Effect of small particles on the near-wall dynamics of a large particle in a highly bidisperse colloidal solution

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We consider the hydrodynamic effect of small particles on the dynamics of a much larger particle moving normal to a planar wall in a highly bidisperse dilute colloidal suspension of spheres. The gap $h_0$ between the large particle and the wall is assumed to be comparable to the diameter $2a$ of the smaller particles so there is a length-scale separation between the gap width $h_0$ and the radius of the large particle $b \gg h_0$. We use this length-scale separation to develop a new lubrication theory which takes into account the presence of the smaller particles in the space between the larger particle and the wall. The hydrodynamic effect of the small particles on the motion of the large particle is characterized by the short time (or high frequency) resistance coefficient. We find that for small particle–wall separations $h_0$, the resistance coefficient tends to the asymptotic value corresponding to the large particle moving in a clear suspending fluid. For $h_0 \gg a$, the resistance coefficient approaches the lubrication value corresponding to a particle moving in a fluid with the effective viscosity given by the Einstein formula.

I. INTRODUCTION

Polydisperse suspensions have a significant presence in many industrial and natural systems. Examples include dairy products, polymeric gels and nearly all complex fluids in biological organisms. Since the dynamics of colloidal systems is often influenced by their confining boundaries [1, 2], the confining effects are important in many emerging applications, e.g., in self-assembly technology involving colloidal crystals [3, 4] and in chemical deposition processes on patterned wall [5]. Hence, it is necessary to understand how polydisperse suspensions behave in the proximity of a bounding surface.

The equilibrium state of confined systems can be fully determined by the particle–wall and interparticle interaction potentials, whereas a description of non-equilibrium phenomena is much more complex. In this paper we study the non-equilibrium dynamics of a wall-bounded bidisperse solution where a large colloidal particle moves in the direction normal to the wall in the presence of smaller particles. Our objective is to find the correction to the near-contact hydrodynamic force on the large particle due to the effect of the smaller particles in the low-concentration regime.

One way to tackle this problem is to treat the suspension in the gap between the wall and the large particle as a fluid with the effective viscosity given by the Einstein’s formula [6]. This approach, however, is valid only if the dimension of the small particles is much smaller than the characteristic flow length scale which is the minimum distance of separation between the surfaces of the wall and the large particle. When the separating distance is comparable to the dimension of the smaller species, a more detailed analysis is necessary to obtain the proper correction to the hydrodynamic friction. Our main purpose is to evaluate this correction in the short time (or high frequency) regime, where the influence of the small particles on the large particle motion results entirely from hydrodynamic effects.

This article is organized in the following way. In section [III] we define our system and discuss assumptions involved in our calculations. In section [IV] we develop a lubrication theory for near-contact approach of the large particle towards the wall and use this theory to derive expressions for modified lubrication pressure and hydrodynamic force on the large particle in the presence of small particles. In section [V] we express the dipolar force on the large particle in the presence of small particles. In section [VI] the results of our theory are used to determine the resistance force acting on the large particle. Our conclusions are drawn in section [VII].

II. HIGHLY ASYMMETRIC BIDISPERSE COLLOIDAL SUSPENSION

We consider a bidisperse colloidal suspension near a solid planar surface. Particles of both species are assumed to be spherical, with high asymmetry in size. We describe the influence of the smaller particles on the motion of a single larger particle in the direction normal to the wall. Our analysis is focused on the effect of the smaller species when the separation between the larger particle and the wall is comparable to the diameter of the smaller particles.

We concentrate on the short-time (or high-frequency) regime; the effect of Brownian motion on the system dynamics can therefore be neglected on the assumption that the deviation of the particle distribution from equilibrium is small. Under these conditions, the smaller particles affect the motion of a large particle only by influencing the velocity and the pressure fields in the suspending fluid. In order to determine these hydrodynamic fields, we first analyze the flow in the presence of a single small particle
in the gap between the wall and the large particle. The cumulative effect of small particles in a dilute suspension is obtained by simple statistical averaging over the position of the smaller particles. This approach is valid in the concentration range where the suspension is dilute enough to neglect mutual interactions between smaller particles and dense enough for meaningful statistical averaging.

**A. System definition**

The geometry of our system is represented in Fig. [1]. The small and the large particles have spherical hydrodynamic cores of radii \(a\) and \(b\), where \(a \ll b\). In typical highly asymmetric bidisperse colloidal mixtures \(b/a\) ranges from \(10^2\) to \(10^3\).

A rigid wall is located at \(z = 0\), and the center of the large sphere is on the \(z\)-axis. Therefore, the surface of this particle can be described by \(z = h(\rho)\) where \(\rho\) is the distance from the axis of symmetry (\(z\)-axis). The minimum distance of separation between the particle surface and the wall is \(h(0) = h_0\). We consider \(h_0 \sim 2a\).

A repulsive screened electrostatic potential between the particles is modeled by additive excluded shells surrounding hydrodynamic core of each particle. The thicknesses of the excluded shells for the small and the large spheres are \(\delta_a\) and \(\delta_b\), respectively. The thickness of the excluded layer associated with the wall is denoted by \(\delta_w\). It is assumed that \(\delta_a, \delta_b, \delta_w \ll b\).

The interaction potential affects the short-time dynamics of the system only through its influence on the equilibrium particle distribution—the effective resistance coefficient is obtained as the equilibrium average of the microscopic stresses produced by the particle motion. The results for a general interaction potential can thus be obtained by evaluating an appropriate equilibrium average of the hydrodynamic functions derived in the following sections. Our explicit numerical results for the excluded-shell potential illustrate the essential features of the near-wall dynamics of large particles in a highly bidisperse colloidal suspension.

**B. Equation for the flow field**

In our calculations, velocity of the large colloidal particle is denoted as \(V^P\) which is in the direction perpendicular to the wall. In this paper, all of our results correspond to the case where the large particle approaches to the wall—the reversal in this motion can be accounted for by simple reversal of computed velocity fields and pressure gradients. The velocity \(V^P\) is small so that the creeping flow approximation is valid. Hence, the hydrodynamic fields are governed by the Stokes equations,

\[
- \nabla P + \eta \nabla^2 u = 0, \quad \nabla \cdot u = 0,
\]

where \(u\) is the velocity field, \(P\) is the pressure field, and \(\eta\) is the viscosity. No-slip boundary condition is assumed at the wall and at the surfaces of all particles.

The hydrodynamic effect of the small particles on the surrounding fluid can be described in terms of the induced force density \(\mathbf{F}\) on surface of the small spheres. Such force density imposes a discontinuity in the gradient of the velocity field at the particle–fluid interface. This discontinuity is such that we can consider the volume
inside the particle as an extension of the fluid domain—the fluid in this region undergoes rigid-body motion corresponding to that of the rigid particle. Therefore, the entire domain (both inside and outside the particle) can be treated as a continuous fluid medium. As a result, the flow field described by Eq. (1) in the presence of the smaller particles is equivalent to the flow field which obeys the inhomogeneous Stokes equations

\[- \nabla P + \eta \nabla^2 \mathbf{u} = \mathbf{F}, \quad \nabla \cdot \mathbf{u} = 0. \tag{2}\]

Hence, if we can determine \( \mathbf{F} \) and solve Eq. (2), we can find the effect of the smaller species on the velocity and the pressure fields. Accordingly, in the first part of our analysis, we solve Eq. (2) to find \( P \) and \( \mathbf{u} \) in the gap between the large particle and the wall for an arbitrary induced-force distribution \( \mathbf{F} \). This analysis is presented in section III.

### C. Statistically averaged force density

In order to quantify the cumulative influence of smaller species on the hydrodynamic resistance of the large particle, we solve an ensemble-averaged flow equation (where the average is taken over all possible positions of the small particles). This reduced description requires the averaging of the force density \( \mathbf{F} \). Such averaging is valid if two conditions are satisfied. Firstly, there should be a sufficient number of small particles in the gap between the large particle and the wall so that the statistical description is physically meaningful. Secondly, the small particles should be well separated and mutually non-interacting. These two conditions are satisfied for

\[ h_0 \ll C^{-\frac{1}{2}} \ll \sqrt{bh_0}, \tag{3} \]

with \( C \) being the number density of the small particles. Under these conditions, the statistically averaged force distribution can be evaluated from the cumulative effect of mutually noninteracting individual small particles.

### III. LUBRICATION SOLUTION IN THE NEAR-CONTACT REGION

In our hydrodynamic calculations, we exploit the fact that for near-contact motion of the large particle the characteristic length scale along the wall is much greater than the characteristic length scale along the perpendicular direction \( z \). As a result of this separation of length scales, we can apply lubrication theory to determine the flow and the pressure fields.

#### A. Lubrication expansion

The predominant hydrodynamic effect on the large particle near a wall comes from the flow field in the near-contact lubrication region. In this lubrication zone, the flow can be locally approximated as a flow between two rigid parallel planes. The extent of the lubrication region is defined by the lubrication length \( l \), which is the characteristic length in the direction along the wall:

\[ l = \sqrt{2ab} \sim \sqrt{bh_0} \gg h_0 \sim 2a. \tag{4} \]

The corresponding characteristic length for the direction perpendicular to the wall is the slowly varying gap width \( h \sim 2a \ll l \). The small parameter that characterizes length-scale separation in the two directions is

\[ \lambda = 2a/l = \sqrt{2a/b}. \tag{5} \]

In our earlier paper [7], we have shown that the scattered flow from a sphere in a slit pore saturates exponentially to an asymptotic Hele–Shaw velocity field at large distances from the sphere. In the asymptotic regime, the scattered flow thus assumes the form of a two-dimensional pressure-driven flow, with a harmonic pressure distribution which is independent of the transverse coordinate \( z \).

There are two ways in which the flow scattered from the small particles contributes to the hydrodynamic normal force acting on the large particle. First, there is the near-field behavior of the scattered field, which produces stresses confined to a localized region of size defined by the length \( h \sim a \). Second, there is also the far-field lubrication pressure.

To estimate the hydrodynamic force resulting from the far-field interactions, we note that there are \( N \sim Cl^2a \) small particles in the lubrication region, and each particle yields an \( O(\phi a b V^P) \) force contribution. We thus find that the cumulative effect of the near-field stresses on the total resistance force acting on the large particle is of the order \( O(\phi a b V^P) \), where \( \phi \) is the volume fraction of the small particles. This force is thus smaller by the order \( O(a/b) \) than the lubrication resistance force

\[ F_0 = 6\pi \eta a V^P b^2/h_0 \]

resulting from the presence of the suspending fluid [8].

The second small-particle contribution to the resistance force originates from the cumulative effect of the far-field pressure associated with the flow scattered from the particles. The far-field pressure decays slowly at large distances, and thus it acts over the whole lubrication area. As shown below, the far-field pressure produces an \( O(\phi F_0) \) contribution to the resistance force. This contribution is thus the dominant correction to the hydrodynamic resistance.

To find the far-field contribution of the scattered flow, we rescale the lateral coordinates \( s \) (parallel to the wall) and transverse coordinate \( z \) (across the gap) by the corresponding lengthscales \( l \) and \( 2a \),

\[ s \to s/l, \quad z \to z/2a. \tag{7} \]

Accordingly, the Stokes equations (2) are transformed into the rescaled form,

\[ -\frac{1}{2a} \frac{\partial P}{\partial z} + \frac{\eta}{4a^2} \left( \frac{\partial^2 u_z}{\partial z^2} + \lambda^2 \nabla^2 u_z \right) = F_z, \tag{8a} \]
\[-\frac{\lambda}{2a} \nabla_s P + \frac{\eta}{4a^2} \left( \frac{\partial^2 u_s}{\partial z'^2} + \lambda^2 \nabla_s^2 u_s \right) = F_s, \tag{8b}\]

\[\lambda \nabla_s \cdot u_s + \frac{\partial u_z}{\partial z} = 0, \tag{8c}\]

where subscripts \(s\) and \(z\) denote the directions parallel and normal to the wall, respectively.

From now on, all coordinates and position vectors will be normalized by the corresponding characteristic lengths. To be consistent with this non-dimensional formulation, we introduce the following dimensionless parameters:

\[\bar{b} = b/2a = 1/\lambda^2, \quad \bar{h}_0 = h_0/2a, \quad \bar{h} = h/2a, \tag{9a}\]

and

\[\bar{\delta}_i = \delta_i/2a. \tag{9b}\]

The subscript \(i\) in Eq. \((9a)\) can be either \(a\) (the small spheres) or \(b\) (the large sphere) or \(w\) (the wall) to indicate the excluded-volume range due to corresponding repulsive potentials. For simplicity, in our calculations, we take

\[\bar{\delta}_a = \bar{\delta}_w = \bar{\delta}_b = \bar{\delta}/2 \tag{10}\]

and use \(\bar{\delta}\) as the only parameter which accounts for the excluded volume. The behavior of more general systems is similar to the one where Eq. \((10)\) is assumed.

The rescaled Stokes equations \((8)\) can be solved asymptotically by scaling the velocity and the pressure fields with proper dimensional quantities and expanding these fields in the small parameter \(\lambda\),

\[P = \frac{V^P}{2a} \frac{\eta}{\lambda^2} \sum_{i=0} \lambda^{2i} P_i, \tag{11a}\]

\[u_s = \frac{V^P}{\lambda} \frac{1}{\lambda} \sum_{i=0} \lambda^{2i} u_{si}, \tag{11b}\]

\[u_s = \frac{1}{2} z(z - \bar{h}) \nabla_s P_0 + \int_0^z \int_0^{z'} f_s dz'' dz' - \frac{z}{\bar{h}} \int_0^{z'} f_s dz'' dz', \tag{14}\]

Then, the velocity perpendicular to the wall can be evaluated by integrating the continuity equation \((12c)\)

\[u_{z0} = -\int_0^z \nabla_s \cdot u_{s0} dz', \tag{15}\]

and using the boundary condition at the surface of the large particle

\[u_{z0}|_{z=h} = -1. \tag{16}\]

The different leading-order powers of \(\lambda\) in the expansion of \(P\), \(u_s\) and \(u_z\) stem from the different orders of various terms in Eqs. \((8)\). By inserting expansion \((11)\) into \((8)\) and collecting terms with the same power of \(\lambda\), a hierarchy of equations corresponding to each order of \(\lambda\) can be obtained. We are particularly interested in the zeroth order terms which satisfy the following leading-order lubrication equations:

\[\frac{\partial P_0}{\partial z} = 0, \tag{12a}\]

\[-\nabla_s P_0 + \frac{\partial^2 u_s}{\partial z'^2} = f_s, \tag{12b}\]

\[\frac{\partial u_{z0}}{\partial z} + \nabla_s \cdot u_{s0} = 0, \tag{12c}\]

where

\[f_s = \frac{4a^2 \lambda}{\eta V^P} F_s. \tag{13}\]

The leading-order hydrodynamic effect is obtained by solving the lubrication equations \((12)\).

### B. Leading order pressure and friction

The momentum equation in the \(z\)-direction \((12a)\) implies that \(P_0\) is independent of \(z\). Using this fact along with the momentum equation in the lateral direction \((12b)\) and the no-slip boundary conditions at the solid surfaces, \(u_{s0}\) can be determined in terms of the pressure field \(P_0\),

\[u_{z0} = \frac{V^P}{\lambda} \frac{1}{\lambda} \sum_{i=0} \lambda^{2i} u_{zi}, \tag{11b}\]

\[u_{s0} = \frac{1}{2} z(z - \bar{h}) \nabla_s P_0 + \int_0^z \int_0^{z'} f_s dz'' dz' - \frac{z}{\bar{h}} \int_0^{z'} f_s dz'' dz', \tag{14}\]

We combine Eqs. \((14)\)–\((10)\) to obtain the lubrication equation for the zeroth order pressure field,

\[\nabla_s \cdot (\bar{h}^3 \nabla_s P_0 + b_s) = -12. \tag{17}\]

The source term \(b_s\) in Eq. \((17)\) is given by

\[b_s(\rho) = \hat{\nabla} f_s(\mathbf{r}), \tag{18}\]

where
\[
\hat{B} f_s = -12 \int_0^{\tilde{h}} \left( \int_0^z \int_0^{z'} f_s dz'' dz' - \frac{z}{\tilde{h}} \int_0^{\tilde{h}} \int_0^{z'} f_s dz'' dz' \right) dz. \tag{19}
\]

In the absence of smaller species (i.e., when \( f_s = 0 \)), well known lubrication equation for the pressure field in a slowly varying gap can be recovered from Eq. (17),
\[
\nabla_s \cdot (\tilde{h}^3 \nabla_s p_L) = -12. \tag{20}
\]
The presence of the smaller spheres produces a pressure correction
\[
p_0 = P_0 - P_L \tag{21}
\]
to the non-dimensional lubrication pressure \( P_L \). The perturbation pressure field \( p_0 \) satisfies the lubrication equation
\[
\nabla_s \cdot (\tilde{h}^3 \nabla_s p_0 + b_s) = 0, \tag{22}
\]
which is obtained by combining Eqs. (17), (20) and (21).

The function \( b_s \) in the above equation plays a key role in our theory. It can be interpreted as the dipolar source density for the far-field lubrication pressure produced by the induced-force distribution \( F_s \).

The correction in friction of the large particle due to the presence of the small spheres has contributions from both perturbation pressure \( p_0 \) and viscous stresses corresponding to the leading order velocity field \( u_0 \). However, comparing the orders of \( \lambda \) in Eq. (11) we conclude that the second contribution is negligible compared to the first one. Thus, the leading order correction in \( \lambda \) to the normal hydrodynamic force acting on the large particle in a solution of small particles stems from the leading-order pressure correction \( p_0 \). As a result, the correction in hydrodynamic force due to the presence of the smaller species can be expressed as
\[
F_0^c = \frac{\eta V^p}{2a} \int p_0 \, d^3 \rho, \tag{23}
\]
where \( p_0 \) is assumed to vanish far away from the contact point.

### IV. DIPOLAR SOURCE DENSITY \( b_s \)

To evaluate the resistance force \( F_0^c \) from Eq. (23), we first need to calculate the lubrication pressure field \( p_0 \). The pressure can be determined from the lubrication equation (22), provided that the dipolar source term (18) is known. In this section, we focus on the key step where we compute the source term \( b_s \) averaged over the positions of small particles.

#### A. Force singularities

The induced force density at the surface of the \( i \)-th sphere is equivalent to a point-force singularity distribution \( F_i \) at the sphere center. This description implies that the induced force density is considered at the surface of an infinitely small hypothetical sphere situated at the center of the \( i \)-th particle. However, the strength of the force density is modified in such a way that only the flow field inside the particle is altered, and the outside flow remains unchanged. Accordingly, the force density for an arbitrary particle \( i \) is
\[
F_i = \frac{\eta V^p}{4a^2 \lambda} \sum_{l_{m\sigma}} f_{l_{m\sigma}} \delta_{l_{m\sigma}} (r - r_i), \tag{24}
\]
where \( r_i \) denotes the position of the center of the particle. The coefficients \( f_{l_{m\sigma}} \) represent the non-dimensional strength of the force singularity and are referred to as the multipolar moments. The force singularities \( \delta_{l_{m\sigma}} \) can be expressed in terms of singular spherical basis solutions of the Stokes equations,
\[
\nabla^2 \nu^r_{l_{m\sigma}} - \nabla p^r_{l_{m\sigma}} = \delta_{l_{m\sigma}}. \tag{25}
\]
The singular spherical basis solutions \( \nu^r_{l_{m\sigma}} \) and pressure solutions \( p^r_{l_{m\sigma}} \) are defined in [9, 10]. These fields satisfy the homogeneous Stokes equation at every point in the flow domain except at the particle center where they are singular and correspond to the point-force singularity \( \delta_{l_{m\sigma}} \).

By considering the cumulative effect from all the spheres, we can compute the statistically averaged normalized force distribution:
\[
F(r) = \frac{\eta V^p}{4a^2 \lambda} \sum_{l_{m\sigma}} f_{l_{m\sigma}}(r) \delta_{l_{m\sigma}} \mu(r - r_0) d^3 r_0, \tag{26}
\]
where the volume fraction of small particles \( \phi \) is given by
\[
\phi = \frac{4\pi}{3} a^3 C. \tag{27}
\]
The force distribution (26) corresponds to the average induced-force density in the ensemble-averaged version of the Stokes equation (2). Equation (26) is valid for an arbitrary distribution of small particles \( \phi \). In our present application the volume fraction is uniform in the available space outside the excluded-volume shells.
B. Local parallel-wall geometry

In order to evaluate the source term $F(r)$, the multipolar moments $f_{lms}$ need to be computed. We obtain these multipolar force distributions by assuming that at the length scale $a \ll b$, the region confined by the large particle and the wall can be locally approximated by the geometry of a channel bounded by two infinite parallel planar walls. For such a geometry, the multipolar moments $f_{lms}$ can be evaluated with high accuracy either using a multiple-scattering technique [13] or a Cartesian-representation algorithm developed in our recent papers [11, 10, 12].

The force multipoles $f_{lms}(r_0)$ are induced as a result of the interaction between the isolated freely moving small sphere situated at $r_0$ and the incident horizontal lubrication flow field $u_{Ls}$ created by motion of the large particle,

$$\frac{\partial^2 u_{Ls}}{\partial z^2} = \nabla_s P_L.$$  \hspace{1cm} (28)

The lubrication pressure $P_L$ satisfies Eq. (20), so that

$$\nabla_s P_L = -\frac{6\rho}{h^3}e_r.$$ \hspace{1cm} (29)

From Eqs. (28) and (29), we find $u_{Ls}$:

$$u_{Ls} = 4A_L \frac{z}{h} \left(1 - \frac{z}{h}\right) \hat{e}_r,$$ \hspace{1cm} (30)

where

$$A_L(\rho) = \frac{3\rho}{4h}.$$ \hspace{1cm} (31)

The amplitude $A_L$ depends on the radial position because both the volume flux and height of the gap are functions of $\rho$.

At the length scale of the small particle diameter, the parabolic lubrication flow (30) can be treated as an external flow coming from infinity in a parallel-wall channel. It is convenient to choose a local coordinate system $(x', y', z'$ with the origin at the center of the small sphere and the $x'$-axis coinciding with the radial direction $e_r$. Hence, the direction of the incident parabolic flow is along the local $x'$ coordinate.

There are three immediate simplifications in the description of $f_{lms}$ for a freely suspended sphere in a parabolic flow. Firstly, the multipolar moments $f_{1\pm 10}$ and $f_{1\pm 11}$ correspond to a Stokeslet and a rotlet, respectively, and therefore they vanish for a force-free and torque-free particle. Secondly, for a parabolic Poiseuille flow (like $u_{Ls}$), the multipolar moments are non-zero only for $m = \pm 1$. Thirdly, our choice of the local coordinates implies that multipolar strength for $m$ is real and is the same as the corresponding value for $-m$. In the following section we evaluate the relevant non-zero coefficients $f_{lms}$ as a function of the gap width and position of the small particle, and we compute the pressure source term.

C. The pressure source term

In order to compute $F_0^s$ from the integral (23), we need to determine $p_0$ in Eq. (22), which involves the dipolar pressure source term $b_s$. We find $b_s$ from $f_s$ by using Eq. (18). Combining Eqs. (13) and (26) along with the proper non-dimensional scaling, we express $f_s$ in the following form:

$$f_s(r) = \frac{3b}{\pi a} \int \phi (r_0) \sum_{lms} f_{lms}(r_0)(I - \hat{e}_z \hat{e}_z) \cdot \delta_{lms}(r - r_0) d^3 r_0,$$ \hspace{1cm} (32)

where $I - \hat{e}_z \hat{e}_z$ is the projection tensor on $x$-$y$ plane. Changing the order of the integrals in Eqs. (18) and (22) we obtain $b_s$:

$$b_s(\rho) = \frac{3b}{\pi a} \int \phi (r_0) \sum_{lms} f_{lms}(r_0) b_{lms}(\rho - r_0) d^3 r_0,$$ \hspace{1cm} (33)

where

$$b_{lms}(\rho - r_0) = (I - \hat{e}_z \hat{e}_z) \cdot \hat{B} \delta_{lms}(r - r_0).$$ \hspace{1cm} (34)

It can be shown that $b_{lms}$ is non-zero only when the following condition is satisfied [13]

$$l + \sigma - |m| \leq 2.$$ \hspace{1cm} (35)

Due to the symmetry of the problem (a parabolic flow in a slit pore), only the terms with $m = \pm 1$ are relevant for our present analysis.

In Appendix A we list the expressions for $\delta_{lms}$ with $m = \pm 1$ and derive the corresponding formulas for the source terms $b_{lms}$, which are obtained by applying the operator $\hat{B}$ directly to $\delta_{lms}$. Our analysis provides a simple derivation of the expressions for the far-field flow resulting from a force singularity in a slit pore. The previously known formulas for the far-field behavior of a Stokeslet [13] and rotlet [13] in a slit pore are special cases of our more general expressions.

Considering Eq. (35) and $m = \pm 1$ for parabolic flows in a slit pore, we find that only $b_{1\pm 10}$, $b_{1\pm 11}$, $b_{1\pm 12}$, $b_{2\pm 10}$, $b_{2\pm 11}$, and $b_{3\pm 10}$ are the nonzero contributions in Eq. (33). Moreover, as pointed out in Sec. IV B we have further simplifications: $f_{1\pm 10} = f_{1\pm 11} = 0$ (freely suspended particle) and $f_{1\pm 12} = 0$ (choice of local coordinates). Hence, only four different coefficients $f_{lms}$
For large gap widths and intermediate positions of the particle where it is neither close to the wall nor near the center of the channel, the curves for different $h$ match with the curve defined by

$$d = 5 \frac{A_L}{h^3} (1 - 2z/h)^2. \quad (40)$$

This can be predicted by calculating the strength of the induced stresslet due to hydrodynamic interactions between a parabolic flow and a sphere in an infinitely wide gap.
V. EVALUATION OF THE EFFECTIVE RESISTANCE FORCE $F_c^0$

In this section, we focus on the evaluation of the correction $F_c^0$ to the hydrodynamic resistance coefficient for the large particle moving near the wall in a solution of small particles. To this end we first determine the pressure field for different ranges of the excluded shell $\bar{\delta}$. The resistance coefficient is then evaluated by integrating the pressure.

A. Evaluation of the pressure field

For a given $d$, we can determine the resistance force $F_c^0$ by combining Eqs. (22), (23) and (38). Here we perform explicit calculations for a model system of spheres interacting via the excluded-shell potential described in Sec. II A. Since in the short-time (high-frequency) limit the ensemble average in Eq. (38) is taken over the equilibrium particle distribution, the volume fraction of small particles is constant in the accessible region,

$$\phi(r) = \phi \quad \text{when} \quad 1/2 + \bar{\delta} < z < \bar{h} - 1/2 - \bar{\delta} \quad (41)$$

and otherwise $\phi = 0$.

Using this model and Eq. (38), we find

$$b_x(\rho) = 12\phi A_L \bar{h}^3 D \hat{e}_\rho, \quad (42)$$

where

$$D = \int_{\frac{1}{2} + \bar{\delta}}^{\bar{h} - \frac{1}{2} - \bar{\delta}} \frac{d(r_0)}{A_L} dz_0. \quad (43)$$

We refer to $D$ as the integrated dipolar strength.

In Fig. 3 we show the magnitude of $D$ as a function of the ratio between the gap width and the diameter of the small particle. Different curves correspond to different values of $\bar{\delta}$. When $h/(2a) \leq 1 + 2\bar{\delta}$ the $D$ is zero because there are no small particles in the gap. The magnitude of $D$ however, increases rapidly to a maximum value when
the gap is wide enough to accommodate the particles. After reaching the maximum, the curves decay with the increasing gap because of the decreasing strength of the induced force multipoles.

When a parabolic flow interacts with a sphere in a large gap, the multipolar moments can be calculated without considering the wall effects. In that case, the form of the induced stresslet in the local shear flow yields

$$D = \frac{5}{3h^2}. \quad (44)$$

Figure 3 shows that the curves approach a slope of $-2$ in the log–log plot for large $h$.

Because of radial symmetry, all associated quantities in Eq. (42) like $A_L$, $\tilde{h}$ and $D$ are functions of the radius $\rho$ only. Hence, $b_s$ can be expressed in terms of the gradient of a scalar

$$b_s(\rho) = \tilde{h}^2 \nabla S(\rho), \quad (45)$$

where

$$\frac{dS}{d\rho} = 12\phi A_L D. \quad (46)$$

Therefore, by substituting Eq. (45) in Eq. (22), we find the perturbative pressure $p_0$:

$$p_0 = -S. \quad (47)$$

As a result, the radial derivative of $p_0$ can be obtained as a radial function by combining Eqs. (46) and (47) along with the expression (41) for amplitude $A_L$ of the incident parabolic lubrication flow

$$\frac{dp_0}{d\rho} = -9\phi \frac{\rho D}{h}. \quad (48)$$

We determine $p_0$ by integrating Eq. (48).

A further simplification can be achieved by noting that in the lubrication region the surface of the large particle is approximately given by

$$\tilde{h}(\rho) = \tilde{h}_0 + \frac{\rho^2}{2}. \quad (49)$$

Assuming (49), the pressure can be expressed as an explicit function of the local gap width:

$$\frac{dp_0}{dh} = -9\phi \frac{D}{h}. \quad (50)$$

In Fig. 4 the perturbation pressure field is plotted as a function of the gap width for different values of $\delta$. The plateau region of the curves corresponds to $D = 0$ in the region depleted of small spheres because of the geometrical constraints. With the increasing range of the excluded-volume potential $\delta$, the plateau region becomes wider, and a smaller number of particles is accommodated in the lubrication region. As a result $p_0$ decreases with increasing $\delta$.

For a large gap, we find from Eq. (44) that

$$p_0 = \frac{15\phi}{2h^2}. \quad (51)$$

which agrees with the result obtained using Einstein’s formula for the effective viscosity. This asymptotic value is independent of the range of the excluded shell, provided that $\delta \ll h_0$. This behavior is seen in Fig. 4 where for a large gap all the curves coincide with an asymptotic line of a slope of $-2$ in the log–log plot.

### B. Friction correction

We now use Eq. (23) to obtain the correction to the normal friction coefficient of the large particle due to the presence of the smaller species. Owing to the axial symmetry, the integral in Eq. (23) is reduced to the following form with the help of Eq. (49):

$$F_0^\delta = \frac{\pi \eta b^2}{a} \left. \int_{h_0}^{\infty} (p_0 - p_0^\infty) \, dh \right|_{h_0} \quad (52)$$

The force $F_0^\delta$, evaluated from Eq. (52), is presented in Fig. 5 as a function of the minimum separation $h_0$ between the wall and the surface of the large particle. The results are normalized by the product of the volume fraction $\phi$, and the lubrication force $F_0$ acting on the large particle in the absence of the small particles. The normalized correction to the friction force decreases with increasing $\delta$ because fewer spheres are accommodated in the lubrication zone. For a larger gap, the ratio $F_0^\delta/F_0$ approaches a value of $2.5\phi$ for all values of $\delta$. This is evident in Fig. 5 and consistent with Einstein’s formula for the effective viscosity of the dilute colloidal solutions.

### VI. CONCLUSIONS

This article presents a new lubrication theory for analyzing the near-wall dynamics of a large colloidal particle in the presence of smaller particles. Our theory is applied to determine the effect of the smaller species on the hydrodynamic friction of the large particle when it moves in the direction normal to the wall. This effect is quantified in terms of the relative contribution $F_0^\delta$ to short-time (or high-frequency) normal friction force acting on the large particle.

We compute $F_0^\delta$ as a function of the minimum separation between the surface of a large particle and the wall. We model the screened electrostatic repulsion between the solid surfaces in terms of excluded volumes and vary the range of the excluded-volume potential to find its effect on the normal friction. Our results show a decrease in friction with an increase in the excluded volume as the number of smaller particles decreases in the near-contact region.
The key simplification in our formulation stems from the fact that the predominant hydrodynamic effect of the small particles is due to the far-field form of the scattered flow from these particles. Our lubrication theory can be applied to evaluate this far-field velocity (which is basically a pressure-driven Hele–Shaw flow in a slit pore). Our analysis provides a concise derivation of the general far-field solution for the flow produced by an arbitrary force singularity between two parallel walls. This derivation is much simpler and more general than the earlier analyses of the Stokeslet \cite{13} and rotlet \cite{14} flow in a slit pore geometry.

We have verified our theory by comparing our calculations with known limiting results. In particular, when the size of the smaller species is much smaller than the separation between the large particle and the wall, the calculated lubrication pressure field and normal friction correction agree with the expressions obtained by using Einstein’s effective viscosity formulation \cite{6}.

Our analysis can be extended to describe a more general near-contact dynamics of bidisperse suspensions. For example, our lubrication theory can also be applied to cases where non-spherical particles and non-planar walls are involved. In the future, we will focus on such a generalization of the present analysis. We will also describe the effect of Brownian motion on the system dynamics \cite{15}.

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APPENDIX A: INTEGRAL DERIVATION OF FAR-FIELD FLOW IN A SLIT PORE

In this Appendix, we present the integral derivation of the far-field results described in section 3. As a corollary of our derivation, we recover the expressions for the well-known far-field flow solutions due to Stokeslet \cite{13} and rotlet \cite{14}.

First, we list the horizontal component of $\delta_{lm\sigma}$ defined in Eq. (24), expressing the higher order multipoles as derivatives of Stokeslets. For our purpose, we only have to consider $m = \pm 1$ which corresponds to the parabolic flow. Moreover, the only multipolar forces $\delta_{lm\sigma}$ that are relevant are those which give non-zero $b_{lm\sigma}$ in Eq. (31). Hence, we take Eq. (35) into account and only analyze the cases where $l + \sigma < 3$.

For $m = 1$, the horizontal component of the relevant $\delta_{lm\sigma}$ is given below:

$$\delta_{110}(r) = -\frac{2\pi}{3} \frac{\partial^2 \delta}{\partial z^2} e, \quad (A1a)$$

$$\delta_{111}(r) = \frac{2\pi}{3} \frac{\partial \delta}{\partial z} e, \quad (A1b)$$

$$\delta_{112}(r) = \sqrt{\frac{2\pi}{3}} \frac{\partial^2 \delta}{\partial z^2} e, \quad (A1c)$$

$$\delta_{210}(r) = -\sqrt{\frac{\pi}{30}} \frac{\partial \delta}{\partial z} e, \quad (A1d)$$

$$\delta_{211}(r) = -\sqrt{\frac{\pi}{30}} \frac{\partial^2 \delta}{\partial z^2} e, \quad (A1e)$$

$$\delta_{310}(r) = \sqrt{\frac{3\pi}{4725}} \frac{\partial^2 \delta}{\partial z^2} e, \quad (A1f)$$

where $\delta(r)$ is the Dirac-delta function and the superscript $\parallel$ denotes the projection of the vector on $x$-$y$ plane. The vector $e$ is defined as

$$e = e_x + ie_y \quad (A2)$$

(except for normalization $e$ is identical to $e_{+1}$ defined in (16)). For $m = 1$, the source terms $\delta_{lm\sigma}$ are the complex conjugates of $\delta_{11\sigma}$. Therefore, we only focus on the force distribution described in Eq. (A1).

In the above expressions for $\delta_{lm\sigma}$, $\delta$, and the derivatives $\partial \delta/\partial z$ and $\partial^2 \delta/\partial z^2$ appear in addition to the combinatorial coefficients. Hence, in order to obtain $b_{lm\sigma}$ by using Eqs. (31) and (A1) we derive the following relations by evaluating the integrals in the definition of operator $\hat{B}$ in Eq. (19):

$$\hat{B} \delta(r - r_0) = 6z_0(h - z_0)\delta(\rho - \rho_0) \quad (A3a)$$

$$\hat{B} \frac{\partial}{\partial z} \delta(r - r_0) = -6(h - 2z_0)\delta(\rho - \rho_0) \quad (A3b)$$

$$\hat{B} \frac{\partial^2}{\partial z^2} \delta(r - r_0) = -12\delta(\rho - \rho_0) \quad (A3c)$$

By combining relations (A1) and (A3) with Eq. (31) we find

$$b_{11\sigma}(r, r_0) = b_{11\sigma}^+(r, r_0) = d_{1\sigma}(r_0) e\delta(\rho - \rho_0), \quad (A4)$$

where

$$d_{10} = -2\sqrt{6\pi z_0(h - z_0)}, \quad (A5a)$$

$$d_{11} = -2\sqrt{6\pi(h - 2z_0)}, \quad (A5b)$$

and the remaining nonzero coefficients are given by Eq. (37). The relations (A5a) and (A5b) are associated with the far-field Hele–Shaw flow produced by a Stokeslet and a rotlet in parallel-plate geometry. Resulting expressions for $b_{110}$ and $b_{111}$ are in agreement with Liron–Mochon’s \cite{13} and Hackborn’s \cite{14} expressions for the far-field solutions whereas the other $b_{lm\sigma}$ described in the article are equivalent to the coefficients derived in our earlier paper \cite{6} by using a more complicated matrix representation.
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