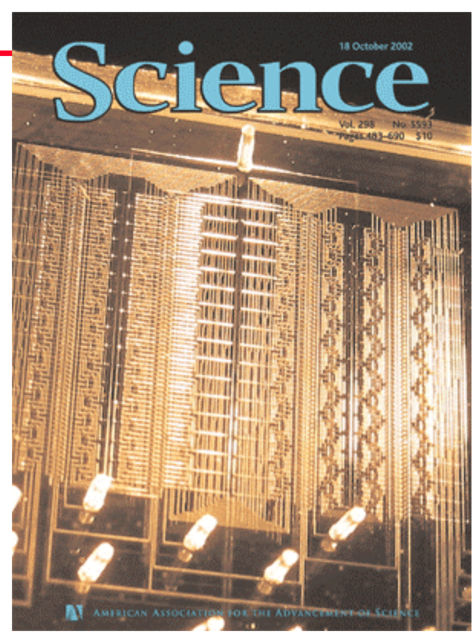
The Micromechanics of Colloidal Dispersions

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

Complex Fluids/Complex Flows



S. Quake

Some Examples/Applications

- Food stuffs & additives
- Personal care products
- Biological fluids & cells
- Ceramics, colored glass
- MR/ER fluids
- Resins, catalysts
- Paints, coatings, inks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March 12, 2004

NEWS
March 24, 2003

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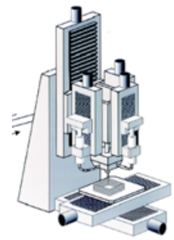
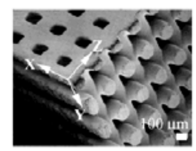
Organic Ink Helps Scientists 'Write' Tiny Fluid Factories

Researchers have developed a new method of "writing" tiny mazes of pipes in millimeter-size devices. Using special ink, they have successfully manufactured three-dimensional networks of channels that can be used to mix microscopic streams of fluid. The findings, published online today by the journal *Nature Materials*, could aid in the development of new biosensors or improved "labs-on-chips."

Image: UNIVERSITY OF ILLINOIS, URBANA-CHAMPAIGN

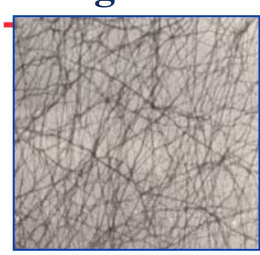
...ventional ...uct ...n flow on ...ssible to ...ne another ..., this procedure is time-consuming because it ...np for each layer. Now Jennifer A. Lewis and





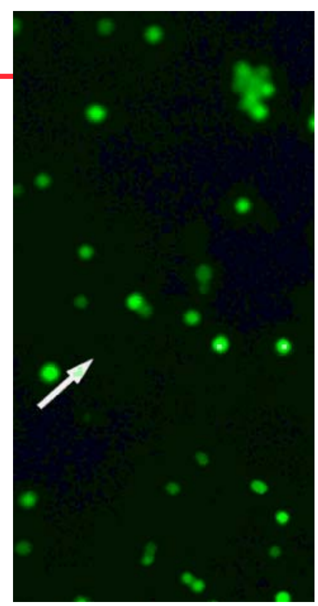
'Nanowriting'

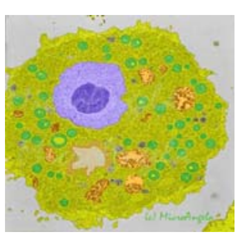
Biological Fluids



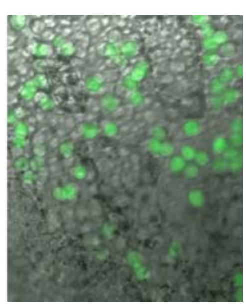
Actin network
Weitz lab., Harvard.

Red blood cells
Microangela EM gallery





Macrophage
Microangela EM gallery



Liz Jones (2002)

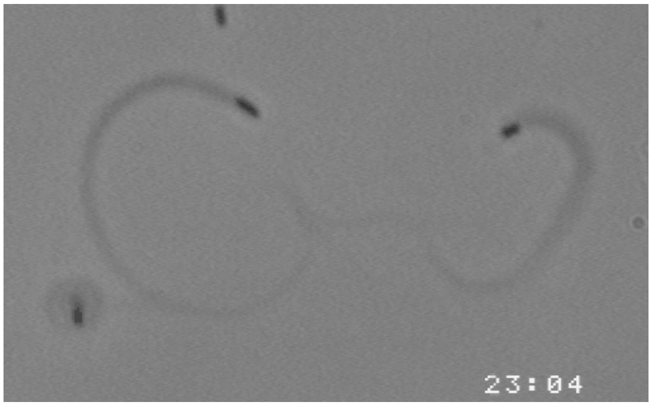
Swimming

Eutreptiella flagellate

Molecular Biology of the Cell, 4th Edition, by Alerts, Johnson, Lewis. Raff, Roberts, Walter

Propelling

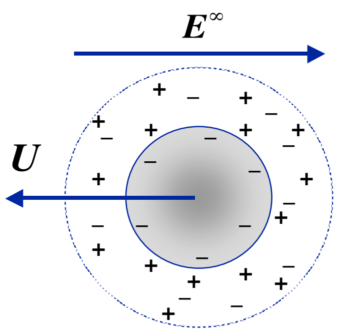
Listeria Bacteria



Propels itself by enzymatic synthesis of actin -- the 'comet tail'

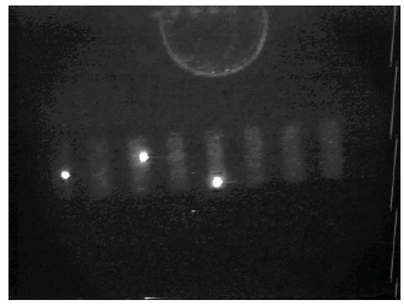
Colloid science & microfluidics

• **Electrophoresis**



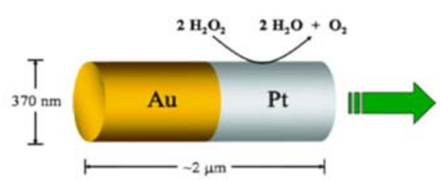
$$\boxed{U = -\frac{\varepsilon\varsigma}{\eta} E^{\infty}}$$

Electrophoresis of DNA



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

Nonliving -- nanomotors



Catalytic nanomotor

Paxton *et al.* (2004)

10 mm

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.

Janus

Autonomous Motion or Science Fiction?

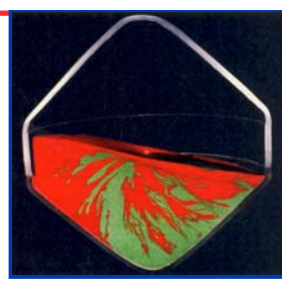
- Design or construct ‘objects’ at the micro-, nano- or molecular scales that can move themselves.
- Have truly portable devices (*e.g.* sensors, drug delivery, lab-on-a-chip).
- Learn something about biological systems.

‘surgeon nanobot’
Erik Viktor

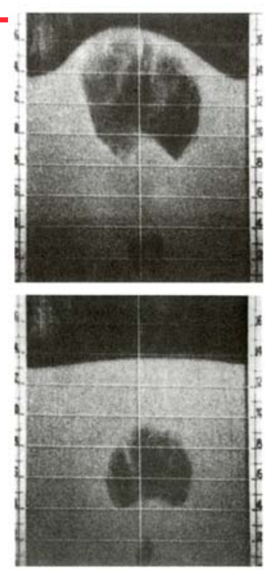
Pattern Formation

Tirumkudulu *et al* (1999)

Shinbrot & Muzzio (2000)

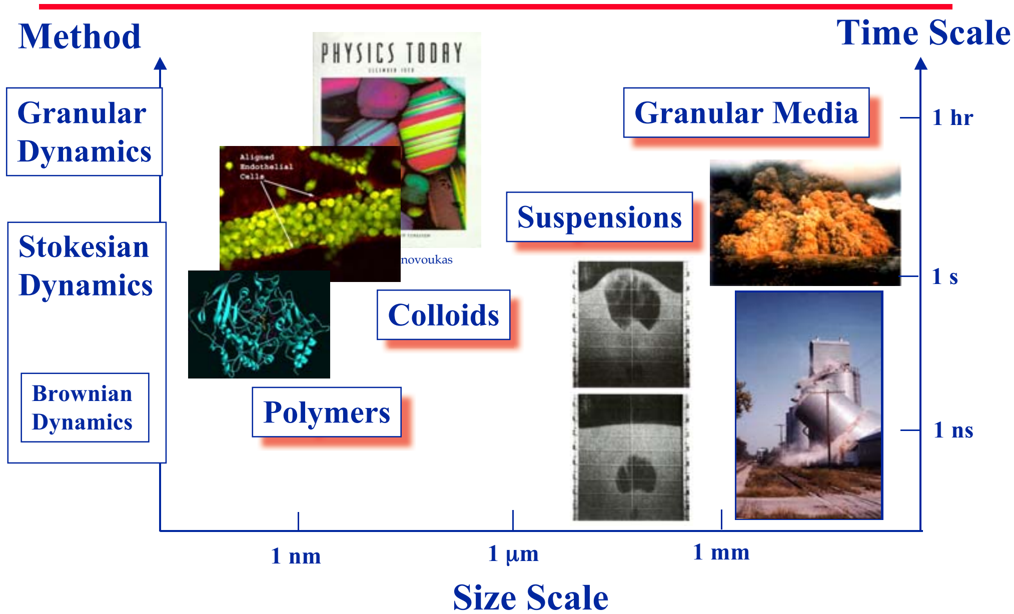


Zoueshtiagh & Thomas (2000)



Fluidized bed (Jackson 2000)

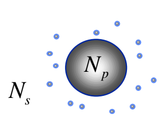
Length and Time Scales of Complex Fluids



Particle Size Scale — Simulation Method

Particle Size Scale		Simulation Method
1 m	10^{0}	Granular Dynamics (St >>1)
	10^{-1}	Bubble Dynamics ($\nabla \times u = 0$)
	10^{-2}	
1 mm	10^{-3}	
	10^{-4}	
	10^{-5}	Stokesian Dynamics (Re << 1)
1µm	10^{-6}	
	10^{-7}	
	10^{-8}	
1 nm	10^{-9}	Molecular Dynamics
1 Å	10^{-10}	

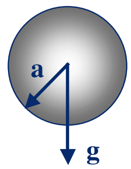
$$Re = \frac{\rho U a}{\eta} < 1 \quad , \quad \left. \begin{array}{l} St = \dfrac{\rho_p}{\rho_f} Re \\ Pe = \dfrac{\nu}{D} Re \end{array} \right\} \text{arbitrary}$$



$$\frac{N_s}{N_p} \sim \left(\frac{a_p}{a_s}\right)^3 \quad , \quad \frac{\tau_p}{\tau_s} \sim \left(\frac{a_p}{a_s}\right)^3 \quad , \quad \text{CPU} \sim \left(\frac{a_p}{a_s}\right)^6 N_p$$

Characteristic Scales: A Simple Example

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



Particle Size: $a = \frac{1}{2}\,\mu\text{m}$

Fall Speed: $U = \frac{1}{2}\,\mu\text{m/s}$

Reynolds Number: $Re = \frac{1}{2}\times 10^{-6}$

Diffusivity: $D = \frac{1}{2}(\mu\text{m})^2/\text{s}$

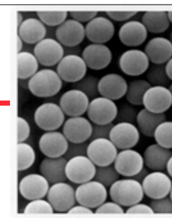
Peclet Number: $Pe = \frac{1}{2}$

$$\left(\frac{inertial}{viscous}\right) \qquad Re = \frac{\rho U a}{\eta}$$

$$\left(\frac{advection}{diffusion}\right) \qquad Pe = \frac{Ua}{D}$$

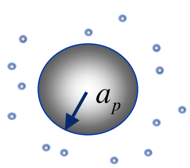
Stokes-Einstein-Sutherland Relation: $D = kTR^{-1} = \dfrac{kT}{6\pi\eta a}$

Micromechanics



Uniform silica microspheres (1 μm diam., × 10,000).

Continuum Approximation: $a_p >> a_s$



$$N_s \sim (a_p/a_s)^3 N_p$$

$$\tau_s \sim a_s\Big/\sqrt{3kT/m} \approx 10^{-13}\,s$$

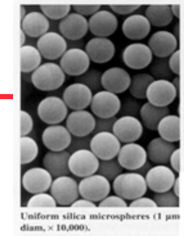
$$\tau_s \sim a_s^2/\nu \;,\; \nu = \eta/\rho$$

$$\tau_p/\tau_s \sim (a_p/a_s)^2$$

Therefore, the solvent can be treated as a continuum :

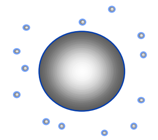
$$Re = \frac{\rho U a}{\eta} << 1 \qquad \cancel{\rho\frac{D\boldsymbol{u}}{Dt}} = -\nabla p + \eta\nabla^2\boldsymbol{u} \;,\; \nabla\cdot\boldsymbol{u} = 0$$

Micromechanics ($Re \ll 1$)



Langevin equation for particle motion:

$$\boldsymbol{m} \cdot \frac{d\boldsymbol{U}}{dt} = \boldsymbol{F}^H + \boldsymbol{F}^B + \boldsymbol{F}^P$$



Hydrodynamic: $\boldsymbol{F}^H = -\boldsymbol{R}_{FU} \cdot \boldsymbol{U} = -6\pi\eta a \boldsymbol{U}$

Stokes drag

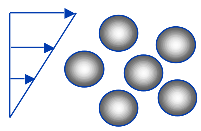
$\tau_p \sim O(m / 6\pi\eta a)$

$\approx 10^{-8} s$

Multiparticle: $\boldsymbol{F}^H = -\boldsymbol{R}_{FU}(\boldsymbol{x}) \cdot \left(\boldsymbol{U} - \boldsymbol{U}^\infty\right)$

Fluid Motion:
Stokes Equations

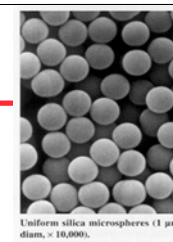
$$0 = -\nabla p + \eta \nabla^2 \boldsymbol{u}$$
$$\nabla \cdot \boldsymbol{u} = 0$$



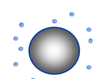
$\boldsymbol{u} = \boldsymbol{U} + \boldsymbol{x} \times \boldsymbol{\Omega}$

no slip at particle surfaces

Micromechanics ($Re \ll 1$)



Langevin equation: $\boldsymbol{m} \cdot \frac{d\boldsymbol{U}}{dt} = \boldsymbol{F}^H + \boldsymbol{F}^B + \boldsymbol{F}^P$



Hydrodynamic: $\boldsymbol{F}^H = -\boldsymbol{R}_{FU}(\boldsymbol{x}) \cdot \left(\boldsymbol{U} - \boldsymbol{U}^\infty\right)$

Stokes drag

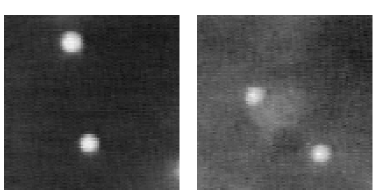
$\tau_p \sim O(m / 6\pi\eta a)$

$\approx 10^{-8} s$

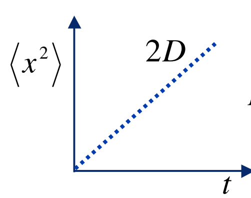
Brownian: $\overline{\boldsymbol{F}^B} = 0 \;,\; \overline{\boldsymbol{F}^B(0)\boldsymbol{F}^B(t)} = 2kT\boldsymbol{R}_{FU}(\boldsymbol{x})\delta(t)$

$O(10^{-13} s)$

$\tau_s \ll \tau_p$



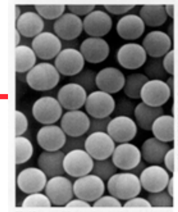
(D. Weitz)



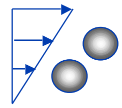
$$D = kTR_{FU}^{-1} = \frac{kT}{6\pi\eta a}$$

Mean-square displacement

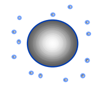
Micromechanics ($Re << 1$)



Uniform silica microspheres (1 μm diam., × 10,000).



Particle Motion: $$\boldsymbol{m}\cdot\frac{d\boldsymbol{U}}{dt} = \boldsymbol{F}^H + \boldsymbol{F}^B + \boldsymbol{F}^P$$



Hydrodynamic: $$\boldsymbol{F}^H = -\boldsymbol{R}(\boldsymbol{x})\cdot(\boldsymbol{U}-\boldsymbol{U}^\infty)$$

Stokes drag

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

$\approx 10^{-8}s$

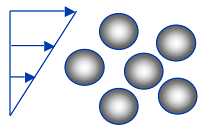
Brownian: $$\overline{\boldsymbol{F}^B} = 0 \;,\; \overline{\boldsymbol{F}^B(0)\boldsymbol{F}^B(t)} = 2kT\boldsymbol{R}(\boldsymbol{x})\delta(t)$$

$O(10^{-13}s)$

Interparticle/ external: $\boldsymbol{F}^P = \Delta\rho V_p \boldsymbol{g}$, electrostatic, etc.

Fluid Motion: Stokes Equations

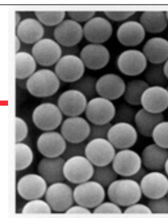
$$0 = -\nabla p + \eta\nabla^2\boldsymbol{u}$$
$$\nabla\cdot\boldsymbol{u} = 0$$



$\boldsymbol{u} = \boldsymbol{U} + \boldsymbol{x}\times\boldsymbol{\Omega}$

no slip at particle surfaces

Micromechanics ($Re << 1$)



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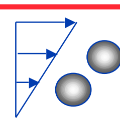
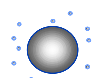


Particle Motion: $$\cancel{\boldsymbol{m}\cdot\frac{d\boldsymbol{U}}{dt}} = \boldsymbol{F}^H + \boldsymbol{F}^B + \boldsymbol{F}^P$$



Hydrodynamic: $$\boldsymbol{F}^H = -\boldsymbol{R}(\boldsymbol{x})\cdot(\boldsymbol{U}-\boldsymbol{U}^\infty)$$

Stokes drag

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

$\approx 10^{-8}s$

Brownian: $$\overline{\boldsymbol{F}^B} = 0 \;,\; \overline{\boldsymbol{F}^B(0)\boldsymbol{F}^B(t)} = 2kT\boldsymbol{R}(\boldsymbol{x})\delta(t)$$

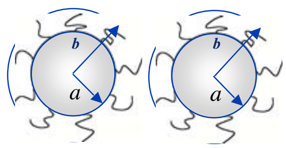
$O(10^{-13}s)$

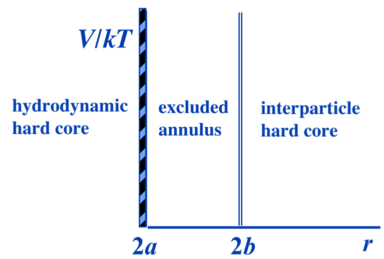
Displacement in momentum relaxation time $$\frac{\Delta x}{a} = Re << 1 \quad\Rightarrow\quad 0 = \boldsymbol{F}^H + \boldsymbol{F}^B + \boldsymbol{F}^P$$

Only configurational degrees of freedom!!

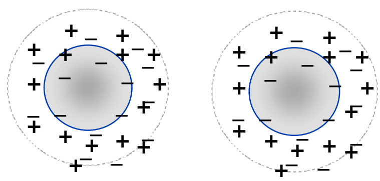
Interparticle forces

Steric Stabilization

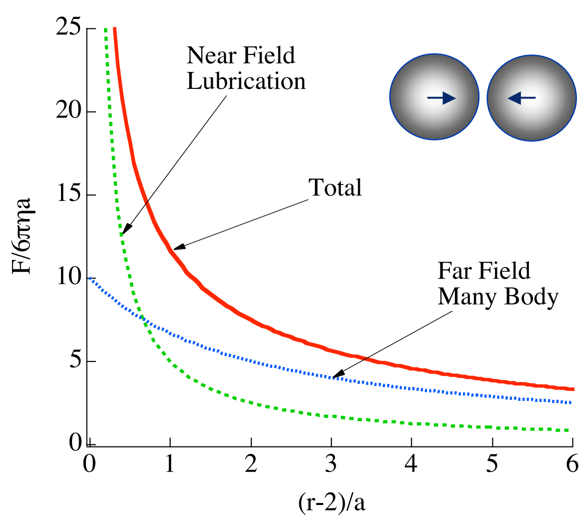




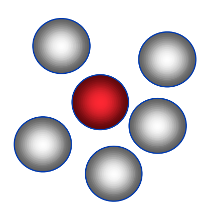
Electrostatic Stabilization



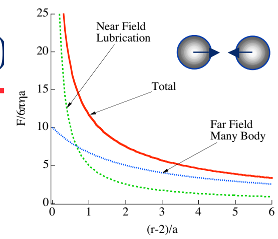
Nature of Hydrodynamic Forces: $F^H = - R(x) \cdot U$



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

$$R_{nf} = R_{nf}^{2B}$$

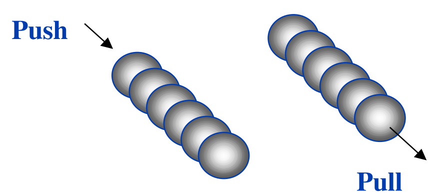
Far field: Many-body effects are computed by representing the particles as force densities on a grid and using Fast Fourier Transforms (FFT) to compute the velocity field.

The force is then computed via Faxen laws and determined iteratively (convergence is rapid after the initial time step).

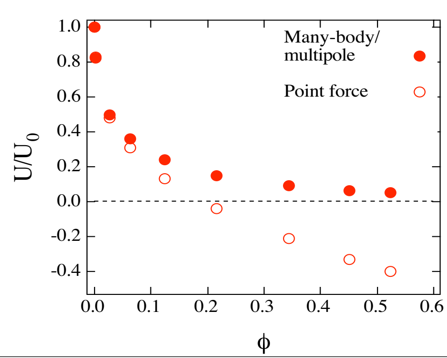
$$F_{ff}^H = -R_{ff} \cdot U$$

Hydrodynamic Interactions

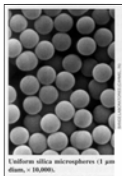
Lubrication: closely spaced particles move as a single (rigid) rod, whether you push or pull.

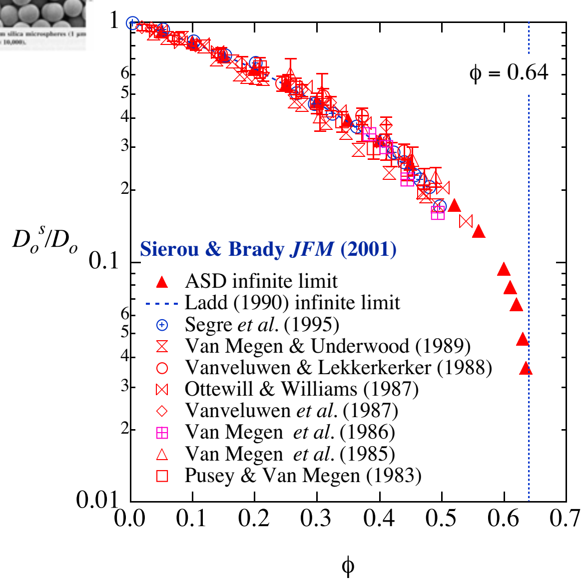


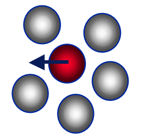
Many-body: "point" particles falling due to gravity have a *negative* fall speed at high concentrations.

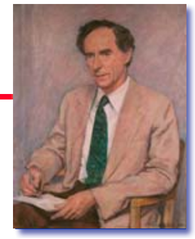


Short-time self-diffusivity









Batchelor (ca. 1995)

$$\boxed{D_0^s(\phi) \;=\; kT\langle \boldsymbol{M}\rangle^{eq}}$$

Dilute limit : $\phi \;\to\; 0$

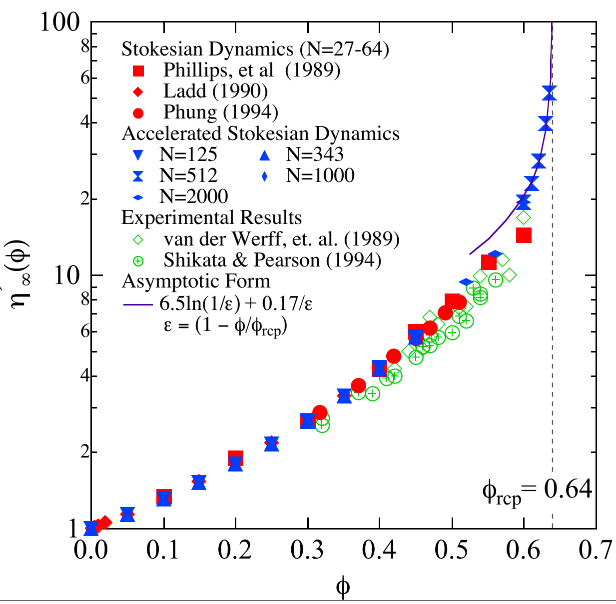
$$D_0^s(\phi) \;\sim\; D_0(1-1.83\phi)$$

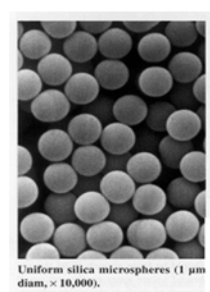
Close packing :

$$\varepsilon = 1-\phi/\phi_{rcp} \to 0$$

$$D_0^s(\phi) \;\sim\; D_0/\ln(1/\varepsilon)$$

Near Equilibrium Behavior: $\omega \to \infty$

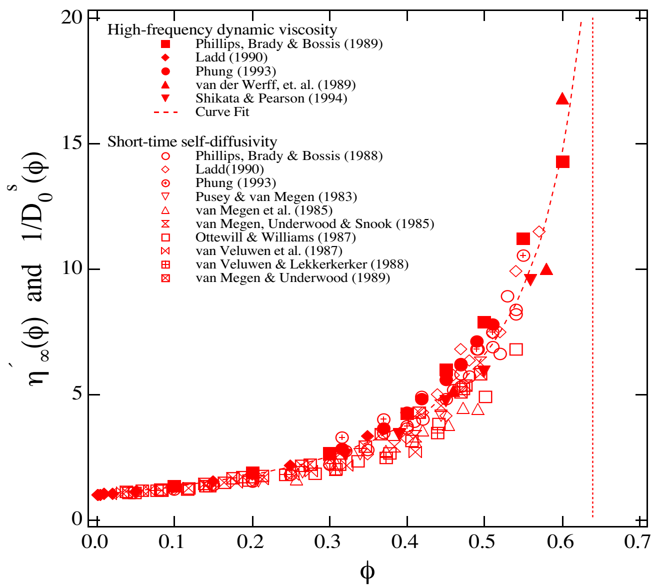




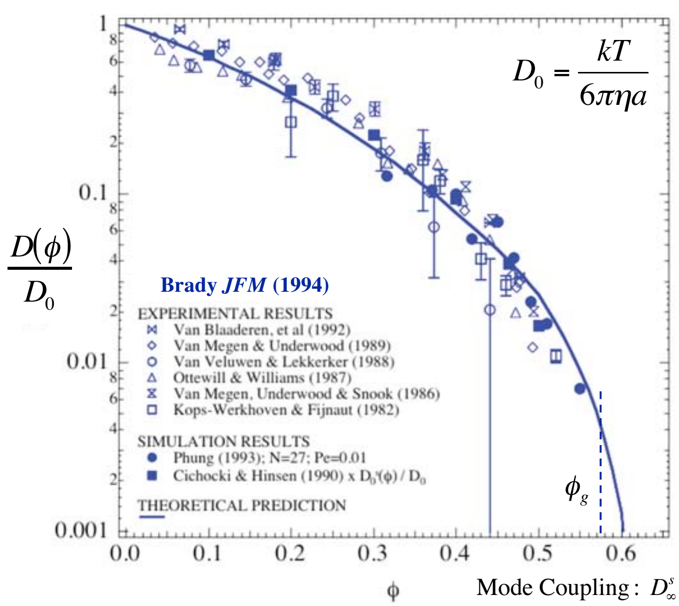
$$\eta'_\infty \sim 1+\tfrac{5}{2}\phi+5\phi^2 \quad \text{as} \quad \phi \to 0$$

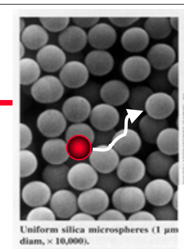
$$\eta'_\infty \sim \ln(1-\phi/\phi_m)^{-1} \quad \text{as} \quad \phi \to \phi_m$$

High-frequency dynamic viscosity & short-time self-diffusivity



Brownian Self-Diffusivity (long-time)



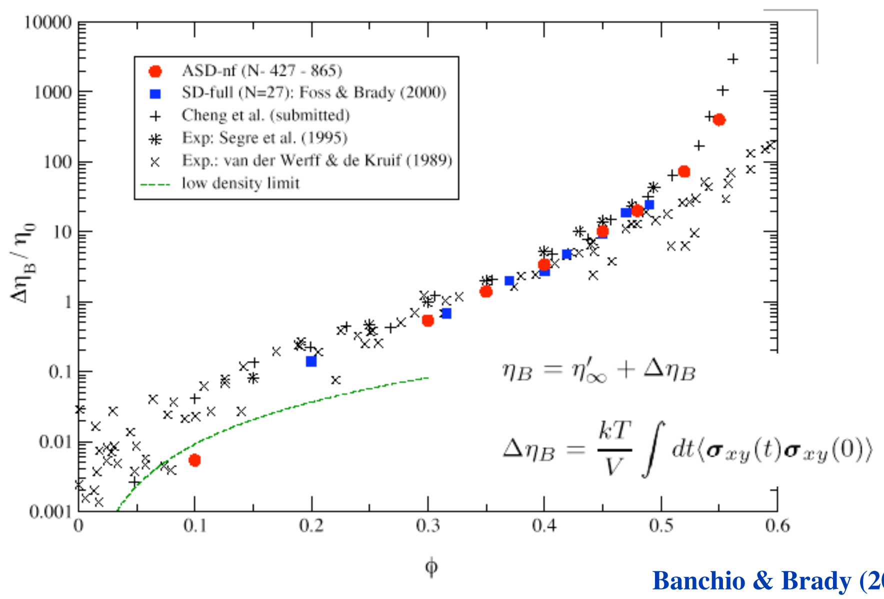


The self-diffusivity decreases with increasing concentration as the diffusing particle must push past its neighbors to move.

Fuchs *et al* (1992)

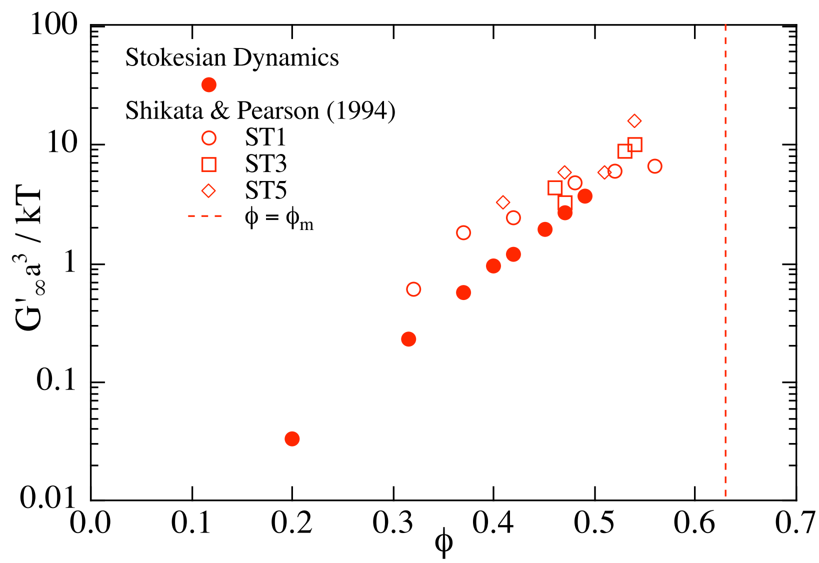
Mode Coupling: $D_\infty^s(\phi) \sim D_0^s(\phi_g - \phi)^{2.62}$

Zero-shear Brownian viscosity (*Pe* = 0)



Banchio & Brady (2002)

High Frequency Elastic Modulus



Summary

Langevin Equation:

$$\underset{\approx}{m} \cdot \frac{d\underset{\sim}{U}}{dt} = \underset{\sim}{F}^H + \underset{\sim}{F}^P + \underset{\sim}{F}^B \leftarrow \text{random or Brownian}$$

hydrodynamic ($\underset{\sim}{F}^H$); interparticle / external ($\underset{\sim}{F}^P$)

$$\overline{\underset{\sim}{F}^B} = 0,$$

$$\overline{\underset{\sim}{F}^B(0)\,\underset{\sim}{F}^B(t)} = 2kT\,\underset{\approx}{R}_{FU}\,\delta(t)$$

$\overline{\cdot}$ = time average over τ_s.

$$\begin{pmatrix} \underset{\sim}{F}^H \\ \underset{\approx}{S}^H \end{pmatrix} = - \begin{pmatrix} \underset{\approx}{R}_{FU} & \underset{\approx}{R}_{FE} \\ \underset{\approx}{R}_{SU} & \underset{\approx}{R}_{SE} \end{pmatrix} \cdot \begin{pmatrix} \underset{\sim}{U} - \underset{\sim}{U}^\infty \\ -\underset{\approx}{E}^\infty \end{pmatrix}$$

Diffusion Equation:

$$\Delta \underset{\sim}{x} = \underbrace{\underset{\sim}{U}^\infty(\underset{\sim}{x})\,\Delta t + \underset{\approx}{R}_{FU}^{-1} \cdot \underset{\approx}{R}_{FE} : \underset{\approx}{E}^\infty \Delta t}_{\underset{\sim}{U}^E \Delta t \text{ hydrodynamic velocity}} + \underbrace{\underset{\approx}{R}_{FU}^{-1} \cdot \underset{\sim}{F}^P \Delta t}_{\underset{\sim}{U}^P \Delta t \text{ interparticle force velocity}}$$

$$+ \, kT\, \nabla \cdot \underset{\approx}{R}_{FU}^{-1}\, \Delta t + \underset{\sim}{X}^B(\Delta t)$$

$$\overline{\underset{\sim}{X}^B} = 0, \quad \overline{\underset{\sim}{X}^B(\Delta t)\,\underset{\sim}{X}^B(\Delta t)} = 2kT\,\underset{\approx}{R}_{FU}^{-1}\,\Delta t$$

Smoluchowski Equation: $P_N(\underset{\sim}{x}, t)$

$$\frac{\partial P_N}{\partial t} + \nabla \cdot \underset{\sim}{j}_N = 0, \qquad t = 0: \; P_N(\underset{\sim}{x}, 0) = P_N^0(\underset{\sim}{x}) \quad \text{initial condition}$$

$$\underset{\sim}{j} = \left(\underset{\sim}{U}^H + \underset{\approx}{R}_{FU}^{-1} \cdot \left[\underset{\sim}{F}^P - kT\nabla \ln P_N \right] \right) P_N$$

$$- \underset{\approx}{R}_{FU}^{-1} \cdot kT\,\nabla \ln P_N = \underset{\sim}{U}^B \quad \text{Brownian velocity}$$

The hydrodynamic resistance tensors, $\underline{\underline{R}}_{FU}$, etc. are functions of the configuration – size, shape, relative separation, orientation, etc. – of the N particles. For a given configuration, $\underline{x}$, of the N particles, determining the resistance tensors is a well posed problem in low Reynolds number hydrodynamics.

With $\underline{\underline{R}}$ 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 shearing motion and with an interparticle force derivable from a potential $\underline{F}^P = -\nabla V$, the equilibrium solution of the Smoluchowski equation $\underline{j} \equiv 0$, is simply

$$P_N \sim \exp(-V/kT).$$

Macroscopic Properties

(1) Sedimentation Velocity: $\langle \underset{\sim}{U} \rangle = \left\langle \frac{1}{N} \sum_{\alpha=1}^{N} \underset{\sim}{U}_\alpha \right\rangle = \left\langle \frac{1}{N} \sum_\alpha \sum_\beta \underline{\underline{M}}_{\alpha\beta} \cdot \underset{\sim}{F}^g_\beta \right\rangle$

avg. over configurations

sum over particles

or, $\langle \underset{\sim}{U} \rangle = \langle \underline{\underline{M}} \rangle \cdot \underset{\sim}{F}^g$ [Note, coupling is M_{UF}]

(2) Permeability: $\langle \underset{\sim}{F}^H \rangle = \left\langle \frac{1}{N} \sum_{\alpha=1}^{N} \underset{\sim}{F}^H_\alpha \right\rangle = \left\langle \frac{1}{N} \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} \underline{\underline{R}}_{\alpha\beta} \right\rangle \cdot \langle \underset{\sim}{U} \rangle$

imposed avg. vel. through bed of fixed particles

$$\langle \underset{\sim}{F}^H \rangle = \langle \underline{\underline{R}} \rangle \cdot \langle \underset{\sim}{U} \rangle$$

Darcy's Law: $\nabla \langle p \rangle = -\eta \underline{\underline{K}}^{-1} \cdot \langle u \rangle$

$\therefore \underline{\underline{K}}^{-1} = n \langle \underline{\underline{R}} \rangle$ [Note, coupling is R_{FU}]

(3) Diffusion:

- Short-time self-diffusivity $\underline{\underline{D}}_0^s \equiv \left\langle \frac{1}{N} \sum_{\alpha=1}^{N} kT \left(\underline{\underline{R}}_{FU}^{-1}\right)_{\alpha\alpha} \right\rangle$

$$= \left\langle \frac{1}{N} \sum_{\alpha=1}^{N} kT\, \underline{\underline{M}}_{\alpha\alpha} \right\rangle$$

- Short-time hindered diffusivity $\underline{\underline{D}}_0^H \equiv \left\langle \frac{1}{N} \sum_{\alpha=1}^{N} \underline{\underline{R}}^{-1}_{\alpha\alpha} \right\rangle$

There are analogous rotational diffusivities.

. Collective / Mutual / Gradient Diffusivity:

$$\underline{\underline{D}}^{c} = \langle \underline{\underline{M}} \rangle \frac{\varphi}{1-\varphi}\left(\frac{\partial \mu}{\partial \varphi}\right)_{P,T} = kT \langle \underline{\underline{M}} \rangle \frac{d}{d\varphi}(\varphi Z(\varphi)),$$

where the osmotic compressibility $Z(\varphi) = \Pi / nkT$, with Π the osmotic pressure.

. Long-time self-diffusivity: $\underline{\underline{D}}^{s}_{\infty} = \lim_{t\to\infty} \frac{1}{2}\frac{d}{dt}\left\langle (\underline{x} - \langle x \rangle)(x - \langle x \rangle)\right\rangle$

$t \gg a^2/D, \quad D = kT/6\pi\eta a$

Must be determined from the dynamics

(4) Bulk or Macroscopic Stress (Low Reynolds #) (no body couples $\underline{L}^{H} = 0$)

$$\langle \underline{\underline{\Sigma}} \rangle = -\langle p \rangle_f \underline{\underline{I}} + 2\eta \langle \underline{\underline{E}} \rangle + n\left\{ \langle \underline{\underline{S}}^{E} \rangle + \langle \underline{\underline{S}}^{P} \rangle + \langle \underline{\underline{S}}^{B} \rangle \right\} - nkT \underline{\underline{I}}$$

$$\langle \underline{\underline{S}}^{E} \rangle = -\left\langle \underline{\underline{R}}_{SU} \cdot \underline{\underline{R}}_{FU}^{-1} \cdot \underline{\underline{R}}_{FE} - \underline{\underline{R}}_{SE} \right\rangle \cdot \langle \underline{\underline{E}} \rangle$$

$$\langle \underline{\underline{S}}^{P} \rangle = -\left\langle \left(\underline{\underline{R}}_{SU} \cdot \underline{\underline{R}}_{FU}^{-1} + \underline{\underline{z}}\,\underline{\underline{I}} \right) \cdot \underline{F}^{P} \right\rangle$$

$$\langle \underline{\underline{S}}^{B} \rangle = -kT \left\langle \nabla \cdot \underline{\underline{R}}_{SU} \cdot \underline{\underline{R}}_{FU}^{-1} \right\rangle \qquad \nabla \cdot \text{ last index of } \underline{\underline{R}}_{FU}^{-1}.$$

$\langle \underline{\underline{S}}^{E} \rangle$ due to the fact that the individual particles do not strain as a fluid element. $\langle \underline{\underline{S}}^{P} \rangle$ "elastic" stress of type found in polymeric systems, and $\langle \underline{\underline{S}}^{B} \rangle$ is the direct contribution from Brownian motion — entropic stress if the structure is out of equilibrium (deviator part).

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