Electrokinetic phenomena in particulate suspensions

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Interactions in dispersed systems

Sedimentation of orientable and deformable particles

Particle dynamics and interactions in electric fields

Pattern formation in swimming suspensions

Gravity-driven suspension jets

Dynamics of confined flexible polymers
Outline

- Review of basic electrokinetics
  - the EDL and electroosmotic flow
  - electrophoresis of an isolated sphere
  - dielectrophoresis and induced-charge electrophoresis

- Particle interactions in sphere suspensions
  - pair interactions
  - multiparticle simulations

- Non-spherical particles
  - arbitrary shapes
  - rodlike particles

- Bounded systems
  - electrophoresis
  - nonlinear interactions
Basic electrokinetics
The electrical double-layer (EDL)

\[ n_+ = n_\infty \]

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The Poisson-Boltzmann equation

- **Steady Nernst-Planck equation** for species \( i \):
  
  \[
  0 = -n_i \nu_i z_i F e \nabla \psi - D_i \nabla n_i
  \]

  Nernst-Einstein relation: 
  \[
  D_i = \frac{\nu_i k T F}{e}
  \]

  \[
  -\frac{z_i e}{k T} \frac{d \psi}{d y} = \frac{1}{n_i} \frac{d n_i}{d y}
  \]

  Boundary conditions: 
  \[
  \begin{align*}
  \psi &\rightarrow 0 \quad \text{as} \quad y \rightarrow \infty \\
n_i &\rightarrow n_i^\infty \quad \text{as} \quad y \rightarrow \infty
  \end{align*}
  \]

  It is easily integrated as: 
  \[
  n_i = n_i^\infty \exp \left( -\frac{z_i e \psi}{k T} \right) \quad \text{(Boltzmann distribution)}
  \]

- **Poisson equation** for the potential: 
  \[
  \nabla^2 \psi = -\frac{\rho e}{\varepsilon}
  \]

  Poisson-Boltzmann equation: 
  \[
  \frac{d^2 \psi}{d y^2} = -\frac{e}{\varepsilon} \sum_{i=1}^{N} z_i n_i^\infty \exp \left( -\frac{z_i e \psi(y)}{k T} \right)
  \]

  For a symmetric electrolyte: 
  \[
  \frac{d^2 \psi}{d y^2} = \frac{2 e z n_\infty}{\varepsilon} \sinh \left( \frac{z e \psi}{k T} \right)
  \]

- **Debye-Hückel approximation:** 
  \[
  \frac{z e \psi}{k T} \ll 1 \quad \psi(y) = \psi_w \exp \left( -y/\lambda_D \right) \quad \lambda_D = \left[ \frac{\varepsilon k T}{2 e^2 z^2 n_\infty} \right]^{1/2}
  \]
Electroosmotic flow

- **Stokes equation** with electric body force:
  
  \[ -\mu \nabla^2 u + \nabla p = \rho_0 E_0 \]
  
  \[ \rho_0 = -\varepsilon \nabla^2 (\Phi_0 + \psi) \]

  For a (locally) uniform field:
  
  \[ \nabla^2 \left( u - \frac{\varepsilon \psi}{\mu} E_0 \right) = \frac{1}{\mu} \nabla p \]

  In the absence of an external pressure gradient, a solution is

  \[ u - \frac{\varepsilon \psi}{\mu} E_0 = -\frac{\varepsilon \zeta}{\mu} E_0 \]

  i.e.

  \[ u = -\frac{\varepsilon \zeta}{\mu} \left( 1 - \frac{\psi(y)}{\zeta} \right) E_0 \]

- On length scales much larger than the Debye length (\( y \gg \lambda_D \)):

  \[ u \approx u_s = -\frac{\varepsilon \zeta}{\mu} E_0 \]

  **Smoluchowski equation** for effective slip velocity

  *IMA, December 5 2009*
Electrophoresis: electric problem

- Laplace’s equation for electric potential outside of the EDL:
  \[ \nabla^2 \phi = 0 \quad E = -\nabla \phi \]
  BC’s:
  \[ \begin{align*}
  n \cdot \nabla \phi &= 0 \quad \text{on } S \\
  \nabla \phi &\to -E_0 \quad \text{as } |x| \to \infty
  \end{align*} \]

- Solution obtained from potential theory (or spherical harmonic expansion):
  \[ \phi(x) = -x \cdot E_0 - \frac{1}{2} \left( \frac{a}{x} \right)^3 x \cdot E_0 \]
  \[ E(x) = E_0 - \frac{1}{2} \left( \frac{a}{x} \right)^3 \left( 3 \frac{x x}{x^2} - 1 \right) \cdot E_0 \]

- Surface electric field and slip velocity (Smoluchowski equation):
  \[ E_s = \frac{3}{2} (1 - nn) \cdot E_0 \]
  \[ u_s = -\frac{\varepsilon \zeta}{\mu} E_s = -\frac{3\varepsilon \zeta}{2\mu} (1 - nn) \cdot E_0 \]
Electrophoresis: flow problem

- **Stokes equations with slip velocity BC:**
  
  \[-\mu \nabla^2 \mathbf{u} + \nabla p = 0, \quad \nabla \cdot \mathbf{u} = 0\]

  BC's:
  \[
  \begin{aligned}
  \mathbf{u} &= \mathbf{U} + \mathbf{\Omega} \times \mathbf{x} + \mathbf{u}_s \quad \text{on } S \\
  \mathbf{u} &\to 0 \quad \text{as } |\mathbf{x}| \to \infty
  \end{aligned}
  \]

  \[\mathbf{u}_s = -\frac{\varepsilon \zeta}{\mu} \mathbf{E}_s = -\frac{3\varepsilon \zeta}{2\mu} (1 - n n) \cdot \mathbf{E}_0\]

  Force and torque balance:

  \[
  \begin{align*}
  \mathbf{F} &= \int_S \boldsymbol{\sigma} \cdot n \, dS = 0 \\
  \mathbf{T} &= \int_S \mathbf{x} \times (\boldsymbol{\sigma} \cdot n) \, dS = 0
  \end{align*}
  \]

- **Solution by method of singularities:**

  \[
  \mathbf{U} = -\frac{1}{4\pi a^2} \int_S \mathbf{u}_s \, dS = \frac{\varepsilon \zeta}{\mu} \mathbf{E}_0
  \]

  \[
  \mathbf{u}(\mathbf{x}) = \frac{1}{2} \left(\frac{a}{x}\right)^3 \left(3 \frac{\mathbf{x} \mathbf{x}}{x^2} - 1\right) \cdot \mathbf{U}
  \]

  (potential dipole flow, irrotational)

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Arbitrary Debye layers

- **Henry solution (1931):**

\[
U = \frac{2 \varepsilon \zeta}{3 \mu} f(\alpha) E_0 \quad \alpha = \frac{a}{\lambda_D}
\]

\[
\begin{aligned}
\alpha < 1 : \quad f(\alpha) &= 1 + \frac{1}{16} \alpha^2 - \frac{5}{48} \alpha^3 - \frac{1}{96} \alpha^4 + \frac{1}{96} \alpha^5 + \frac{1}{8} \alpha^4 e^\alpha \left(1 - \frac{\alpha^4}{12}\right) \int_\alpha^\infty \frac{e^{-t}}{t} \, dt \\
\alpha \geq 1 : \quad f(\alpha) &= \frac{3}{2} - \frac{9}{2\alpha} - \frac{75}{2\alpha^2} - \frac{330}{\alpha^3}
\end{aligned}
\]

\[
U \to \frac{2 \varepsilon \zeta}{3 \mu} E_0 \quad \text{as } \alpha \to 0
\]

(thick Debye layer)

\[
U \to \frac{\varepsilon \zeta}{\mu} E_0 \quad \text{as } \alpha \to \infty
\]

(thin Debye layer)
Dielectrophoresis

A dielectric force/torque can arise when a particle is placed in a nonuniform electric field.

Maxwell stress tensor:

\[ \Sigma^m = \varepsilon \left( EE - \frac{1}{2} E^2 I \right) \]

DEP force and torque:

\[ F = \int_S (\Sigma^m \cdot n) dS \quad T = \int_S (x - x_c) \times (\Sigma^m \cdot n) dS \]  

(\[ T = 0 \] for a sphere)

They are most easily obtained by means of multipolar expansions:

External potential:

\[ \phi^e(x) = \phi_0 - x \cdot E_0 - \frac{1}{2} xx : G_0 - \frac{1}{6} x xx : H_0 - \ldots \]

Disturbance potential:

\[ \phi^d(x) = \frac{1}{4\pi \varepsilon} \left[ \frac{q}{r} + \frac{x \cdot p}{x^3} + \frac{1}{2} \frac{x xx : Q}{x^5} + \ldots \right] \]

\[ p = -2\pi \varepsilon a^3 E_0 \quad Q = -\frac{8\pi \varepsilon a^5}{3} G_0 \]

\[ F = qE_0 + p \cdot G_0 + \frac{1}{6} Q : H_0 + \ldots \quad T = p \times E_0 + \ldots \]

In a linear electric field:

\[ F = -2\pi \varepsilon a^3 E_0 \cdot G_0 = -\pi \varepsilon a^3 \nabla |E|^2 \]
Induced-charge electrophoresis


A polarizable particle in an electric field attracts counterions, that accumulate near its surface, forming a non-uniform electric double layer (EDL).

At steady state, the particle and its EDL behave like an insulator. Electric potential satisfies:

\[ \nabla^2 \Phi = 0 \]

\[
\begin{cases}
  n \cdot \nabla \Phi = 0 & \text{as } r \in \partial S \\
  \nabla \Phi \to -E_\infty & \text{as } r \to \infty
\end{cases}
\]

Potential drop across the EDL modifies the \( \zeta \)-potential:

\[ \zeta = \zeta_0 - \Phi_s \]

A fluid flow (solution of the Stokes equations) is driven by the slip on the surface:

\[ u_s = -\frac{\epsilon \zeta}{\mu} \mathbf{E}_s \]

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Induced-charge electrophoresis


- **Electric problem:** same solution as previously for standard EP

\[
\phi(x) = -x \cdot E_0 - \frac{1}{2} \left( \frac{a}{x} \right)^3 x \cdot E_0 \\
E(x) = E_0 - \frac{1}{2} \left( \frac{a}{x} \right)^3 \left( 3 \frac{x x}{x^2} - 1 \right) \cdot E_0
\]

- **Effective zeta-potential and slip velocity:**

\[
\zeta(x) = \frac{3}{2} a n \cdot E_0 \\
E_s(x) = \frac{3}{2} (1 - nn) \cdot E_0
\]

\[
u_s(x) = -\frac{9 \varepsilon a}{4 \mu} (1 - nn) \cdot E_0 E_0 \cdot n
\]

- **Flow problem:** velocity field driven by the slip velocity

\[
u(x) = \frac{9 \varepsilon a^3}{8 \mu} \left( 1 + \frac{a^2}{6} \nabla^2 \right) S(x) \cdot E_0 E_0
\]

“stresslet”: \( S_{ijk}(x) = -\frac{\delta_{ij} x_k}{x^3} + \frac{\delta_{ik} x_j}{x^3} + \frac{\delta_{jk} x_i}{x^3} - 3 \frac{x_i x_j x_k}{x^5} \)

No longer a potential flow!
Particle interactions
Interactions in electrophoresis

Governing equations:

- **Electric problem**
  \[
  \nabla^2 \phi = 0
  \]
  \[
  \begin{aligned}
  \nabla \phi &\to -E_0 \quad \text{as } |x| \to \infty \\
  n_\alpha \cdot \nabla \phi & = 0 \quad \text{on } S_\alpha
  \end{aligned}
  \]

- **Flow problem**
  \[
  -\mu \nabla^2 u + \nabla p = 0, \quad \nabla \cdot u = 0
  \]
  \[
  \begin{aligned}
  u & = U_\alpha + \Omega_\alpha \times x_\alpha + u^\alpha_s \quad \text{on } S_\alpha \\
  u &\to 0 \quad \text{as } |x| \to \infty
  \end{aligned}
  \]
  \[
  u^\alpha_s = -\frac{\varepsilon \zeta_\alpha}{\mu} E
  \]
  \[
  F_\alpha = \int_{S_\alpha} \sigma \cdot n_\alpha \, dS = 0 \quad T_\alpha = \int_{S_\alpha} x \times (\sigma \cdot n_\alpha) \, dS = 0
  \]

No analytical solution for arbitrary configurations, even for only two particles!
Method of reflections: introduction

The method of reflections in asymptotic method for large separations, which iteratively corrects the potential induced by the sphere to satisfy the no-flux BC on the sphere surfaces.

\[ \phi \approx \phi^{(0)} + \phi^{(1)} + \phi^{(2)} + \phi^{(2)} + \ldots \]

\[ \phi^{(j)} \] is the potential disturbance induced by particle \( \alpha \) when placed in

\[ \phi^{(j-1)} \]

\( \phi^{(j)} \) is the potential disturbance induced by particle \( \alpha \) when placed in \( \phi^{(j-1)} \).

It is obtained using the following, which expresses the disturbance \( \phi^d(x) \) induced by an insulating sphere in the external potential \( \phi^e(x) \):

\[
\begin{cases}
\phi^e(x) = \phi^e(0) + x \cdot \nabla \phi^e(0) + \frac{1}{2} xx : \nabla \nabla \phi^e(0) + \ldots \\
\phi^d(x) = \frac{1}{2} \left( \frac{a}{x} \right)^3 x \cdot \nabla \phi^e(0) + \frac{1}{3} \left( \frac{a}{x} \right)^5 xx : \nabla \nabla \phi^e(0) + \ldots
\end{cases}
\]

More accurate methods:

- method of twin multipole expansions
- boundary-element methods
Interactions in electrophoresis

Relative motion of two spheres in electrophoresis:

**Assumptions:** thin Debye layer, weak applied field, zero polarizability, no surface conduction.

Reed & Morrison, *J. Colloid Interface Sci.*, 54 117 (1976)


\[
U_1 = \frac{\varepsilon \zeta_1}{\mu} E_0 + \frac{\varepsilon (\zeta_2 - \zeta_1)}{\mu} \left[ \frac{1}{2} \frac{a_2^3}{r^3} (3ee - 1) + \frac{1}{4} \frac{a_1^3 a_2^3}{r^6} (27ee - 1) \right] \cdot E_0 + O(r^{-8})
\]

⇒ No relative motion for particles with same zeta potential!

This result holds for any number of particles with same zeta potential, regardless of size.

**Consequences:** no relative motions, no separation, no hydrodynamic dispersion, little fluid mixing.
Nonlinear interactions

If some assumptions are relaxed, nonlinear EK phenomena may arise and result in relative motions. Here we focus on:

- **dielectrophoresis** (moderate fields): distortion of the electric field by the particles creates field gradients, leading to non-zero DEP forces;

- **induced-charge electrophoresis** (moderate fields, polarizable particles): disturbance flows induced by ICEP result in relative motions by symmetry breaking.

\[
\begin{align*}
U_{\text{DEP/ICEP}} &= O \left( \frac{\varepsilon a E_0^2}{\mu} \right) \\
U_{\text{EP}} &= O \left( \frac{\varepsilon \zeta E_0}{\mu} \right)
\end{align*}
\]

DEP and ICEP become significant when

\[
\frac{a E_0}{\zeta} = O(1)
\]

In a typical experiment:

\[
\begin{align*}
E_0 &\sim 10 - 100 \text{ V/cm} \\
a &\sim 1 - 10 \text{ \(\mu\)m} \\
\zeta &\sim 10 - 100 \text{ mV}
\end{align*}
\]

\[
\frac{a E_0}{\zeta} \sim 0.01 - 10
\]
Pair interactions

Force on sphere 1, relative velocity, and angular velocity:

\[
\begin{align*}
F &= 4\pi \varepsilon a^2 \mathbf{F}(\lambda, \hat{R}) : E_0 E_0 \\
U &= \frac{\varepsilon a}{\mu} \mathbf{M}(\lambda, \hat{R}) : E_0 E_0 \\
\Omega &= \frac{\varepsilon}{\mu} \mathbf{W}(\lambda, \hat{R}) : E_0 E_0
\end{align*}
\]

where \( \lambda = 2a/R \in [0, 1] \) \( \hat{R} = R/R \)

\[
\begin{align*}
F_{ijk}(\lambda, \hat{R}) &= f(\lambda)(\delta_{ij} \hat{R}_k + \delta_{ik} \hat{R}_j) + g(\lambda) \hat{R}_i \delta_{jk} \\
&\quad + h(\lambda) \hat{R}_i \hat{R}_j \hat{R}_k \\
M_{ijk}(\lambda, \hat{R}) &= l(\lambda)(\delta_{ij} \hat{R}_k + \delta_{ik} \hat{R}_j) + m(\lambda) \hat{R}_i \delta_{jk} \\
&\quad + n(\lambda) \hat{R}_i \hat{R}_j \hat{R}_k \\
W_{ijk}(\lambda, \hat{R}) &= w(\lambda) \varepsilon_{ijk} \hat{R}_l \hat{R}_k
\end{align*}
\]

Unknown functions of \( \lambda \) were obtained by (i) method of reflections, (ii) method of twin multipole expansions, (iii) boundary-element calculations.

Relative motion and pairing dynamics

Radial velocity between two spheres:

\[ \frac{U \cdot \hat{R}}{U_0} = [2l(\lambda) + n(\lambda)] \cos^2 \Theta + m(\lambda) \]

Far-field flow disturbance

Flow field generated by a pair of interacting spheres:

- **Standard electrophoresis**

  \[ u^{\text{EP}}(x) \approx \frac{\varepsilon \zeta}{\mu} \left( \frac{a}{r} \right)^3 (3\hat{x}\hat{x} - 1) : E_0 \]

  Potential flow, irrotational, fast decay

- **Dielectrophoresis**

  \[ u^{\text{DEP}}(x) \approx \frac{1}{2} \frac{\varepsilon R}{\mu} \left( \frac{a}{r} \right)^2 \left[ \hat{x}\hat{R} + \hat{R}\hat{x} - (\hat{x} \cdot \hat{R})(1 + 3\hat{x}\hat{x}) \right] \cdot F(\lambda, \hat{R}) : E_0 E_0 \]

  Stokes dipole flow, rotational, slow decay

- **Induced-charge electrophoresis**

  \[ u^{\text{ICEP}}(x) \approx \frac{9}{4} \frac{\varepsilon a}{\mu} \left( \frac{a}{r} \right)^2 \hat{x}(1 - 3\hat{x}\hat{x}) : E_0 E_0 \]

  Stokes dipole flow, rotational, slow decay

Multiparticle simulations

Park & Saintillan, in preparation (2009)

- **Far-field velocities** from the method of reflections are rewritten in terms of fundamental solutions of the Stokes equations. They are then calculated in periodic boundary conditions using an efficient Smooth Particle-Mesh Ewald (SPME) algorithm with $N\log(N)$ scaling, allowing the simulation of very large systems.


- **Near-field velocities** are corrected pairwise using the method of twin multipole expansions (using the tabulated functions $l(\lambda)$, $m(\lambda)$, and $n(\lambda)$ and cubic spline interpolation).

- **Excluded volume interactions** are resolved using a contact algorithm (no artificial repulsive forces).
Smooth Particle-Mesh Ewald algorithm


We want to evaluate sums of the form:

\[ u(x_i) = \sum_{j=1}^{N} \sum_{p} G(x_i - x_j + p) F_j \]

This can be recast into the Ewald summation formula (Hasimoto 1959):

\[ u(x_i) = \sum_{j=1}^{N} A(x_i - x_j, \alpha) F_j + \sum_{k} e^{-2\pi ik \cdot x} B(k, \alpha) \hat{F}_k \]

with:

\[ \hat{F}_k = \sum_{j=1}^{N} e^{2\pi ik \cdot x_j} F_j \]

- **REAL SUM** (short-range interactions): Evaluated directly over nearest neighbors.
- **FOURIER SUM** (smooth long-range interactions): Evaluated on a Cartesian grid using the Fast Fourier Transform. Interpolation to and from the grid is done using Cardinal B-splines.

*Total cost in \( O(N \log N) \)*
Dynamics in suspension

Dynamics in a periodic suspension with no linear EP (ICEP and DEP only)
Electric field points in the z-direction

100 particles

\[ \phi = 0.052 \]
\[ L_x \times L_y \times L_z = 20^3 \]

200 particles

\[ \phi = 0.105 \]
\[ L_x \times L_y \times L_z = 20^3 \]
Pairing dynamics
Pair distribution functions

- Pairing regions at the poles
- Depletion at the equator
- Weaker pairings at high volume fractions owing to stronger fluctuations
- Qualitative agreement with previous studies on rod suspensions


Hydrodynamic dispersion

- Particle/particle interactions result in chaotic and hydrodynamic diffusion at long times.
- Track mean square displacements as a function of time: $\langle (x(t) - x_0)(x(t) - x_0) \rangle$

(a) linear

(b) log-log

- Ballistic regime ($\sim t^2$) at short times.
- Diffusive regime ($\sim t$) at long times.

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Hydrodynamic dispersion

Hydrodynamic diffusion tensor: \[ D = \lim_{t \to \infty} \frac{d}{dt} \langle (\mathbf{x} - \mathbf{x}_0)(\mathbf{x} - \mathbf{x}_0) \rangle \]

- Anisotropic diffusivities
  \[ \frac{D_{zz}}{D_{xx}} \approx 3.2 \]

- Increase at low volume fractions: stronger hydrodynamic interactions between particles.

- Decrease at high volume fractions: hindered diffusion due to excluded volume and more frequent pairings.
Velocity statistics

\[ \phi = 0.01465 \]

\[ \phi = 0.117 \]

- \( \sigma_{u_x} < \sigma_{u_z} \)

- Non-Gaussian tails, especially in the transverse direction.

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Velocity statistics

Particle velocity standard deviation

\[ \sigma_{u_x}, \sigma_{u_z} \sim \phi^{0.46} \]

\[ \frac{\sigma_{u_z}}{\sigma_{u_x}} \approx 1.46 \]
Summary

- Standard linear electrophoresis does not result in relative motions for particles with identical zeta-potentials (electrophoretic velocity is unchanged by interactions).

- Dielectrophoresis and induced-charge electrophoresis can both result in relative motions in suspensions of spheres undergoing electrophoresis (moderate particle size or field strength, or low native zeta potential).

- These interactions can be either attractive (particles aligned with field direction) or repulsive (particles aligned in transverse direction), and will result in transient particle pairings in suspension.

- Computer simulations confirm particles pairings, which are clearer in dilute suspensions. They also manifest strong hydrodynamic diffusion and velocity fluctuations.
Anisotropic particles
Electrophoresis of nonspherical particles

In classical electrophoresis (thin Debye layer limit), the velocity of an isotropic (nonspherical) particle is still given by:

\[ U^{EP} = \frac{\epsilon \zeta}{\mu} E_0 \]

No rotation occurs.

Morrison, J. Colloid Interface Sci., 34 210 (1970)
Anisotropic particles are subject to an electrorotational (DEP) torque, causing them to align in the direction of the field.

For a slender axisymmetric particle:

\[ \phi(x) = -x \cdot E_0 + \frac{1}{4\pi \varepsilon} \frac{p \cdot x}{x^3} + ... \]

\[ p = \frac{8}{3} \pi \varepsilon l^3 \alpha^2 \mathbf{P} \cdot E_0 \]

\[ T = p \times E_0 \]

\[ \Omega = \frac{3 \log 2 \gamma}{8\pi \mu l^3} T = \frac{\varepsilon \log 2 \gamma}{\mu \gamma^2} (\mathbf{P} \cdot E_0) \times E_0 \]

Han & Yang, *J. Colloid Interface Sci.*, 177 132 (1996)

ICEP of nonspherical particles

Slightly deformed cylinder:

\[ R(\theta) = a[1 + \epsilon P_3(\cos \theta)] \]

External potential:

\[ \phi^e(r, \theta) = -E_0 r \cos(\theta - \gamma) \]

Squires & Bazant,


\[ U_{\text{ICEP}} = -\frac{5}{8} \epsilon \left( \frac{\varepsilon a E_0^2}{\mu} \right) [\cos(-2\gamma)\hat{x} + \sin(-2\gamma)\hat{y}] \]
ICEP of nonspherical particles

$P_2(\cos \theta)$  $P_3(\cos \theta)$

Nonlinear interactions in rod suspensions

Sedimentation in an electric field shows particle pairings

(Movie courtesy of K. A. Rose and J. G. Santiago, Stanford)

Single-rod model: electric problem

- Ideally polarizable spheroid:
  - aspect ratio $A = \alpha^{-1}$
  - unit director $p$
  - linear abscissa $s$ along its axis

- At steady state, the effect of the counterions is to deflect the electric field lines: the body and its EDL behave like an insulator $^{1,2}$.

- In the thin EDL limit, the electric potential outside of the EDL satisfies:

\[
\nabla^2 \Phi = 0
\]

\[
\begin{align*}
\n\mathbf{n} \cdot \nabla \Phi &= 0 & \text{as } r \in \partial S \\
\n\nabla \Phi &\rightarrow -E_\infty & \text{as } r \rightarrow \infty
\end{align*}
\]

$^2$ Squires & Bazant, J. Fluid Mech. 2004

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Single-rod model: electric problem

- Analytical solution of the electric problem around an insulating spheroid is classic\(^1,2\).

\[
E(x) - E_\infty \propto E_\infty \alpha^2 \left( \frac{L}{|x|} \right)^3
\]

⇒ Electric interactions are very weak for particles of high aspect ratio

- On the surface of the spheroid:

\[
\begin{align*}
\Phi_s &= -x \cdot G \cdot E_\infty \\
E_s &= (I - nn) \cdot G \cdot E_\infty
\end{align*}
\]

where: \( G = G_{||} pp + G_{\perp} (I - pp) \)

---

\(^1\) Stratton, *Electromagnetic theory*, 1941.

\(^2\) Fair & Anderson, *J. Colloid Interface Sci.*, 1989
Single-rod model: flow problem

- Solution of the electric problem provides boundary condition for flow problem:

\[
\mathbf{u}_s = -\frac{\varepsilon \zeta}{\mu} \mathbf{E}_s, \quad \zeta = \zeta_0 - \Phi_s
\]

- Fluid velocity satisfies Stokes equations with slip BC:

\[
-\mu \nabla^2 \mathbf{u} + \nabla p = 0, \quad \nabla \cdot \mathbf{u} = 0
\]

\[
\begin{align*}
\mathbf{u}(\mathbf{x}) &= \mathbf{U} + \mathbf{\Omega} \times \mathbf{x} + \mathbf{u}_s(\mathbf{x}) & \text{as } \mathbf{x} \in \partial S, \\
\mathbf{u}(\mathbf{x}) &\to 0 & \text{as } |\mathbf{x}| \to \infty
\end{align*}
\]

- Approximate solution obtained using slender-body theory\(^1,2\):

\[
\mathbf{U} + s\mathbf{\Omega} \times \mathbf{p} + \tilde{\mathbf{u}}_s(s) - \mathbf{u}_\infty(\mathbf{x} + sp) = \frac{\log 2A}{4\pi \mu} (1 + pp) \cdot \mathbf{f}(s)
\]

\(^1\) Batchelor, *J. Fluid Mech.*, 1971

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Single-rod model: Slender-body formulation

Circumferentially averaged slip velocity\(^1\):  
\[ \tilde{u}_s(s) = \frac{1}{2\pi} \int_0^{2\pi} u_s(s, \theta) d\theta \]

- After linearization, the fluid slip velocity along the rod becomes:

\[ u_s(s) \approx -\frac{\epsilon}{\mu} s (\mathbf{p} \cdot \tilde{E}_\infty) \tilde{E}_\infty \quad \text{where} \quad \tilde{E}_\infty = \left[ G_{\|}pp + \frac{1}{2} G_\perp (\mathbf{I} - pp) \right] \cdot E_\infty \]

\(^1\) Solomentsev & Anderson, J. Fluid Mech., 1994
Single-rod model: slender-body formulation

- **Slender-body theory** shows that ICEP can be modeled by a linear slip velocity:

\[
\tilde{u}_s(s) \approx -\frac{\epsilon}{\mu} s \left( p \cdot \tilde{E}_\infty \right) \tilde{E}_\infty \quad \text{where} \quad \tilde{E}_\infty = \left[ G_\parallel pp + \frac{1}{2} G_\perp (I - pp) \right] \cdot E_\infty
\]

The component normal to the rod causes **alignment of the rod with the field**, at the angular velocity:

\[
\Omega = \frac{\epsilon}{\mu} \left( p \times \tilde{E}_\infty \right) \left( p \cdot \tilde{E}_\infty \right)
\]

The component tangential to the rod, to leading order, **drives a stresslet flow** in the surrounding fluid, of magnitude:

\[
S = \frac{2\pi \epsilon l^3}{3 \log 2A} \left( p \cdot \tilde{E}_\infty \right)^2 \left( pp - \frac{I}{3} \right)
\]
Pair interactions: semi-analytical model

- Consider two particles aligned in the z-direction. Assume a linear distribution of point-forces along their axes (stresslet interactions).
- Solve for the relative velocity analytically.

Hydrodynamic interactions result in particle pairings
Multiparticle simulations: non-Brownian case

Simulation method includes:

- far-field hydrodynamic interactions based on slender-body theory
- lubrication and contact forces
- (Brownian motion)
- ICEO slip velocity
- Smooth-Particle Mesh Ewald algorithm


\[ 128 \text{ rods} \]
\[ nL^3 = 0.8 \]
\[ A = 10 \]

⇒ Qualitative agreement with the theoretical pair distribution function obtained from two-particle model

IMA, December 5 2009
Non-Brownian systems: Hydrodynamic dispersion

- Superposition of the relative motions leads to diffusive behavior at long times.

- Hydrodynamic diffusivity tensor:

\[
D = \lim_{t \to \infty} \frac{1}{2} \frac{d}{dt} \langle (x(t) - x_0)(x(t) - x_0) \rangle
\]

\[
\frac{D}{\varepsilon E_\infty^2 L^2 / \mu}
\]

![Graphs showing mean square displacements and diffusivity as functions of time and aspect ratio.](image)
Multiparticle simulations: Brownian systems

- Simulation method includes: far-field hydrodynamic interactions, lubrication and contact forces, ICEP slip, and Brownian motion in periodic BCs.

\[ P_e = \frac{\epsilon E^2}{\mu D_T} = \frac{8\pi \epsilon E^2 l^3}{3kT \log 2A} \]

Comparison to experiments

(Rose and Santiago 2006)

60 rods, \( nl^3 = 0.1 \), \( A = 10 \)
Bounded systems
Wall effects in EP

- Electrophoresis in direction parallel to an insulating planar wall:

\[ U_\parallel = \left[ 1 - \frac{1}{16} \lambda^3 + \frac{1}{8} \lambda^5 + \ldots \right] \frac{\varepsilon}{\mu} (\zeta_p - \zeta_w) E_0 \]

- Electrophoresis in direction normal to a planar electrode:

\[ U_\perp = \left[ 1 - \frac{5}{8} \lambda^3 + \frac{1}{4} \lambda^5 + \ldots \right] \frac{\varepsilon \zeta_p}{\mu} E_0 \]

\[ \lambda = \frac{a}{h} \]

\( \Rightarrow \) Motion is slowed down by presence of wall (but not as much as in sedimentation)

The DEP force on a spherical particle next to a wall is non-zero by symmetry breaking, and causes motion away from the wall.

\[ F = \varepsilon a^2 E_0^2 \left[ \frac{3\pi}{16} \lambda^4 + O(\lambda^7) \right] N \]

\[ \lambda = \frac{a}{h} \]

Wall effects in ICEP

- ICEP disturbance flow causes migration away or towards the wall depending on the direction of the electric field.

  Kilic & Bazant, in review (2009)

- Migration velocity can be obtained by method of reflections. For a particle next to a dielectric wall:

  \[ U = \frac{\varepsilon E_0^2 a}{\mu} \left[ \frac{27}{64} \lambda^2 + \frac{3}{16} \left( \frac{\varepsilon_w \lambda D}{\varepsilon a} \right) \lambda^3 + O(\lambda^4) \right] \]

  \[ \lambda = \frac{a}{h} \]

Electrophoretic deposition

**Future work:** simulations of electrophoretic colloid deposition, with aim of predicting deposit microstructure and quantifying the influence of the dynamics in suspension.

**Preliminary simulations:** small system, no electric or hydrodynamic interactions with boundaries

\[
\frac{aE_0}{\zeta} = 1 \quad \phi = 0.0262 \quad L_x \times L_y \times L_z = 20^3
\]

Collaboration with K. Rose (LLNL)
Particle interactions at electrodes

- EHD flow driven by particles at electrodes can result in particle interactions, leading to (reversible) particle aggregation.

Ristenpart, Aksay & Saville,
J. Fluid Mech., 575 83 (2007)
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- For more details, reprints etc....:
  http://mechse.illinois.edu/research/dstn

Thank you!