-q(z+z_0)} \right] - \frac{1}{4\eta q} \frac{\omega}{\omega_q + i\omega_q} (1 + qz)(1 + qz_0) e^{-q(z+z_0)}, \tag{B5}
\]

for \( z \geq 0 \), and

\[
\tilde{G}_{zz}(\mathbf{q}, z, z_0, \omega) = \frac{1}{4\eta q} \left( \frac{2}{1 + \lambda} \right) q^2 z_0 e^{q(z-z_0)} + \frac{1}{4\eta q} \frac{\omega}{\omega_q + i\omega_q} (1 - qz)(1 + qz_0) e^{q(z-z_0)}, \tag{B6}
\]

for \( z \leq 0 \).
3. Normal-longitudinal component

In order to get the component $\tilde{G}_{nl}$ of the Oseen tensor, we perform the same analysis expect that we now keep $\tilde{F}_l \neq 0$, whereas we set $\tilde{F}_z = 0$. This time, the discontinuity imposed by $\delta'$ in Eq. (11) has an incidence on the second derivative of the velocity at $z = z_0$

$$\frac{\partial^2 \tilde{v}_z}{\partial z^2} \bigg|_{z_0} - \frac{\partial^2 \tilde{v}_z}{\partial z^2} \bigg|_{z_0} = \frac{iq\tilde{F}_l}{\eta_1}, \quad (B7)$$

the velocity, its first and its third derivative being continuous. The algebra being quite similar to that of the previous section, we shall skip the details. Once again, the velocity field depends on the deformation of the interface. Interestingly, a point force exerted parallel to the surface is responsible for a normal displacement of the fluid-fluid interface. Evaluating the velocity at height $z = 0$ leads to the result

$$\tilde{h}(q, \omega) = \frac{1}{\omega - i\omega_q} q z_0 e^{-q z_0} \tilde{F}_l \frac{1}{4\eta q} . \quad (B8)$$

Bringing everything together, we find the normal-longitudinal component of the Green function

$$\tilde{G}_{zl}(q, z, z_0, \omega) = \frac{i}{4\eta q} \left[ q(z_0 - z) e^{-q(z-z_0)} + \left( \frac{1 - \lambda}{1 + \lambda} qz - qz_0 - \frac{2q^2 z z_0}{1 + \lambda} \right) e^{-q(z+z_0)} \right]$$

$$+ \frac{i}{4\eta q} \frac{\omega}{\omega - i\omega_q} (1 + qz) q z_0 e^{-q(z+z_0)}, \quad (B9)$$

for $z \geq 0$, and

$$\tilde{G}_{zl}(q, z, z_0, \omega) = -\frac{i}{4\eta q} \left( \frac{2}{1 + \lambda} \right) qz(1 - qz_0) e^{q(z-z_0)} + \frac{i}{4\eta q} \frac{\omega}{\omega - i\omega_q} (1 - qz) q z_0 e^{q(z-z_0)}, \quad (B10)$$

for $z \leq 0$.

APPENDIX C: LONGITUDINAL COMPONENT OF THE VELOCITY

To obtain the longitudinal component of the velocity, there is actually no need to solve the corresponding differential equation (7). Indeed, from the incompressibility condition (10), $\tilde{v}_l$ is related to $\tilde{v}_z$ thanks to $\tilde{v}_l = (i/q) \partial \tilde{v}_z / \partial z$. From the definition of the Oseen tensor $\tilde{v}_l = \tilde{G}_{lt} \tilde{F}_l + \tilde{G}_{lz} \tilde{F}_z$ (since, of course, $\tilde{G}_{lt} = 0$), it is straightforward to get

$$\tilde{G}_{ll}(q, z, z_0, \omega) = \frac{1}{4\eta q} \left[ (1 - q(z - z_0)) e^{-q(z-z_0)} - \left( \frac{1 - \lambda}{1 + \lambda} \right) \left( 1 - q(z + z_0) + \frac{2q^2 z z_0}{1 - \lambda} \right) e^{-q(z+z_0)} \right]$$

$$+ \frac{1}{4\eta q} \frac{\omega}{\omega - i\omega_q} q^2 z z_0 e^{-q(z+z_0)}, \quad (C1)$$

for $z \geq 0$, and

$$\tilde{G}_{ll}(q, z, z_0, \omega) = \frac{1}{4\eta q} \left( \frac{2}{1 + \lambda} \right) (1 + qz)(1 - qz_0) e^{q(z-z_0)} + \frac{1}{4\eta q} \frac{\omega}{\omega - i\omega_q} q^2 z z_0 e^{q(z-z_0)}, \quad (C2)$$

for $z \leq 0$.

Regarding the longitudinal-normal component, $\tilde{G}_{lz}$, no additional algebra is required since it can directly be deduced from $\tilde{G}_{zl}$ using the symmetry relation of the Green function.

[1] J. Happel and H. Brenner, Low Reynolds Number Hydrodynamics (Kluwer, Dordrecht, 1983).
[2] H. A. Lorentz, Abhandl. Theor. Phys. 1, 23 (1907).
[3] K.H. Lan, N. Ostrowsky, and D. Sornette, Phys. Rev. Lett. 57, 17 (1986).
[4] P. Holmqvist, J.K.G. Dhont, and P.R. Lang, Phys. Rev. E 74, 021402 (2006).
[5] L.P. Faucheux and A.J. Libchaber, Phys. Rev. E 49, 515 (1994).
[6] A. Pralle, E.-L. Florin, E.H.K. Stelzer, and J.K.H. Hörber, Appl. Phys. A 66, 571 (1998).
[7] E.R. Dufresne, T.M. Squires, M.P. Brenner, and D.G. Grier, Phys. Rev. Lett. 85, 3317 (2000).
[8] B. Lin, J. Yu, and S.A. Rice, Phys. Rev. E 62, 3909 (2000).
[9] F. Benmouna and D. Johannsmann, Eur. Phys. J. E 9, 435 (2002).
[10] L. Joly, C. Ybert, and L. Bocquet, Phys. Rev. Lett. 96, 046101 (2006).
[11] M. Joanicot and A. Ajdari, Science 309, 887 (2005).
[12] C. Neto, D.R. Evans, E. Bonaccurso, H.-J. Butt, and V.S.J. Craig, Rep. Prog. Phys. 68, 2859 (2005).
[13] E. Lauga and T.D. Squires, Phys. Fluids 17, 103102 (2005).
[14] J. Blawzdziewicz, V. Cristini, and M. Loewenberg, Phys. Fluids 11, 251 (1999).
[15] B.U. Felderhof, J. Chem. Phys. 124, 124705 (2006).
[16] R.B. Jones, J. Chem. Phys. 121, 483 (2004).
[17] B.U. Felderhof, J. Phys. Chem. B 109, 21406 (2005).
[18] S.H. Lee, R.S. Chadwick, and L.G. Leal, J. Fluid Mech. 93, 705 (1979).
[19] T. Bickel, Eur. Phys. J. E 20, 379 (2006).
[20] S.H. Lee and L.G. Leal, J. Colloid Int. Sci. 87, 81 (1982).
[21] For a recent overview, see S.-M. Yang and L.G. Leal, Int. J. Multiphase Flow 16, 507 (1990).
[22] J.K.G. Dhont, An Introduction to Dynamics of Colloids (Elsevier, Amsterdam, 1996).
[23] S.A. Safran, Statistical Thermodynamics of Surfaces, Interfaces, and Membranes (Addison-Wesley, NY, 1994).
[24] D.G.A.L. Aarts, M. Schmidt, and H.N.W. Lekkerkerker, Science 304, 847 (2004).
[25] U. Seifert, Adv. Phys. 46, 13 (1997).
[26] R.G. Larson, The Structure and Rheology of Complex Fluids (Oxford University Press, NY, 1999).
[27] C. Pozrikidis, Boundary Integral and Singularity Methods for Linearized Viscous Flow (Cambridge University Press, Cambridge, 1992).
[28] As a matter of fact, the integral can be expressed in terms of Sine Integrale and Cosine Integral functions, though the final result is quite complicated and not really more transparent than Eq. (32).
[29] C. Berdan, II and L.G. Leal, J. Colloid Int. Sci. 87, 62 (1982).
[30] B.U. Felderhof, J. Chem. Phys. 125, 144718 (2006).
[31] V.W.A. de Villeneuve, D.G.A.L. Aarts, and H.N.W. Lekkerkerker, Colloids Surf. A: Physicochem. Eng. Aspects 282, 61 (2006).