Suspensions: From Micromechanics to Macroscopic Behavior

John F. Brady

Divisions of Chemistry & Chemical Engineering
and Engineering & Applied Science
California Institute of Technology, Pasadena, CA

With help from: P. Nott, D. Foss & A. Sierou

Multiscale Modeling and
Simulation of Complex Fluids
University of Maryland
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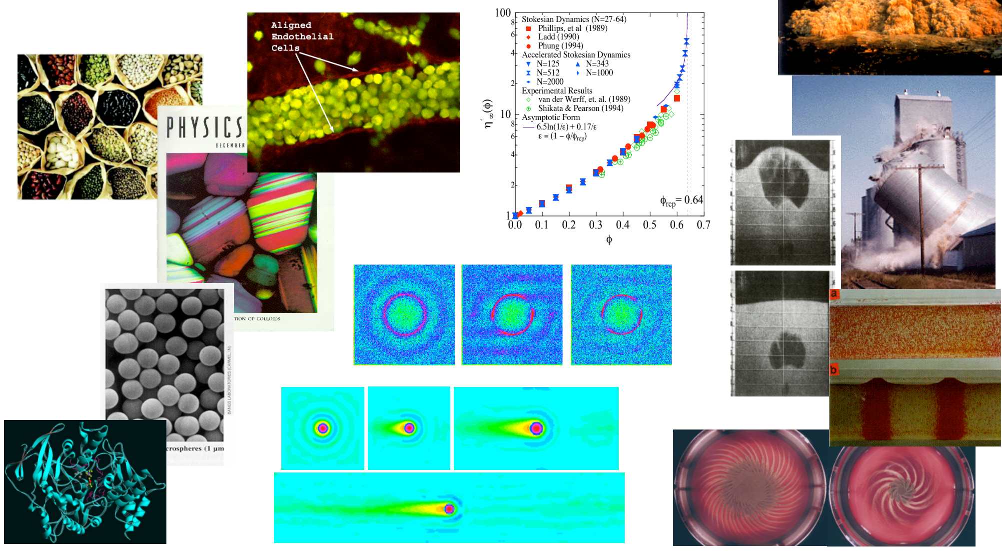
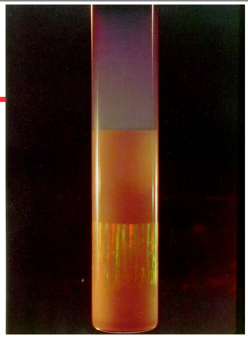
Multilevel Modeling: Micro to Macro



Micro --> Meso --> Macro

Suspensions as 'Complex Fluids'

- **Many complex fluids are composed of (or can be modeled as) small particles dispersed in a viscous fluid where Brownian forces (*kT*) compete against interparticle (*V*) and hydrodynamic (*Re* << 1) forces to set structure and determine properties**



Russel, Saville & Schowalter (1989)

- **What makes complex fluids interesting is that they are 'soft'**

$$\frac{\text{colloidal}}{\text{molecular}} \sim \left(\frac{a_m}{a_p}\right)^3 \; ; \; \text{time scales} \sim \left(\frac{a_p}{a_m}\right)^3$$

- **And often <u>far</u> from equilibrium**

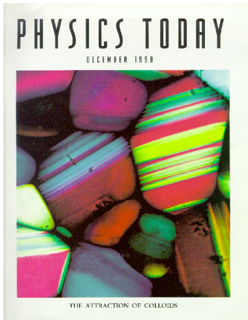
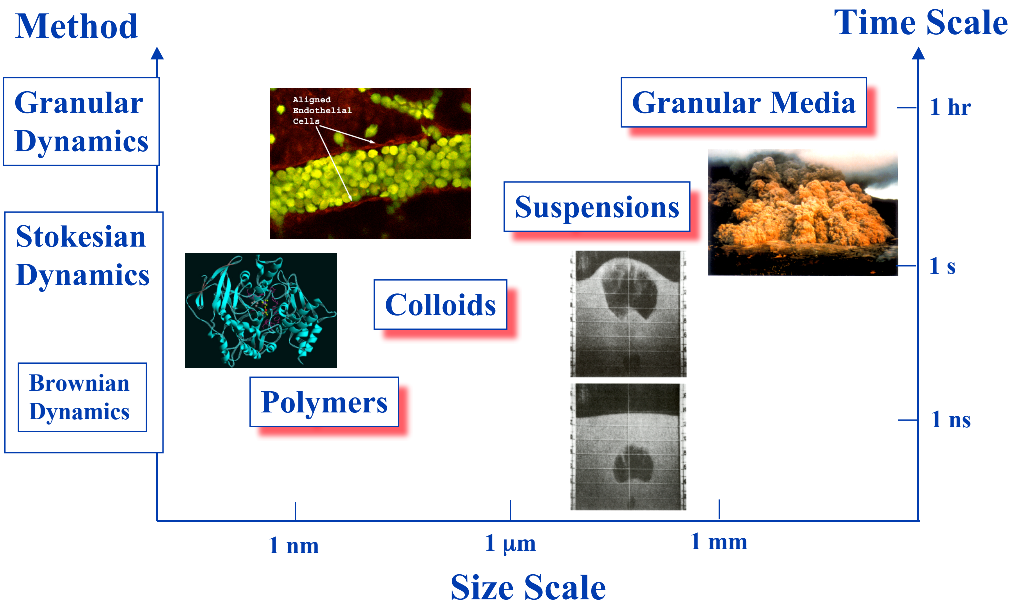


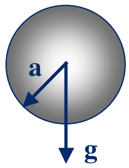
Photo by Y. Monovoukas

Length and Time Scales of Complex Fluids



Characteristic Scales: A Simple Example

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



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

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

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

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

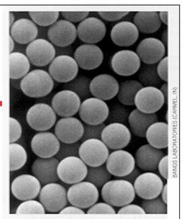
Diffusivity: $D = \tfrac{1}{2}(\mu\text{m})^2/\text{s}$

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

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

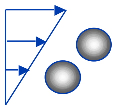
Stokes - Einstein - Sutherland Relation: $D = kTR^{-1} = \dfrac{kT}{6\pi\eta a}$

Micromechanics ($Re << 1$)



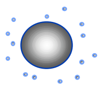
Uniform silica microspheres (1 µm diam., × 10,000).

Particle Motion: $\cancel{m \cdot \dfrac{dU}{dt}} = \boldsymbol{F}^H + \boldsymbol{F}^B + \boldsymbol{F}^P$



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

Stokes drag



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

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

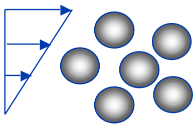
Brownian: $\overline{\boldsymbol{F}^B} = 0 \;, \quad \overline{\boldsymbol{F}^B(0)\boldsymbol{F}^B(t)} = 2kT\boldsymbol{R}(\boldsymbol{x})\delta(t)$

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

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

Fluid Motion: Stokes Equations

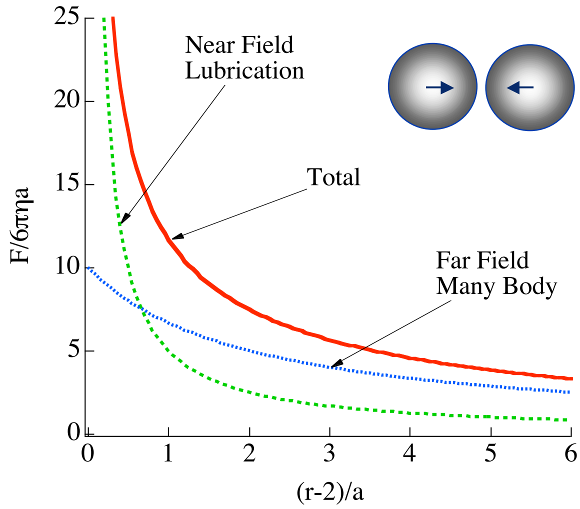
$$0 = -\nabla p + \eta \nabla^2 \boldsymbol{u}$$
$$\nabla \cdot \boldsymbol{u} = 0$$



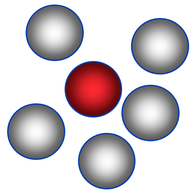
$\boldsymbol{u} = \boldsymbol{U} + \boldsymbol{x} \times \boldsymbol{\Omega}$

no slip at particle surfaces

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



Interactions decay as $\frac{1}{r}$



Model "Hard-Sphere" Suspensions

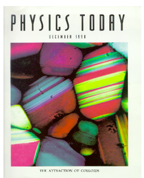
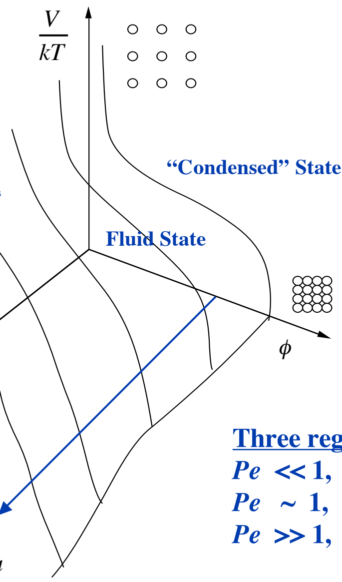
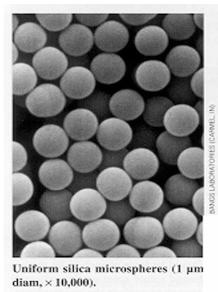


Photo by Y. Monovoukas





$$Pe = \frac{6\pi\eta a^3 \dot{\gamma}}{kT}$$

$$= \frac{\text{Brownian Time}}{\text{Flow Time}}$$

$$= \frac{a^2 / D}{1/\dot{\gamma}}, \quad D = kT / 6\pi\eta a$$

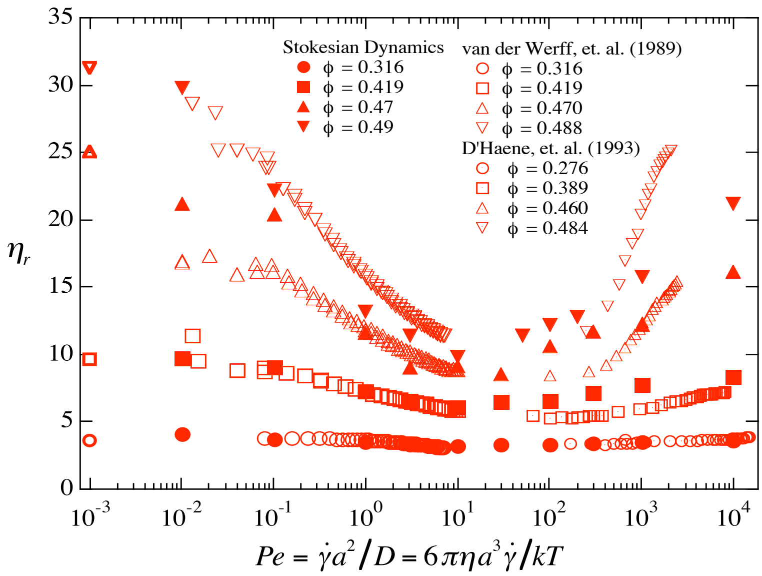
Three regimes:

Pe **<< 1, Brownian dominated**

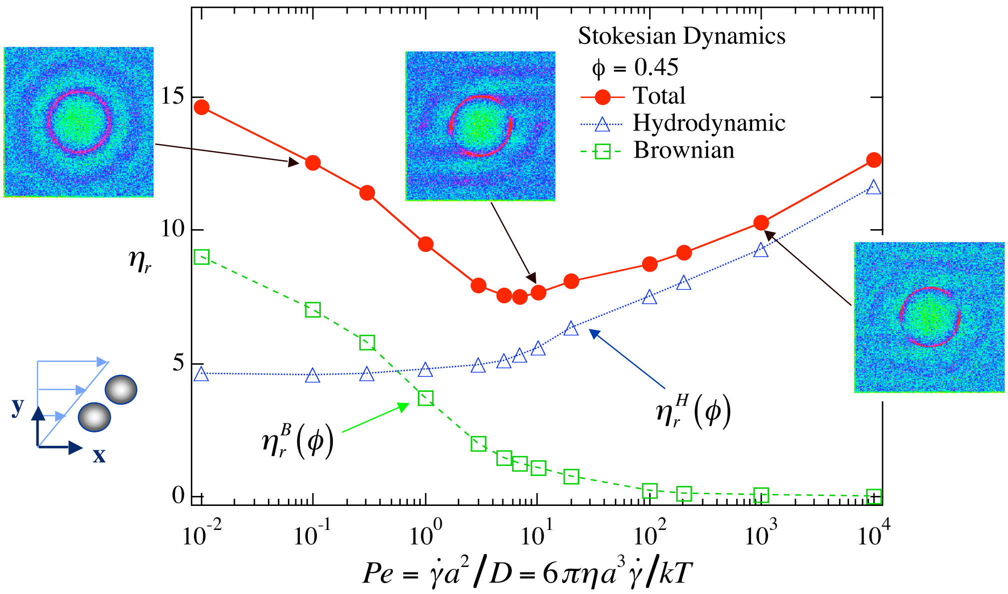
Pe **~ 1, Balance**

Pe **>> 1, Hydrodynamic dominated**

Rheology: Simulation vs. Experiment

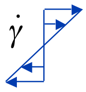


Brownian & hydrodynamic contributions to stress

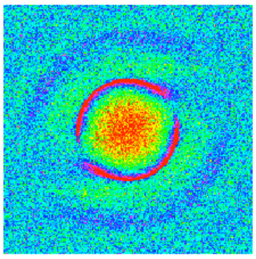


Shear Thickening:

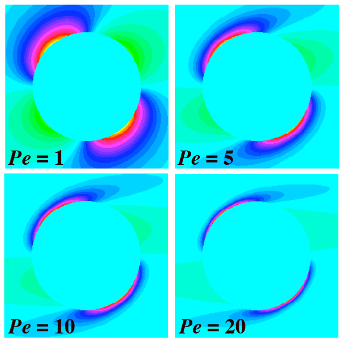
Boundary Layer at Particle Contact: $r-2 \sim \overline{Pe}^{-1}$



$g(x,y)$



$Pe = 10^4$



$$\boldsymbol{S}^H_{b.l.} \sim -n^2 \int_{b.l.} \boldsymbol{rF}^{shear} g(\boldsymbol{r}) d\boldsymbol{r} \ ,$$

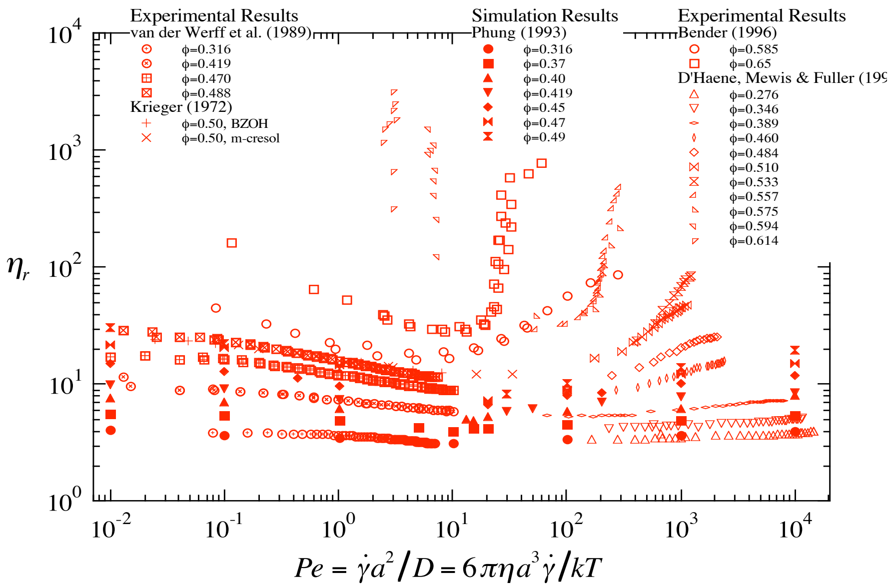
$$\boldsymbol{S}^H_{b.l.} \sim \eta'_\infty(\phi)\dot{\gamma}\phi^2 g(2;\phi)$$

$$\boldsymbol{F}^{shear} \sim -3\pi\eta'_\infty(\phi)a^2\dot{\gamma} \times \hat{\boldsymbol{r}}\left(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{E}}\cdot\hat{\boldsymbol{r}}\right)$$

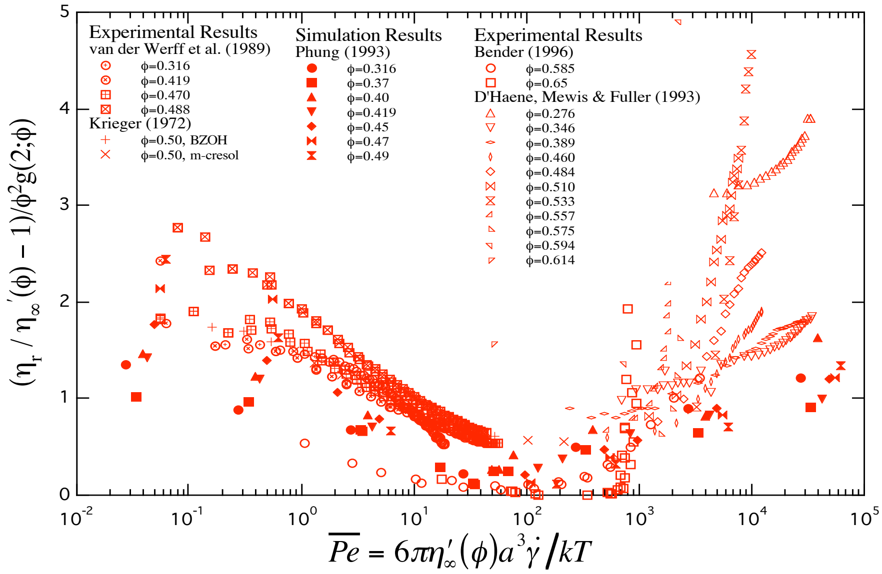
$$\overline{Pe} = 6\pi\eta'_\infty(\phi)a^3\dot{\gamma}/kT$$

$$\boxed{\frac{\eta_r/\eta'_\infty(\phi)-1}{\phi^2 g^\infty(2;\phi)} = \mathcal{F}\left(\overline{Pe}\right)}$$

Shear Viscosity for all *Pe*

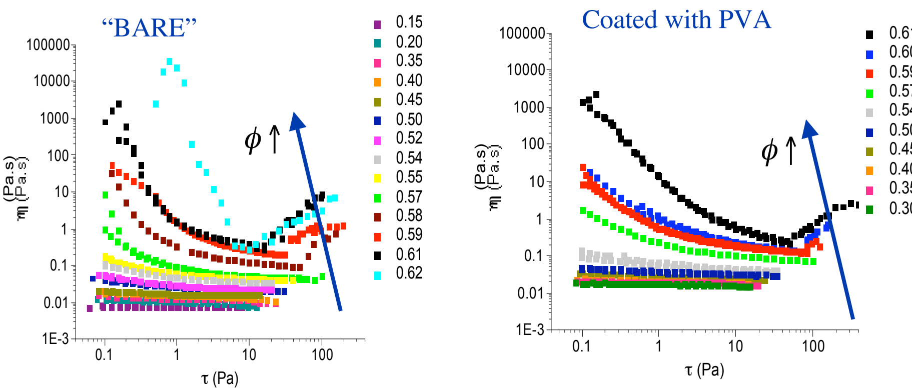


Collapse of Shear Viscosity for all *Pe*



Flow Curves for bare and coated silica

(pH 9.1, T = 25 C, satd. polymer layer)

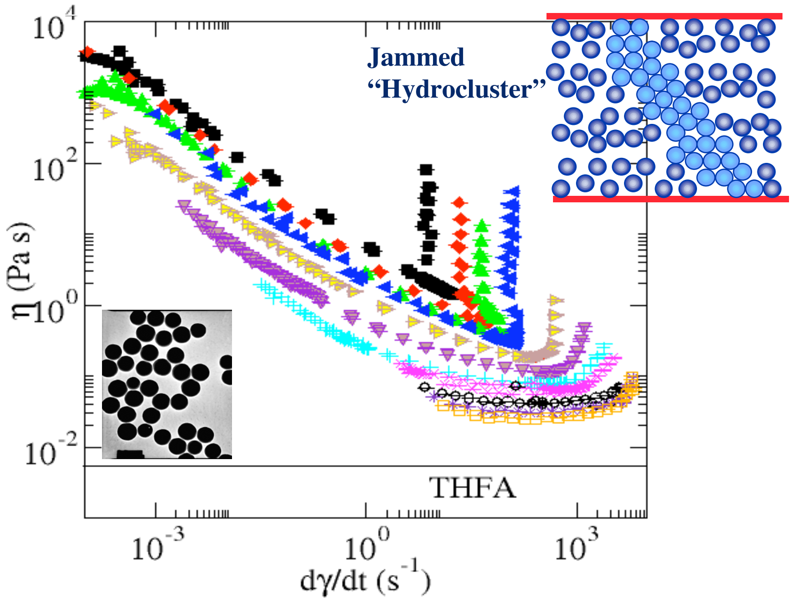


Adsorbed PVA shifts the Shear Thickening to higher Stresses

N. Wagner (2001)

Sudden Shear Thickening

Maranzano & Wagner, JOR 2001, JCP 2002



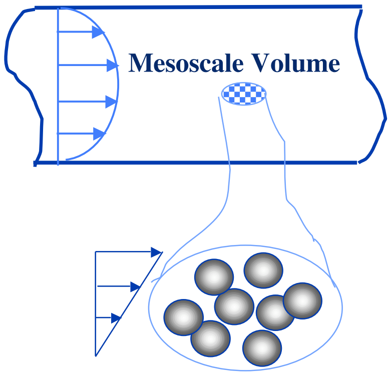
What's It Good For?

Walking on water!

http://www.youtube.com/watch?v=f2XQ97XHjVw

Microscale → Mesoscale → Macroscopic

Macroscale Flow Geometry



Microscale Distribution

- **Rheology: Stress--strain-rate constitutive relations**

$$\sigma(\dot{\gamma},\ \phi,\ \text{microstructure, etc.})$$

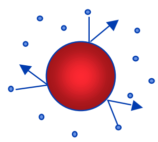
- **Diffusion: Particle distribution within each (rheology) and between volume elements**

$$\boldsymbol{u}_p - \boldsymbol{u} = f(\dot{\gamma},\ \phi,\ \text{microstructure, etc})$$

Particle Diffusion: $D \sim (v')^2 \times \tau$

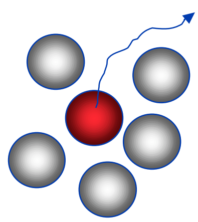
- **Brownian motion**

$$(v')^2 \sim \frac{3kT}{m}, \quad \tau \sim \frac{m}{6\pi\eta a}, \quad D \sim \frac{kT}{2\pi\eta a}$$

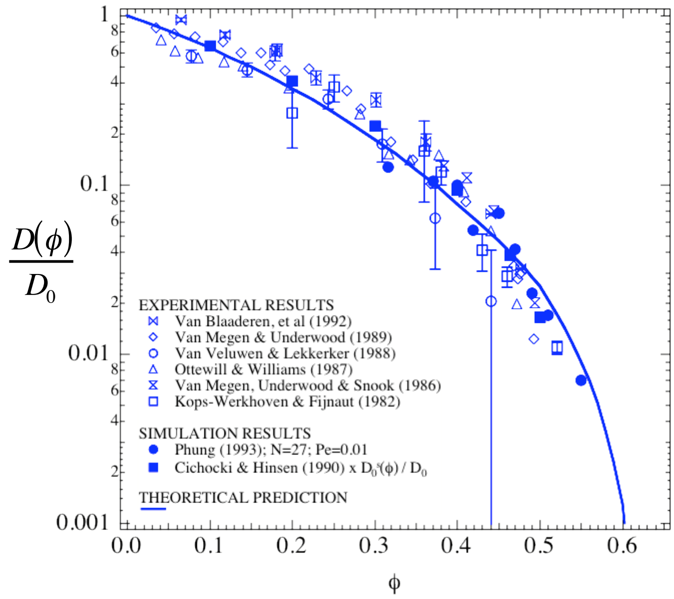


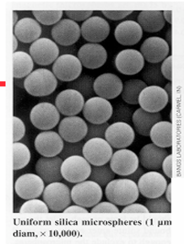
- **Time to diffuse the order of the particle size**

$$t_a \sim \frac{a^2}{D} \sim \frac{2\pi\eta a^3}{kT} \approx 1s \text{ for } a = 0.5\mu\text{m}$$



Brownian Self-Diffusivity (long-time)





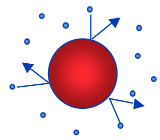
The self-diffusivity decreases with increasing concentration as the diffusing particle must push past its neighbors to move.

Brady (1994)

Particle Diffusion: $D \sim (v')^2 \times \tau$

- **Brownian motion**

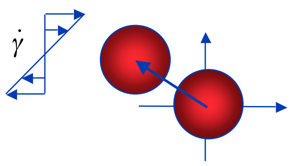
$$(v')^2 \sim \frac{3kT}{m}\,, \quad \tau \sim \frac{m}{6\pi\eta a}\,, \quad D \sim \frac{kT}{2\pi\eta a}$$



$$t_a \sim \frac{a^2}{D} \sim \frac{2\pi\eta a^3}{kT} \approx 1s \text{ for } a = 0.5\mu m$$
$$\approx 1000s \text{ for } a = 5\mu m$$
$$\approx 10^9 s \sim 30\,yrs \text{ for } a = 500\mu m$$

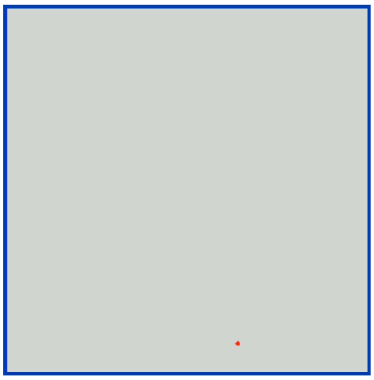
- **Shear-induced:** $Pe = \dot{\gamma} t_a = \frac{\dot{\gamma} a^2}{D_B} >> 1$

$$(v')^2 \sim (\dot{\gamma} a)^2\,, \quad \tau \sim \dot{\gamma}^{-1}\,, \quad D \sim \dot{\gamma} a^2$$



GI Taylor film: "Low Reynolds Number Flows"

Does shear-induced diffusion exist? You Judge!

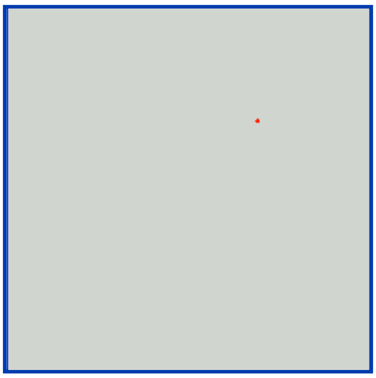


Run A

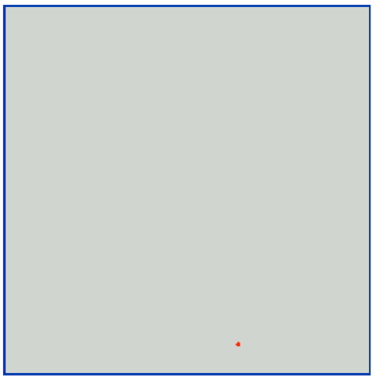
View is in the velocity-gradient -- vorticity plane

Simple Shear Flow
ϕ = 0.35, *Re* << 1
***Pe* = 0, ∞**

Run B



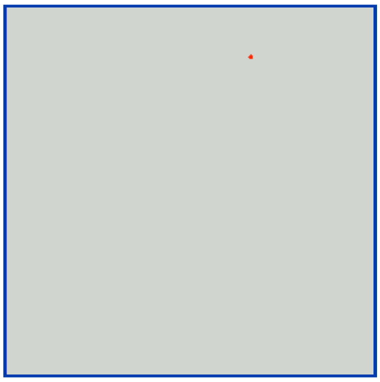
Which one is which?



Run C

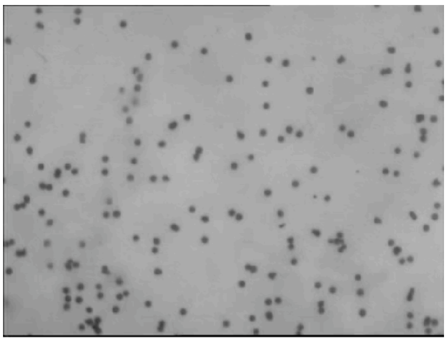
Same as previous runs, but at a finer time scale

Run D

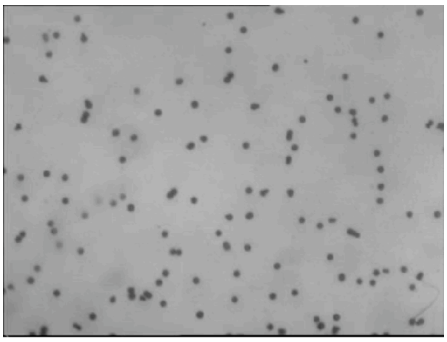


Oscillatory Shear: Chaos & Reversibility

[Pine, Gollub, Brady & Leshansky *Nature* (2005)]

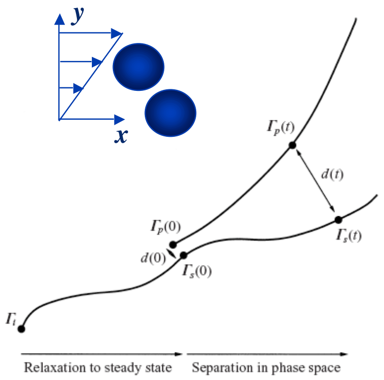


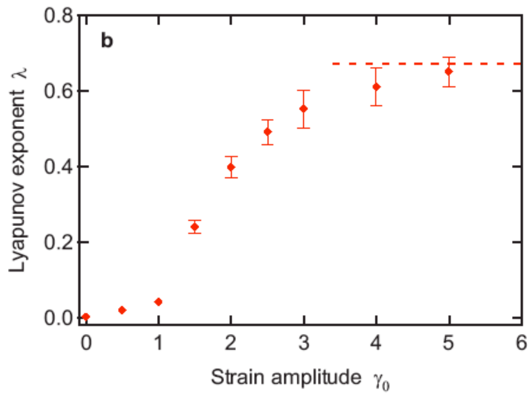
Small Strain Amplitude



Large Strain Amplitude

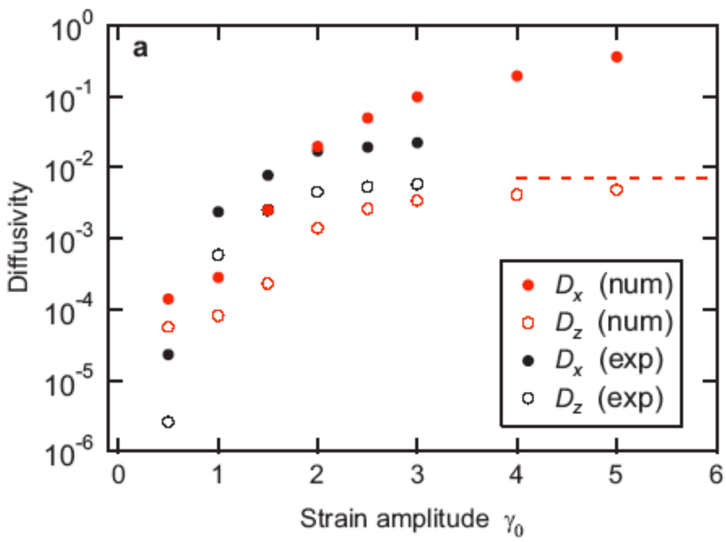
Oscillatory Shear: Lyapunov Exponent

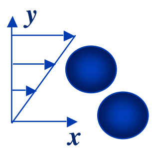




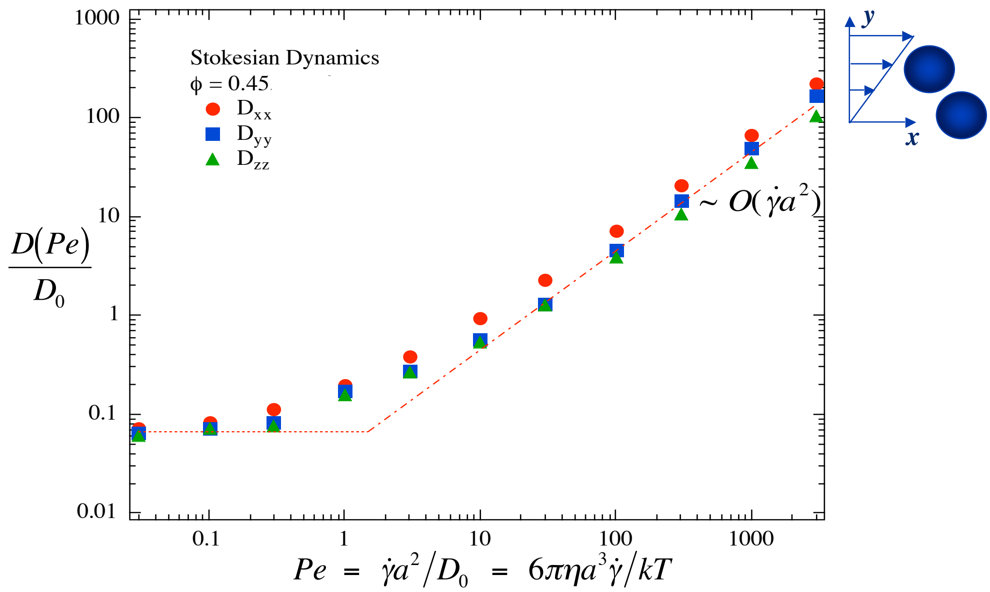
$$\lambda = \frac{d}{dt} \ln\left[d(t)/d(0)\right]$$

Oscillatory Shear: Diffusivities

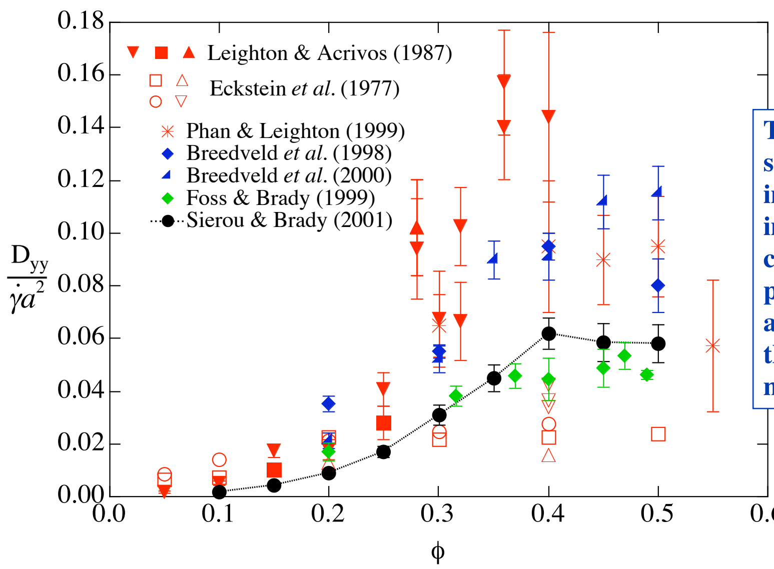




Shear-Induced Diffusivity



Shear-Induced Self-Diffusivity



The shear-induced self-diffusivity increases with increasing concentration as particle collisions are responsible for the diffusive motion.

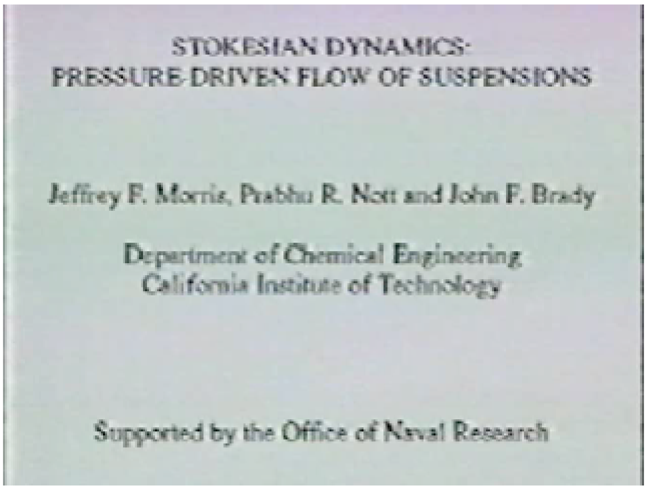
Shear-Induced Particle Diffusion

- We see that particles undergo a random walk and diffuse, even though there are no thermal effects.
- But what does this have to do with the phase behavior in two-phase flow?
- Diffusion usually smoothes out concentration variations and makes the system more homogeneous.
- But …

$$D \;\sim\; \dot{\gamma} a^2 d(\phi)$$

- If the shear rate varies in a flow, then particles will migrate to regions of low shear rate (Leighton & Acrivos 1987).

Pressure-driven flow of suspensions ($H/a = 30$, $\phi_A = 0.4$)

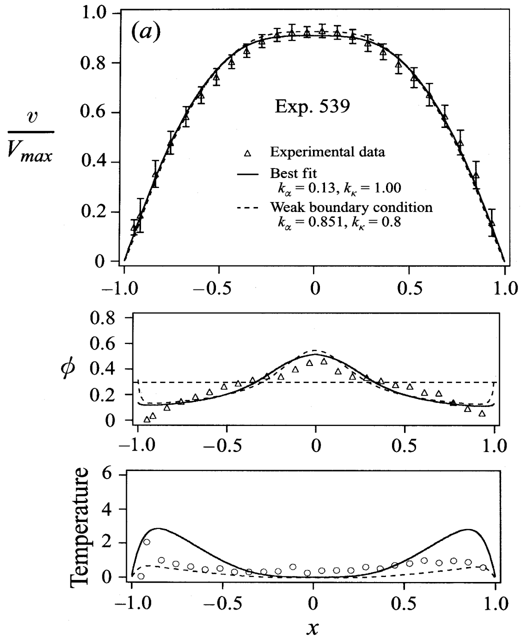


Particle Migration

- Because the diffusivity is proportional to the shear rate, when the shear rate varies as in pressure-driven flow, the particles migrate from regions of high shear rate to low, much as molecules migrate from high temperature to low -- the Soret effect.

- This behavior can be modeled by writing mass and momentum balances for the particles and fluid -- two-phase flow equations.

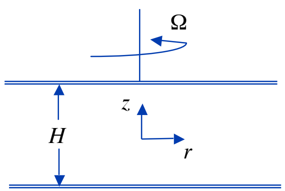
Lyon & Leal (1998)



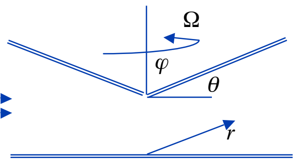
Another Issue: Flows with curved streamlines

Parallel Plate: $\dot{\gamma} = \Omega \frac{r}{H}$

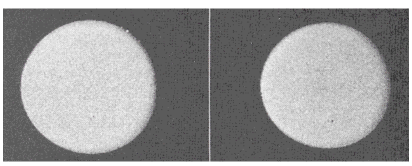
Cone & Plate: $\dot{\gamma}$ is constant



suspension

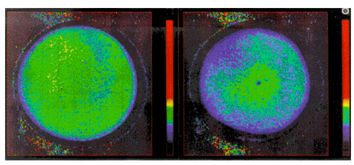


NMR images of fluid fraction (Chow, *et al., Phys. Fluids* 1994)



before after

$a = 50\mu m$
$\phi = 0.5$

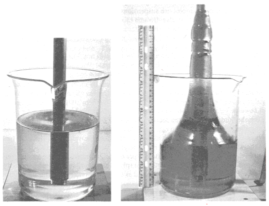


before after

$\boxed{N_1 = -\frac{5}{4}N_2 - \frac{3}{4}\Pi}$ ⇐ stress balance: no migration ⇒ $\boxed{N_1 = -2N_2}$

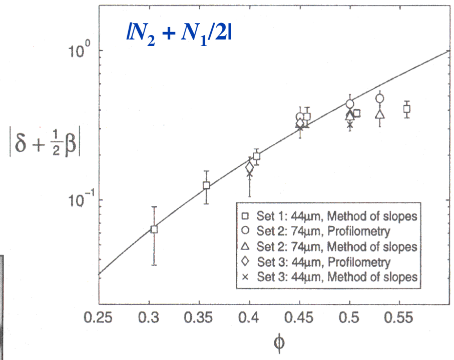
Normal Stress Effects

Rod climbing ($N_1 > 0$)



(From DPL1, Bird, Armstrong & Hassager)

Zarraga, *et al.*, *J. Rheol.* (2000)



Rod falling ($N_2 + N_1/2 < 0$)

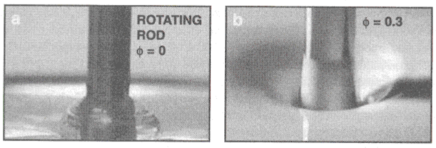


FIG. 14. Weissenberg rod climbing effect at 298 K. (a) pure PDMS polymer, (b) suspension at $\phi = 0.3$.

Aral & Kalyon, *J. Rheol.* (1997)

The Minimal Model

- **Stress is function of concentration and shear rate.**
- **Normal stresses are important**
- **Motion of concentration relative to the mean**

Suspension Balance Model (Nott & Brady, *JFM* 1994)

Bulk suspension:

$$\rho \frac{D\boldsymbol{u}}{Dt} = \nabla \cdot \sigma \ , \quad \nabla \cdot \boldsymbol{u} = 0$$

Particle phase:

$$\rho_p \phi \frac{D\boldsymbol{u}_p}{Dt} = -\phi R(\phi)\left(\boldsymbol{u}_p - \boldsymbol{u}\right) + \nabla \cdot \sigma_p \ , \quad \frac{\partial \phi}{\partial t} + \nabla \cdot \phi \boldsymbol{u}_p = 0$$

The Minimal Model

- **Stress is function of concentration and shear rate.**
- **Normal stresses are important**
- **Motion of concentration relative to the mean**

Particle phase:

$$\rho_p \phi \frac{D\boldsymbol{u}_p}{Dt} = -\phi R(\phi)(\boldsymbol{u}_p - \boldsymbol{u}) + \nabla \cdot \sigma_p \ , \quad \frac{\partial \phi}{\partial t} + \nabla \cdot \phi \boldsymbol{u}_p = 0$$

No particle inertia:

$$\phi(\boldsymbol{u}_p - \boldsymbol{u}) = \frac{1}{R(\phi)} \nabla \cdot \sigma_p \quad \Rightarrow \quad \frac{\partial \phi}{\partial t} + \nabla \cdot \phi \boldsymbol{u} = -\nabla \frac{1}{R(\phi)} \nabla \cdot \sigma_p$$

Stress-induced diffusion

The Minimal Model

- **Stress is function of concentration and shear rate.**
- **Normal stresses are important**
- **Motion of concentration relative to the mean**

Bulk suspension: $\sigma = -p\boldsymbol{I} + 2\eta \boldsymbol{e} + \sigma_p \ , \quad \rho \frac{D\boldsymbol{u}}{Dt} = \nabla \cdot \sigma \ , \quad \nabla \cdot \boldsymbol{u} = 0$

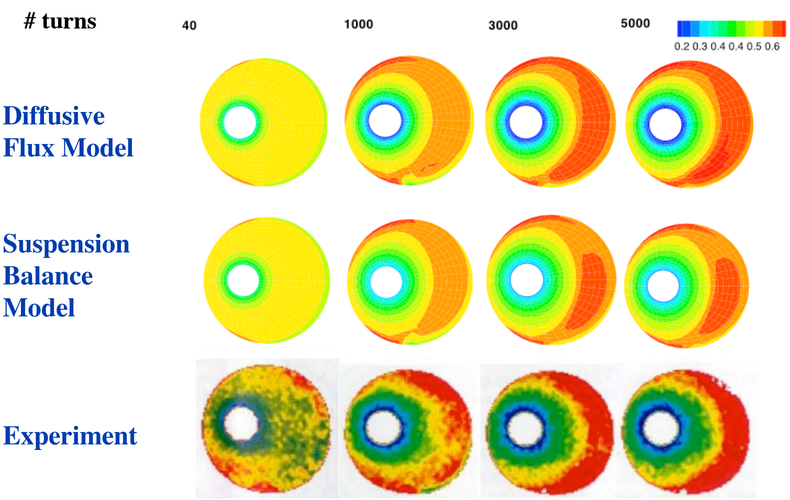
Particle phase: $\sigma_p = -\Pi(\phi,\dot{\gamma})\boldsymbol{I} + 2\eta_p(\phi,\dot{\gamma})\boldsymbol{e} + \boldsymbol{N}_p(\phi,\dot{\gamma})$

Osmotic pressure | **Shear viscosity** | **Normal stress differences**

$$\frac{\partial \phi}{\partial t} + \nabla \cdot \phi \boldsymbol{u} = -\nabla \frac{1}{R(\phi)} \nabla \cdot \sigma_p \quad \Rightarrow \quad D(\phi,\dot{\gamma}) = \frac{1}{R(\phi)} \frac{\partial \Pi(\phi,\dot{\gamma})}{\partial \phi}$$

Modeling Suspension Flows (Fang *et al* 2002)

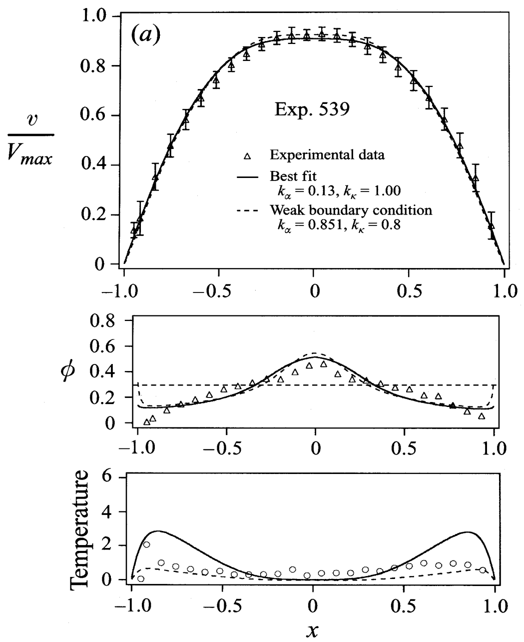
Eccentric journal bearing, e/c = 1/2, $\phi = 0.5$, (H/a) = 35.3



Particle Migration

- Because the diffusivity is proportional to the shear rate, when the shear rate varies as in pressure-driven flow, the particles migrate from regions of high shear rate to low, much as molecules migrate from high temperature to low -- the Soret effect.
- This behavior can be modeled by writing mass and momentum balances for the particles and fluid -- two-phase flow equations.

Lyon & Leal (1998)



The (next) Minimal Model

- **Stress is function of concentration and shear rate.**
- **Normal stresses are important**
- **Motion of concentration relative to the mean**
- **Nonlocal behavior:** $\sigma_p(\boldsymbol{x},t) = \int \eta_p(\boldsymbol{x}-\boldsymbol{x}')\boldsymbol{e}(\boldsymbol{x}')d\boldsymbol{x}'$

Suspension Temperature: $T = \frac{1}{2}\left(\boldsymbol{u}'_p \cdot \boldsymbol{u}'_p\right)$

Energy balance:

$$\rho C_p \frac{DT}{Dt} = \sigma : e - \alpha(\phi)T - \nabla\cdot\boldsymbol{q} \quad , \quad \boldsymbol{q} = -k(\phi)\nabla T$$

$$\Pi(\phi,\dot{\gamma}) = p(\phi)T$$

Particle Migration

- **Because the diffusivity is proportional to the shear rate, when the shear rate varies as in pressure-driven flow, the particles migrate from regions of high shear rate to low, much as molecules migrate from high temperature to low -- the Soret effect.**
- **This behavior can be modeled by writing mass and momentum balances for the particles and fluid -- two-phase flow equations.**

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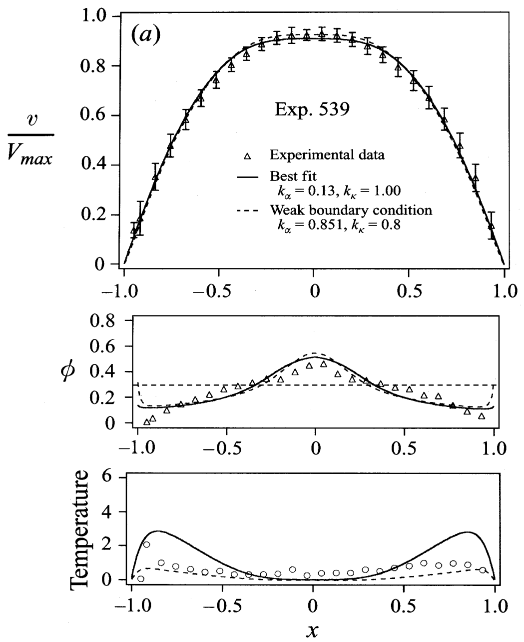
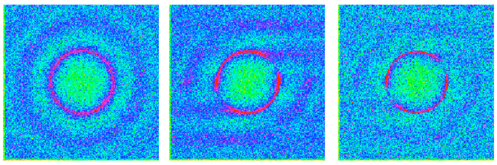


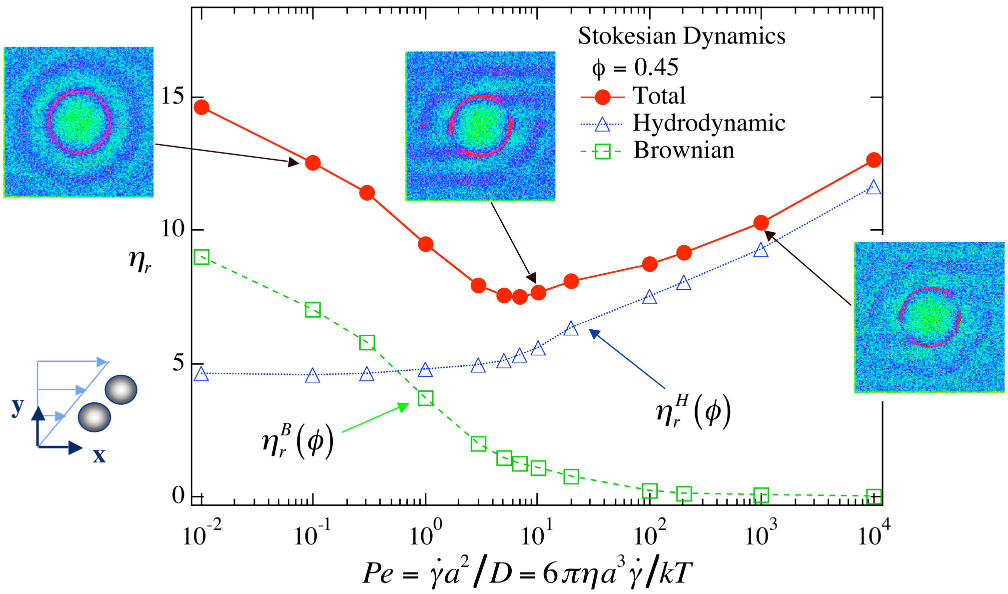
The (next next) Minimal Model

- Stress is function of concentration and shear rate.
- Normal stresses are important
- Motion of concentration relative to the mean
- Nonlocal behavior

- Microstructural evolution

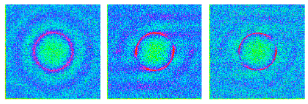


Brownian & hydrodynamic contributions to stress



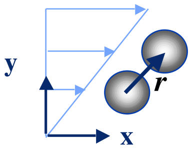
The (next next) Minimal Model

- Stress is function of concentration and shear rate.
- Normal stresses are important
- Motion of concentration relative to the mean
- Nonlocal behavior
- Microstructural evolution:



$$\sigma_p^H \sim -n^2 \int \boldsymbol{r}\boldsymbol{F}^{shear} g(\boldsymbol{r})d\boldsymbol{r} \quad , \quad \boldsymbol{F}^{shear} \sim -3\pi\eta'_\infty(\phi)a^2\dot{\gamma} \times \hat{\boldsymbol{r}}(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{e}}\cdot\hat{\boldsymbol{r}})$$

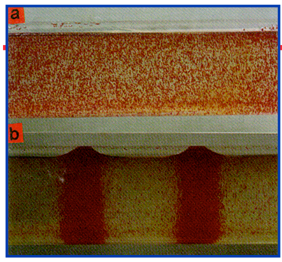
$$\sigma_p^B \sim -n^2 \int \boldsymbol{r}\boldsymbol{F}^{B} g(\boldsymbol{r})d\boldsymbol{r} \quad , \quad \boldsymbol{F}^{B} \sim -\boldsymbol{D}(\phi,\dot{\gamma})\cdot\nabla \ln g(\boldsymbol{r})$$



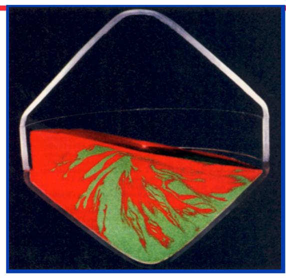
$$\frac{\partial g(\boldsymbol{r},t)}{\partial t} + \nabla\cdot\boldsymbol{v}_{rel}\, g = \nabla\cdot\boldsymbol{D}\cdot\nabla g \quad + \quad \cdots$$

Pattern Formation

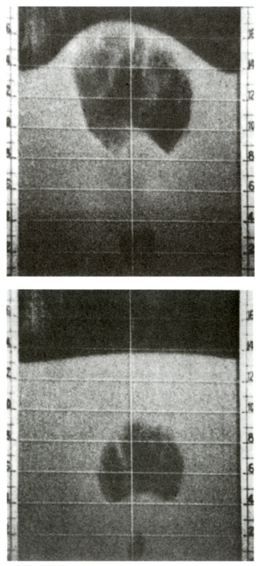
Tirumkudulu *et al* (1999)



Shinbrot & Muzzio (2000)

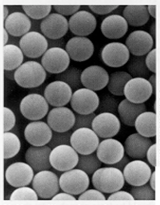


Zoueshtiagh & Thomas (2000)



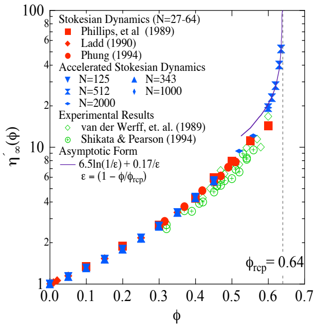
Fluidized bed (Jackson 2000)

Multilevel Approach



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

Particle-level (Microscopic) Interactions



Average (Mesoscopic) Behavior

Bulk (Macroscopic) Flows

The End