ELECTRO-VISCOUS INTERACTIONS BETWEEN SEDIMENTING PARTICLES

Ehud Yariv*[a)], Itzchak Frankel** & Ory Schnitzer*
*Department of Mathematics, Technion — Israel Institute of Technology, Technion City 32000, Israel
**Department of Aerospace Engineering, Technion — Israel Institute of Technology, Technion City 32000, Israel

Summary Colloidal particles moving in electrolyte solutions experience electro-viscous forces driven by osmotic perturbation to the driving Stokes flow. This phenomenon is manifested in irreversible repulsion between a pair of spherical particles sedimenting side-by-side in an unbounded fluid domain. At near-contact separations, the singular pressure associated with particle counter-rotation leads to a large salt polarization within the narrow gap. This results, through osmotic slip, in particle repulsion scaling inversely with the second power of gap separation.

INTRODUCTION

Electrokinetic phenomena generically reflect distortion of mechanical equilibrium within the diffuse Debye layer surrounding charged solid surfaces suspended in liquid electrolytes. One such mechanism is streaming potential, driven by an imposed Stokes flow. Flow within the thin Debye layer generate effective surface currents of both charge and salt. Since these are generally nonuniform, charge and salt conservation necessitates comparable currents from the electro-neutral 'bulk' surrounding this layer, resulting in bulk electric field and salt polarization. These, in turn, lead to osmotic slip, manifested in electrokinetic flow above and beyond the original driving flow. The resulting "electro-viscous" forces may be the key to resolving paradoxes manifested in a variety of low-Reynolds-number experimental observations which are apparently inconsistent with established properties of Stokes flows [1].
The proper modeling of streaming-potential phenomena in the limit of thin double layers has been a matter of ongoing controversy [2, 3]. In a recent paper [4] we have demonstrated that the product the Hartmann and Péclet Pe numbers scales as δ^{-2} ($\delta \ll 1$ being the dimensionless Debye thickness) thereby resolving part of the confusion. Most of that paper has dealt with the large-Pe limit, usually appropriate to particles moving under imposed shear flows.

MODERATE-Pe MACROSCALE MODEL

In sedimentation problems, Pe is actually moderate. We have accordingly developed a companion thin-double-layer scheme for $O(1)$ Péclet numbers, where the Debye-layer physics appears as effective 'boundary' conditions. We consider a generic problem animated by the imposed Stokes flow (magnitude v^*) of a symmetric electrolyte (valencies $\pm z$, viscosity μ^*, dielectric permittivity ϵ^*) around charged solid surfaces (typical dimension a^*). Far from the surfaces the two ionic concentrations approach the equilibrium value c^* and the electric field vanishes. The macroscale model governing the transport in the electro-neutral bulk outside the Debye layer is described in a dimensionless notation, where electric potentials are normalized by the thermal voltage $\varphi^* = k^*T^*/\mathscr{Z}e^*$ (wherein k^*T^* is the Boltzmann temperature and e^* the elementary charge), the salt concentration c by c^*, the velocity $\mathbf{v}$ by v^*, and the pressure p by μ^*v^*/a^*. In this bulk region the following expansion hold:

$$\varphi = \delta^2\varphi_2 + \cdots, \quad c = 1 + \delta^2 c_2 + \cdots, \quad \mathbf{v} = \mathbf{v}_0 + \delta^2\mathbf{v}_2 + \cdots, \quad p = p_0 + \delta^2 p_2 + \cdots. \tag{1}$$

Here $(\mathbf{v}_0, p_0)$ is the driving Stokes flow, satisfying no-slip on the solid surface and approaching the imposed flow at infinity, while the induced flow $(\mathbf{v}_2, p_2)$, which also satisfies the Stokes equations, decay at large distances. The harmonic potential φ_2 and salt concentration c_2 also decay at infinity; the latter is governed by the advection–diffusion equation

$$\nabla^2 c_2 = \mathrm{Pe}\left(\frac{\partial c_2}{\partial t} + \mathbf{v_0}\cdot\nabla c_2\right), \tag{2}$$

in which $\mathrm{Pe} = a^*v^*/D^*$, D^* being the ionic diffusivity. The appropriate boundary conditions reflect matching with the Debye-layer fields. Thus, both φ_2 and c_2 are governed by *inhomogeneous* Neumann conditions

$$\frac{\partial\varphi_2}{\partial n} = \zeta\,\mathrm{Pe}\frac{\partial p_0}{\partial n}, \quad \frac{\partial c_2}{\partial n} = -\mathscr{H}(\zeta)\,\mathrm{Pe}\frac{\partial p_0}{\partial n}. \tag{3}$$

while the velocity is driven by the effective slip condition

$$\mathbf{v}_2 = \frac{\alpha}{\mathrm{Pe}}\left\{\zeta\boldsymbol{\nabla}_s\varphi_2 - \mathscr{H}(\zeta)\boldsymbol{\nabla}_s c_2\right\}. \tag{4}$$

In these, the the 'zeta potential' ζ is the voltage drop (normalized by φ^*) across the debye layer, $\mathscr{H}(\zeta) = -2\ln\left(1-\tanh^2(\zeta/4)\right)$, $\boldsymbol{\nabla}_s$ is the surface gradient, and $\alpha = \epsilon^*{\varphi^*}^2/\mu^*D^*$. This parameter is independent of particle dimension and salt concentration; it is ≈ 0.5 for typical ionic diffusivities.

a) Corresponding author. E-mail: udi@technion.ac.il.

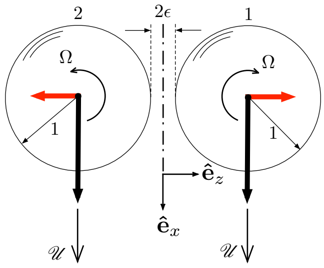

Figure 1. Two identical spheres sedimenting perpendicularly to their line of centers. In the absence of electrokinetic effects the particles settle in the external-force direction with velocity $\mathscr{U}^*$ and counter-rotate with angular velocities $\pm\Omega^*$. In an electrolyte solution, the associated flow induces an electro-viscous repulsive force between the charged particles.

ILLUSTRATION: TWO PARTICLES SEDIMENTING SIDE-BY-SIDE

Consider two identical torque-free spherical particles (radius a^*) settling perpendicularly to their line of centers under an external force F^* (gravity, buoyancy, etc.) in an otherwise quiescent unbounded fluid. In standard Stokes flows (i.e. in the absence of electrokinetic effects), simple symmetry arguments show that the particles retain a constant separation distance; the particles settle with equal velocities $\mathscr{U}^*$ along the force direction and counter-rotate with an angular speed Ω^*. For a given separation, these rigid-body velocities are determined by the specified force together with the vanishing of the torque. As usual in Stokes flows, the velocities are linear in the external force, i.e. the motion is reversible.

For charged particles settling in an electrolyte, electro-viscous forces upset this reversibility, giving rise to a nonlinear repulsive force $\mathscr{R}$, at $O(\delta^2)$, acting along the line of centers. This force was calculated by [5] for large Péclet numbers, where it was dominated by Maxwell stresses [2, 4]. In what follows we employ the present moderate-Péclet-number macroscale model to calculate particle repulsion using F^*/μ^*a^* as the velocity scale v^*.

The leading-order field $(\mathbf{v}_0, p_0)$, corresponding to the flow in the absence of electrokinetic effects, is considered as known. The electro-viscous force on a particle is calculated by integrating the viscous stresses corresponding to the flow perturbation $\mathbf{v}_2$ on the particle surface. In principle, this flow depends on both the streaming potential φ_2 and the salt-concentration perturbation c_2. However, owing to the linearity of the governing problem the flow perturbation $(\mathbf{v}_2, p_2)$ can be superposed of two subfields: one induced by streaming-potential gradients (electro-osmotic flow) and the other induced by salinity gradients (diffusio-osmotic flow). While the electro-osmotic subfield is clearly linear in the driving flow, the diffusio-osmotic subfield is *nonlinear*, by virtue of the presence of the advection term in (2) governing c_2. By symmetry arguments, it is readily verified that only terms which are nonlinear in the driving flow may contribute to repulsion [5]. Thus it is sufficient to consider only the diffusio-osmotic part of the flow perturbation, with no need to calculate the streaming potential φ_2.

We focus upon the near-contact limit $\epsilon \ll 1$ (but still $\delta \ll \epsilon$), which is naturally analyzed using a lubrication approximation. This limit was already addressed in the large-Pe régime [5]. The driving flow $\mathbf{v}_0$ was analyzed in the near-contact limit by [6] in a laboratory-fixed reference frame, where it was decomposed into two parts: (i) two particles translating with velocity $\mathscr{U}_0$ perpendicular to their line of centers without rotating, (ii) two particles counter-rotating with velocities $\pm\Omega_0$ without translation. These two parts differ significantly: while the former problem is described at leading order by simply setting $\epsilon = 0$ (i.e. two spheres touching), the latter is singular in ϵ (due to the intense shear rate within the narrow gap) and therefore requires the use of matched asymptotic expansions, with an $O(\epsilon^{-3/2})$ large pressure within the inner gap region. The intense pressure gives rise to a singular salt polarization within the narrow gap of the same order; due to symmetry, however, it is only the salt perturbation of $O(\epsilon^{-1})$ that contributes to leading-order repulsion, scaling as ϵ^{-2}

$$\mathscr{R} = \frac{6\pi}{25}\epsilon^{-2}\alpha\mathscr{H}^2(\zeta)\mathrm{Pe}\,\Omega_0^2. \tag{5}$$

Note the nonlinear dependence upon Ω_0. Remarkably, no need arises to explicitly solve for the salt perturbation since the linear operator acting on it appears in the forcing term of the equation governing the pressure perturbation.

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