The Micromechanics of Colloidal Dispersions

John F. Brady

Divisions of Chemistry & Chemical Engineering
and Engineering & Applied Science
California Institute of Technology
Pasadena, CA 91125, USA
jfbrady@caltech.edu

Multiscale Modeling and Simulation of Complex Fluids
University of Maryland
13 April 2007
Some Examples/Applications

• Food stuffs & additives
• Personal care products
• Biological fluids & cells
• Ceramics, colored glass
• MR/ER fluids
• Resins, catalysts
• Paints, coatings, inks

Organic Ink Helps Scientists ‘Write’ Tiny Fluid Factories

Researchers have developed a new method of “writing” tiny etchings into a plane of glass, like those made by a laser printer. By using an ink that is too small to be seen with the naked eye, they may have succeeded in miniaturizing the microscopic elements of devices that can be used to manipulate streams of liquid. The finding, published online today by the journal Nature Materials, could aid in the development of microfabrication or improved “lab-on-chips.”

‘Nanowriting’

Biological Fluids

Actin network
Weitz lab., Harvard.

Macrophage
Microangelo EM gallery

Red blood cells
Microangelo EM gallery

Liz Jones (2002)
Swimming

*Eutreptiella flagellate*


Propelling

*Listeria Bacteria*

Propels itself by enzymatic synthesis of actin -- the ‘comet tail’
Colloid science & microfluidics

• Electrophoresis

\[ U = -\frac{\varepsilon E}{\eta} \]

Electrophoresis of DNA

J. Han and H.G. Craighead, Cornell University
http://www.hgc.cornell.edu/biofab/video.htm

Nonliving -- nanomotors

Catalytic nanomotor

The mechanism of self-propulsion is unknown. Some candidates: surface tension gradients caused by the catalytic reaction on the Pt surface, electrochemical flows between Pt and Au, etc.

Paxton et al. (2004)
Autonomous Motion or Science Fiction?

- Design or construct ‘objects’ at the micro-, nano- or molecular scales that can move themselves.
- Have truly portable devices (e.g. sensors, drug delivery, lab-on-a-chip).
- Learn something about biological systems.

‘surgeon nanobot’
Erik Viktor

Pattern Formation


Zoueshtiagh & Thomas (2000) Fluidized bed (Jackson 2000)
Length and Time Scales of Complex Fluids

<table>
<thead>
<tr>
<th>Method</th>
<th>Time Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granular Dynamics</td>
<td>1 hr</td>
</tr>
<tr>
<td>Stokesian Dynamics</td>
<td>1 s</td>
</tr>
<tr>
<td>Brownian Dynamics</td>
<td>1 ns</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Size Scale</th>
<th>Particle Size Scale</th>
<th>Simulation Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mm</td>
<td></td>
<td>Granular Dynamics (St &gt;&gt; 1)</td>
</tr>
<tr>
<td>1 µm</td>
<td></td>
<td>Bubble Dynamics (∇ × u = 0)</td>
</tr>
<tr>
<td>1 nm</td>
<td></td>
<td>Stokesian Dynamics (Re &lt;&lt; 1)</td>
</tr>
<tr>
<td>1 Å</td>
<td></td>
<td>Molecular Dynamics</td>
</tr>
</tbody>
</table>

\[
N_i \sim \left( \frac{a_p}{a_i} \right)^3, \quad \tau_p \sim \left( \frac{a_p}{a_i} \right)^3, \quad \text{CPU} \sim \left( \frac{a_p}{a_i} \right)^6 N_p
\]
Characteristic Scales: A Simple Example

Spherical particle of 0.5µm of specific gravity 2 falling in water.

- Particle Size: \( a = \frac{1}{2} \) µm
- Fall Speed: \( U = \frac{1}{2} \) µm/s
- Reynolds Number: \( Re = \frac{\rho U a}{\eta} \)
- Diffusivity: \( D = \frac{1}{2} (\mu m)^2 / s \)
- Peclet Number: \( Pe = \frac{U a}{D} \)

Stokes - Einstein - Sutherland Relation: \( D = \frac{kT}{6\pi\eta a} \)

Micromechanics

Continuum Approximation: \( a_p \gg a_s \)

- \( N_s \sim \left(\frac{a_p}{a_s}\right)^3 N_p \)
- \( \tau_s \sim a_s / \sqrt{3kT/m} = 10^{-13} \) s
- \( \tau_s \sim a_s^2 / \nu \) , \( \nu = \eta / \rho \)
- \( \tau_p / \tau_s \sim \left(\frac{a_p}{a_s}\right)^2 \)

Therefore, the solvent can be treated as a continuum:

\[ Re = \frac{\rho U a}{\eta} \ll 1 \]
\[ \frac{\rho}{\rho D} \frac{D u}{D t} = -\nabla p + \eta \nabla^2 u \] , \( \nabla \cdot u = 0 \)
Micromechanics ($Re << 1$)

Langevin equation for particle motion:

$$ m \cdot \frac{dU}{dt} = F^H + F^B + F^P $$

**Hydrodynamic:**

$$ F^H = -R_{FU} \cdot U = -6\pi \eta a U $$

Stokes drag

$$ \tau_p \sim O(m / 6\pi \eta a) $$

$$ \approx 10^{-8} \text{s} $$

**Multiparticle:**

$$ F^H = -R_{FU}(x) \cdot (U - U^w) $$

**Fluid Motion:**

$$ 0 = -\nabla p + \eta \nabla^2 u $$

Stokes Equations

$$ \nabla \cdot u = 0 $$

$$ u = U + x \times \Omega $$

no slip at particle surfaces
Micromechanics ($Re \ll 1$)

Particle Motion: \[ m \frac{dU}{dt} = F^H + F^B + F^p \]

Hydrodynamic: \[ F^H = -R(x) \cdot (U - U^n) \]
Stokes drag \[ \tau_p \sim O(m / 6\pi \eta a) \]

Brownian: \[ \overline{F^B} = 0, \quad \overline{F^B}(0)\overline{F^B}(t) = 2kTR(x)\delta(t) \]
\[ O(10^{-13} s) \]

Interparticle/external: \[ F^p = \Delta \rho V g, \text{ electrostatic, etc.} \]

Fluid Motion:
Stokes Equations \[ 0 = -\nabla p + \eta \nabla^2 u \]
\[ \nabla \cdot u = 0 \]
\[ u = U + x \times \Omega \]
no slip at particle surfaces

Displacement in momentum relaxation time \[ \frac{\Delta x}{a} = Re \ll 1 \quad \Rightarrow 
0 = F^H + F^B + F^p \]

Only configurational degrees of freedom!!
Interparticle forces

Steric Stabilization

Electrostatic Stabilization

Nature of Hydrodynamic Forces: $F^H = -R(x) \cdot U$

Interactions decay as $\frac{1}{r}$
**Stokesian Dynamics Method: O(N ln N)**

Split the hydrodynamic interactions into near- and far-field parts:

\[ F^H = -R \cdot U = -R_{nf} \cdot U - R_{ff} \cdot U \]

**Near field:** Lubrication interactions are two-body effects and can be added pairwise. Calculations can be done in \( O(N) \) operations

\[ R_{nf} = R_{nf}^2 B \]

**Far field:** Many-body effects are computed by representing the particles as force densities on a grid and using Fast Fourier Transforms (FFT) to compute the velocity field. The force is then computed via Faxen laws and determined iteratively (convergence is rapid after the initial time step).

\[ F_{ff}^H = -R_{ff} \cdot U \]

**Hydrodynamic Interactions**

**Lubrication:** closely spaced particles move as a single (rigid) rod, whether you push or pull.

**Many-body:** “point” particles falling due to gravity have a negative fall speed at high concentrations.
Short-time self-diffusivity

\[ D_0^s(\phi) = kT \langle \mathcal{M} \rangle^{eq} \]

Dilute limit: \( \phi \to 0 \)

\[ D_0^s(\phi) \sim D_0(1 - 1.83\phi) \]

Close packing:

\[ \varepsilon = 1 - \frac{\phi}{\phi_{rcp}} \to 0 \]

\[ D_0^s(\phi) \sim D_0 / \ln(1/\varepsilon) \]

Near Equilibrium Behavior: \( (\omega) \to \infty \)

\[ \eta' = 1 + \frac{5}{2} \phi + 5\phi^2 \] as \( \phi \to 0 \)

\[ \eta' \sim \ln(1 - \phi/\phi_{m})^{-1} \] as \( \phi \to \phi_m \)
High-frequency dynamic viscosity & short-time self-diffusivity

Brownian Self-Diffusivity (long-time)

The self-diffusivity decreases with increasing concentration as the diffusing particle must push past its neighbors to move.

Fuchs et al (1992)

\[ D_0 = \frac{kT}{6\pi \eta a} \]

\[ D(\phi) = D_0 (1 - \phi)^{2.62} \]

\[ D' = kT \frac{D_0}{6\pi \eta a} (1 - \phi) \]

\[ D(\phi) \approx D_0 (1 - \phi)^{2.62} \]
Zero-shear Brownian viscosity ($Pe = 0$)

\[
\eta_B = \eta'_\infty + \Delta \eta_B
\]

\[
\Delta \eta_B = \frac{kT}{V} \int dt (\sigma_{xy}(t) \sigma_{xy}(0))
\]

High Frequency Elastic Modulus

\[
G'_{\infty} \frac{a^3}{kT}
\]
Summary

Langevin Equation:

\[ m \frac{dx}{dt} = F^H + F^P + F^B + \xi \text{ random or Brownian} \]

\[ F^B = 0 \]

\[ F^P(0) F^B(t) = 2kT \frac{\partial f}{\partial x} \]

\[ \frac{F^H}{S_u} = \frac{R_{uu}}{R_{EE}} \left( \frac{U - U^\infty}{-E^\infty} \right) \]

Diffusion Equation:

\[ \Delta x = U^\infty \Delta t + R_{FV}^{-1} \frac{\partial f}{\partial x} \Delta x + R_{FV} \cdot F^P \Delta t + kT \nabla \cdot R_{FV}^{-1} \Delta t + \chi^B(\Delta t) \]

\[ \chi^B = 0, \quad \chi^B(\Delta t) \chi^B(\Delta t) = 2kT \frac{R_{FV}^{-1}}{R_{FV}} \Delta t \]

Smoluchowski Equation:

\[ \frac{\partial P_N}{\partial t} + \nabla \cdot \mathbf{J} = 0, \quad t = 0: \ P_N(x, 0) = N^0(x) \text{ initial condition} \]

\[ \mathbf{J} = \left( U^H + R_{FV}^{-1} \left( F^P - kT \nabla \ln P_N \right) \right) P_N \]

\[ -R_{FV}^{-1} \cdot kT \nabla \ln P_N = U^B \text{ Brownian velocity} \]
The hydrodynamic resistance tensor, $R_p$, etc., are functions of the configuration — e.g., shape, relative separation, orientation, etc. — of $N$ particles. For a given configuration, $X$, of $N$ particles, determining the resistance tensor is a well-posed problem in low Reynolds number hydrodynamics.

With $R$ determined for each (and every) configuration, we then need to either integrate the diffusion equation numerically to have the configuration evolve from some initial state (Stokesian Dynamics), or solve the Smoluchowski equation, analytically if possible. Note that the diffusion equation is just a discretized version of the Smoluchowski equation.

This completes the description of the microdynamics. We now turn to the computation of macroscopic properties from these microdynamics. (We shall also revisit the long-range interactions and convergence problems.)

Note, in the absence of a shear flow motion and with an interparticle force derivable from a potential $F_p = -\nabla \psi$, the equilibrium solution of the Smoluchowski equation $\mathbf{J} \equiv 0$, is simply

$$P_n \sim \exp(-\mathbf{V}/kT).$$
Macrosopic Properties

(1) Sedimentation Velocity: \[ \langle \mathbf{U} \rangle = \left( \frac{1}{N} \sum_{\alpha=1}^{N} \mathbf{U}_{\alpha} \right) = \left( \frac{1}{N} \sum_{\alpha=1}^{N} \frac{M_{\alpha}}{\beta_{\alpha} \rho_{\alpha}} \mathbf{F}_{\alpha} \right) \]

\[ \sum \text{ over particles} \]

\[ \alpha \rightarrow \langle \mathbf{U} \rangle = \langle \mathbf{M} \rangle \cdot \mathbf{F} \]

[Note: coupling is \( \mu \mathbf{F} \)]

(2) Permeability:

\[ \langle \mathbf{F}^H \rangle = \left( \frac{1}{N} \sum_{\alpha=1}^{N} \mathbf{F}_{\alpha}^H \right) = \left( \frac{1}{N} \sum_{\alpha=1}^{N} \frac{R_{\alpha}}{\rho_{\alpha} \kappa} \mathbf{F}_{\alpha} \right) \cdot \langle \mathbf{U} \rangle \]

imposed avg. vel. through bed of fixed particles

\[ \langle \mathbf{F}^H \rangle = \langle \mathbf{R} \rangle \cdot \langle \mathbf{U} \rangle \]

Darcy's Law: \[ \nabla \langle p \rangle = - \nabla \langle \mathbf{F} \rangle \cdot \langle \mathbf{U} \rangle \]

\[ \therefore \kappa^{-1} = n \langle \mathbf{R} \rangle \]

[Note: coupling is \( \kappa \mathbf{F} \mathbf{U} \)]

(3) Diffusion:

\[ \text{Short-time self-diffusion} \quad D^S_0 = \left( \frac{1}{N} \sum_{\alpha=1}^{N} \mathbf{h} \mathbf{F} \mathbf{h}^{-1} \right) \mathbf{U}_{\alpha} \]

\[ = \left( \frac{1}{N} \sum_{\alpha=1}^{N} \mathbf{h} \mathbf{T} \mathbf{h}^{-1} \right) \mathbf{U}_{\alpha} \]

\[ \text{Short-time hindered diffusion} \quad D^H_0 = \left( \frac{1}{N} \sum_{\alpha=1}^{N} \mathbf{h} \mathbf{h}^{-1} \right) \mathbf{U}_{\alpha} \]

There are analogous rotational diffusions.
Collective / Mutual / Gradient Diffusivity

\[ \mathcal{D} = \left\langle \mathbf{M} \right\rangle \frac{\partial \left( \mathcal{E} \right)}{\partial \tau} p_T = \kappa T \left\langle \mathbf{M} \right\rangle \frac{\partial \left( \phi \tau \right)}{\partial \tau} p_T \]

when the osmotic compressibility \( \tau (\phi) = \Pi \Pi / \kappa T \), with \( \Pi \)
\( \theta \)-osmotic pressure.

Long-time self-diffusion: \( \mathcal{D} \approx \lim_{t \to \infty} \frac{1}{2} \frac{d}{dt} \left\langle (x_i - x_j)(x_i - x_j) \right\rangle \)

\( t \gg a^2 / D, \quad D = \kappa T \pi \eta a \)

Not be determined from the dynamic.

(4) Bulk macropore shear (low Reynolds #) (no body couple \( \mathcal{E} = 0 \))

\[ \left\langle \mathcal{E} \right\rangle = - \left\langle \mathcal{E}_E + 2 \eta \left\langle \mathcal{E} \right\rangle \right\rangle + \eta \left\{ \left\langle \mathcal{E}^E \right\rangle + \left\langle \mathcal{E}^p \right\rangle + \left\langle \mathcal{E}^b \right\rangle \right\} - \kappa T \Pi \]

\[ \left\langle \mathcal{E}^E \right\rangle = - \left\langle \mathbf{R} \cdot \frac{1}{2} \mathbf{R}^{-1} \cdot \mathbf{F} \cdot \mathbf{R}^{-1} \cdot \mathbf{F} \cdot \mathbf{R}^{-1} \right\rangle \cdot \left\langle \mathcal{E} \right\rangle \]

\[ \left\langle \mathcal{E}^p \right\rangle = - \left\langle \left( \mathbf{R} \cdot \mathbf{R}^{-1} \cdot \mathbf{Z} \right) \cdot \mathbf{F} \cdot \mathbf{R}^{-1} \right\rangle \]

\[ \left\langle \mathcal{E}^b \right\rangle = - \kappa T \left\langle \nabla \cdot \mathbf{R} \cdot \mathbf{R}^{-1} \right\rangle \quad \nabla: \text{ last index} \mathbf{R}^{-1} \]

\( \left\langle \mathcal{E}^E \right\rangle \) due to the fact that the individual particles do not strain as a fluid element. \( \left\langle \mathcal{E}^p \right\rangle \) "elastic" shear of type found in polymer systems, and \( \left\langle \mathcal{E}^b \right\rangle \) is the direct contribution from Brownian motion - entropic shear of local structure is out of equilibrium (dynamic part).
References

. Russel, Saville & Schowalter 1989 "Colloidal Dispersions", CVP

. Wax 1954 "Noise & Stochastic Processes", Dover


• Sangani, A. & Acrivos, A. 1982 "

Int. J. Multiphase Flow, 8, 343-


