The Micromechanics of Colloidal Dispersions

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And backed by: NSF, NASA, ONR, PRF

ICI Distinguished Lecture
University of Alberta
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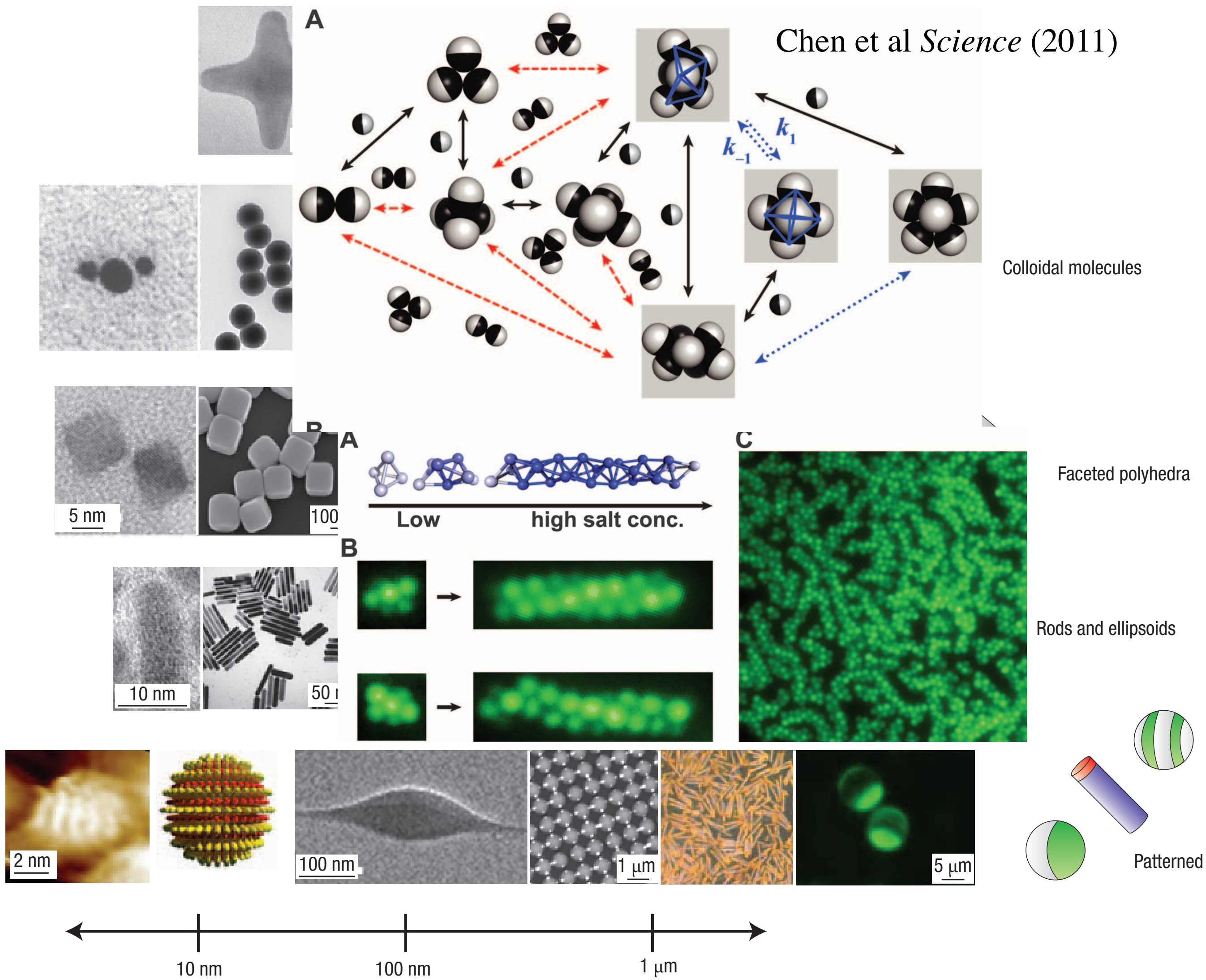
Outline

- What's a colloid and why do we care?
- How did the field start?
- The amazing rheology of spheres. (Or how to walk on water and make a bullet-proof vest.)
- How does random diffusion de-mix a suspension?
- What can we do with active matter?
- Conclusions

What's a Colloid?

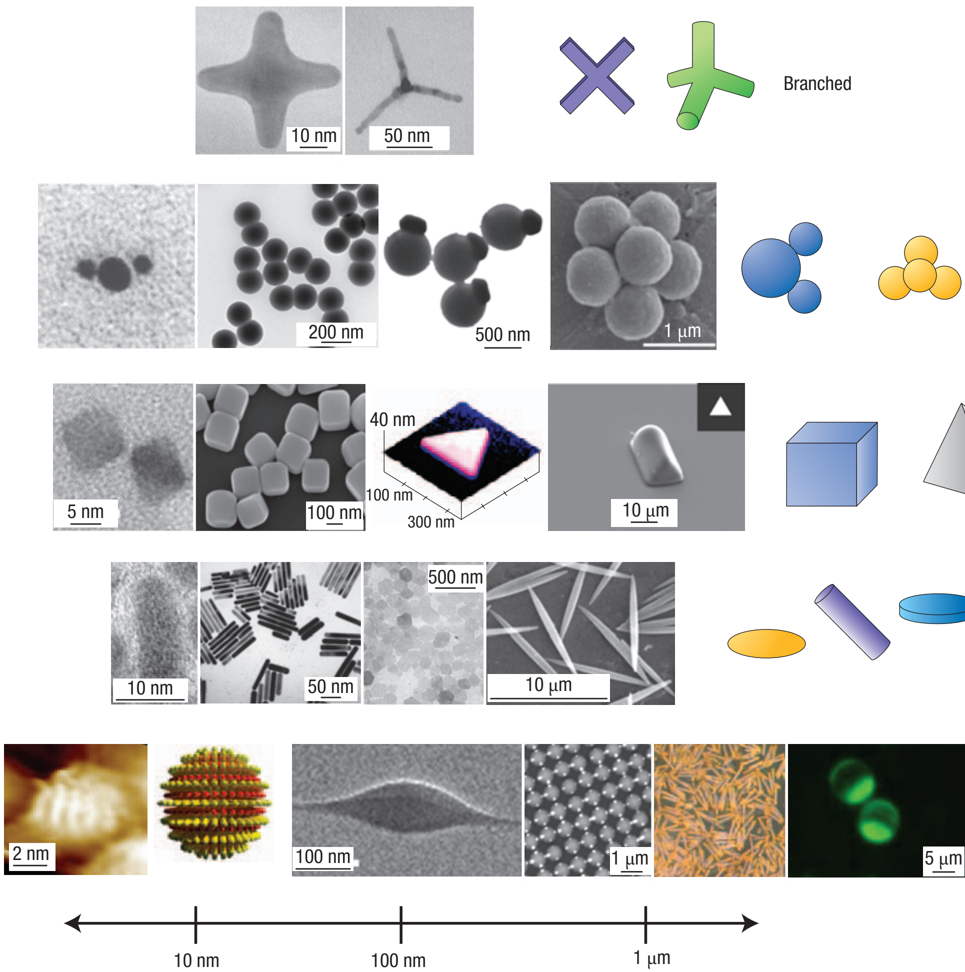
Colloids are small particles dispersed in a liquid. They come in a variety of sizes - typically from 10nm to 10µm - shapes and colors.

Because of their small size, Brownian forces (kT) compete against interparticle forces (V) and hydrodynamics to set the structure and determine properties.



Glotzer & Solomon, *Nature Materials* (2007)

Why do we care?



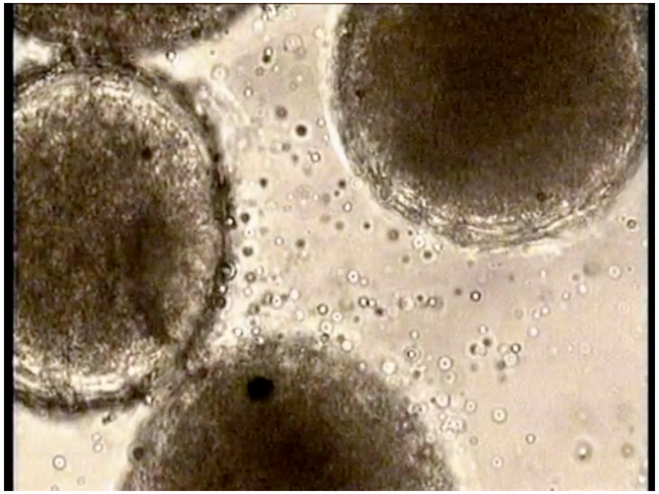
Glotzer & Solomon, *Nature Materials* (2007)

How did the field start?

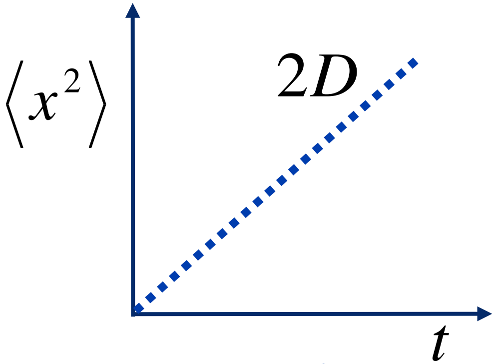
The answer is Einstein.

Einstein (circa 1905)

Brownian Motion



Brown (circa 1827)



Mean-square displacement

Stokes-Einstein Relation

$$D = kTM \quad \left(= \frac{kT}{6\pi\eta a} \right)$$

$$\boldsymbol{F}^H = -6\pi\eta a \boldsymbol{U}$$

$$Re = \rho U a/\eta \ll 1$$

Stokes (circa 1851)

W. Sutherland (1905)

(age 20)

(1859-1911)

LXXV. *A Dynamical Theory of Diffusion for Non-Electrolytes and the Molecular Mass of Albumin.* By WILLIAM SUTHERLAND ‡.

IN a paper communicated to the Australian Association for the Advancement of Science at Dunedin, 1904, on the Measurement of Large Molecular Masses, a purely dynamical theory of diffusion was outlined, with the aim of getting a formula for calculating from the data of diffusion those large molecular masses for which the ordinary methods fail. The formula obtained made the velocity of diffusion of a substance through a liquid vary inversely as the radius a of its molecule and inversely as the viscosity of the liquid. On applying it to the best data for coefficients of diffusion D it was found that the products aD, instead of being constant, diminished with increasing a in a manner which made extrapolation with the formula for substances like albumin seem precarious. After looking a little more closely into the dynamical conditions of the problem, it seems to me that the diminution of aD can be accounted for, and can be expressed by an empirical formula which enables us to extrapolate with confidence for a value of a for albumin, and so to assign for the molecular mass of albumin a value whose accuracy depends on that with which D is measured.

The theory is very similar to that of "Ionization, Ionic Velocities and Atomic Sizes" (Phil. Mag. Feb. 1902). Let a molecule of solute of radius a move with velocity V parallel to an x axis through the dilute solution of viscosity η. Then the resistance F to its motion is given by Stokes's formula

$$F = 6\pi V \eta a \frac{1+2\eta/\beta a}{1+3\eta/\beta a} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

* A theorem attributed to Weber. See Gray and Matthews' 'Bessel's Functions,' p. 228.
† See 'Theory of Sound,' § 203, equations (14), (16).
‡ Communicated by the Author.

where β is the coefficient of sliding friction if there is slip between the diffusing molecule and the solution. For N molecules of solute per c.c. of solution the total resistance will be N times this, and in the steady state of diffusion will equilibrate the driving force due to variation of the osmotic pressure of the solute, namely dp/dx, which by the osmotic laws is $RTdc/dx$, if c is the concentration of the solute at x and R is the gas constant. Hence

$$RT\frac{dc}{dx} = 6\pi V \eta a N \frac{1+2\eta/\beta a}{1+3\eta/\beta a}; \quad . \quad . \quad . \quad (2)$$

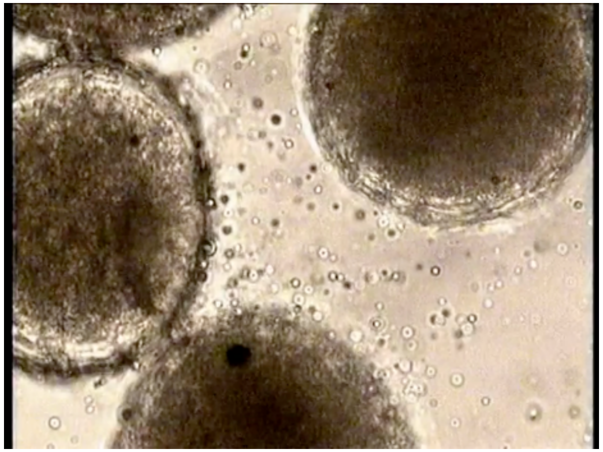
and the required formula for the coefficient of diffusion with C for the number of molecules in a gramme-molecule is

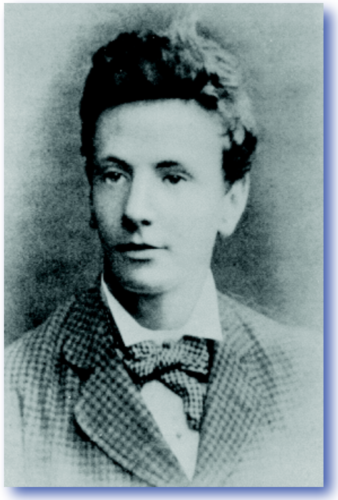
$$D = \frac{RT}{6\pi\eta a C} \frac{1+3\eta/\beta a}{1+2\eta/\beta a} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

How did the field start?

Brownian Motion

Einstein (circa 1905)





Sutherland (circa 1879)

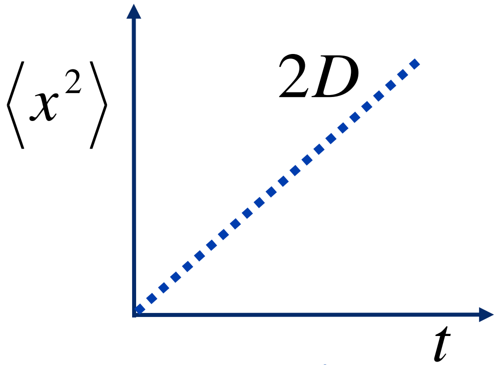
Stokes-Einstein-Sutherland Relation

$$D = kTM \quad \left(= \frac{kT}{6\pi\eta a} \right)$$

$$\boldsymbol{F}^H = -6\pi\eta a \boldsymbol{U}$$

$$Re = \rho U a/\eta \ll 1$$

Stokes (circa 1851)



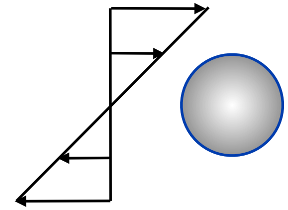
Mean-square displacement

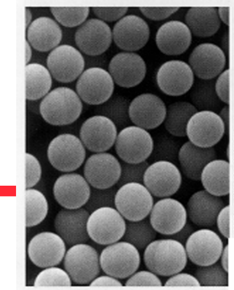
Einstein and the effective viscosity

Einstein (circa 1905)

In *Annalen der Physik* (1906; corrected 1911)

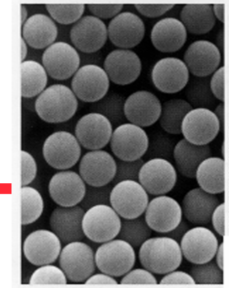
$$\eta_{eff} = \eta\left(1 + \tfrac{5}{2}\phi\right) \quad , \quad \phi = \tfrac{4}{3}\pi a^3 n$$





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

Einstein and Avagadro's Number



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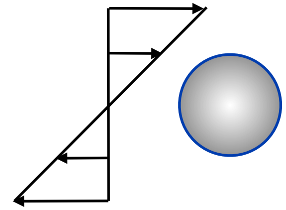


$$\frac{\eta_{eff}}{\eta} - 1 = \frac{5}{2}\frac{4}{3}\pi\left(\frac{\text{gm} - \text{mole}}{\text{vol}}\right) N_A a^3$$

Avagadro (circa 1811)

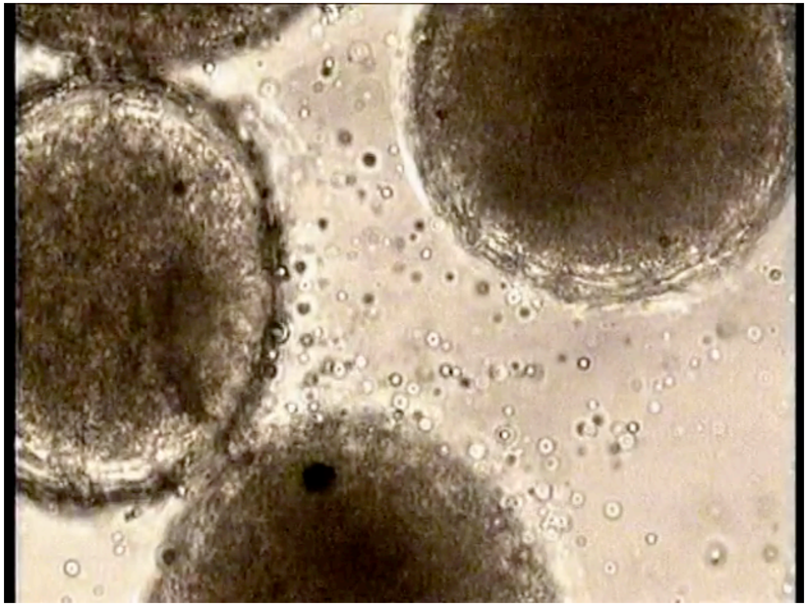
Stokes-Einstein-Sutherland Relation: $D = \dfrac{RT}{6\pi\eta}\dfrac{1}{N_A a}$

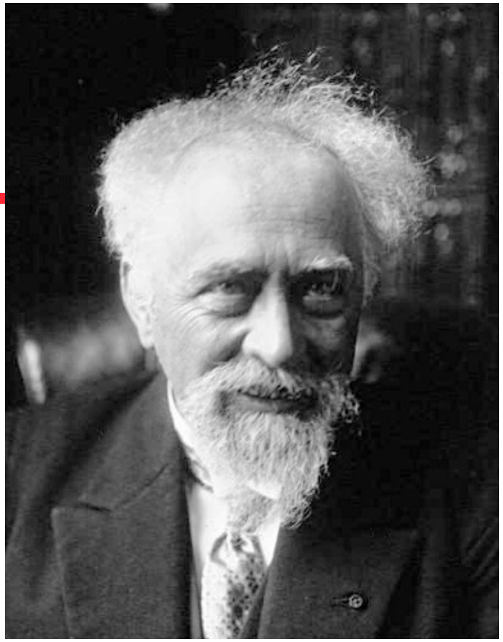
For a sugar molecule:

$$N_A = 6.56 \times 10^{23}$$

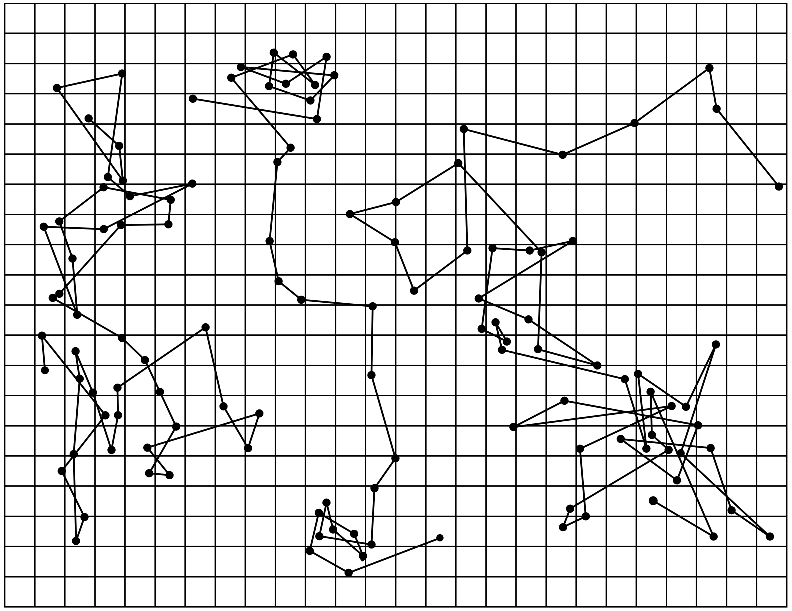
$$a = 4.9\,\mathring{A}$$

Jean B. Perrin (1926 Nobel Prize)

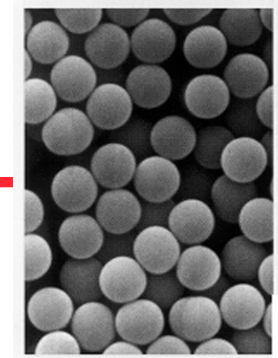




Definitive proof of the atomic nature of matter

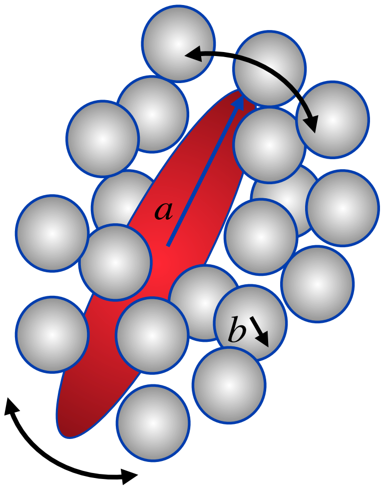


‘Generalized’ Stokes-Einstein-Sutherland Relation



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

solvent molecules



Rotational Diffusivity:

$$D_{rot} = kTM_{rot} \left(= \frac{kT}{8\pi\eta a^3} \right)$$

- **Separation of length and time scales between the motion of the ‘particle’ and that of a solvent molecule: *a/b* >> 1**

particle/ solvent time: $\tau_p/\tau_s \sim (a/b)^2$

 # collisions in particle time: $N_c \sim (a/b)^4$

# of solvent molecules per particle $N_s/N_p \sim (a/b)^3$

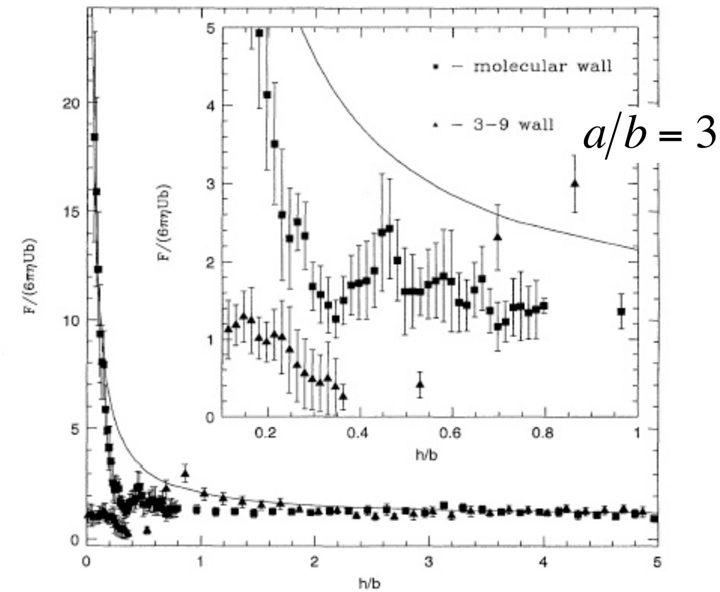
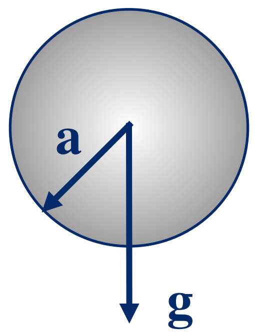


FIG. 2. The force of the fluid resistance acting on ball A approaching a solid molecular or 3-9 wall, $U = 2.0$, $b = 3.0$. The solid line represents the exact continuum result [2].

Vergeles, *et al* *PRL* (1995)

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

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

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

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

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

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

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

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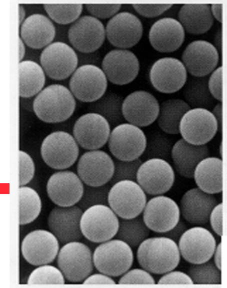
The amazing rheology of spheres

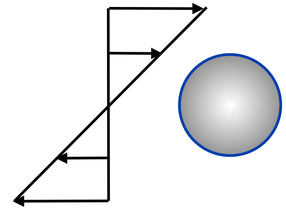


Uniform silica microspheres (1 µm diam, × 10,000).

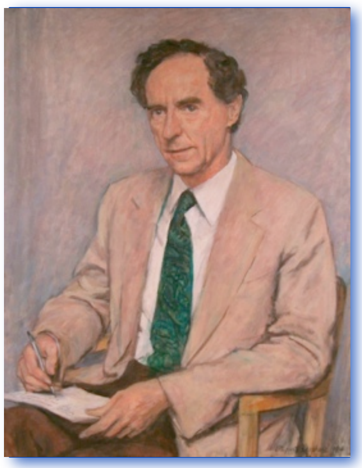
Einstein (1905)

In *Annalen der Physik* (1906; corrected 1911)

$$\eta_{eff} = \eta\left(1 + \tfrac{5}{2}\phi\right) \quad , \quad \phi = \tfrac{4}{3}\pi a^3 n$$



The next correction, $O\left(\phi^2\right)$, took 70 years! Why?



Batchelor

1) Long-range interactions

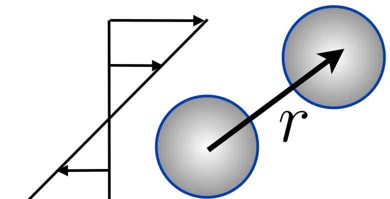
$$u' \sim 1/r^2 \quad , \quad S \sim 1/r^3$$

2) Microstructure

$$g(\boldsymbol{r})$$

3) Brownian contribution to stress

$$\boldsymbol{S}^B$$

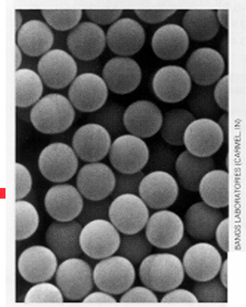


force dipole or ‘Stresslet’ : *S*

$$\Delta\eta^H = 5.0\phi^2$$

$$\Delta\eta^B = 1.2\phi^2$$

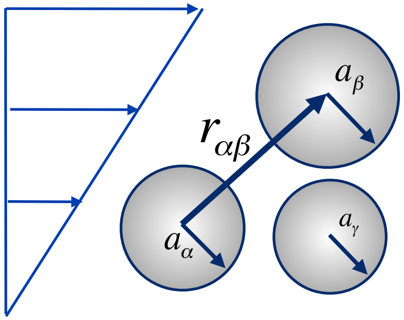
The amazing rheology of spheres



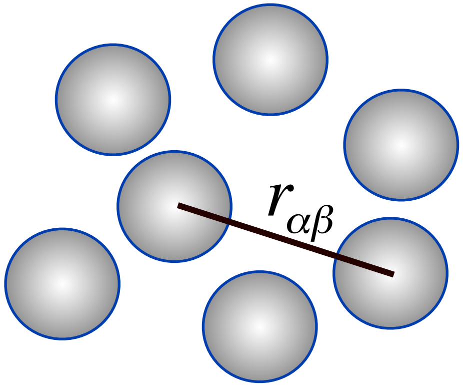
$$\eta^{eff} = \eta\left(1 + \tfrac{5}{2}\phi + 5.0\phi^2 + 1.2\phi^2 + O(\phi^3)\right)$$

Einstein (1906) **Batchelor (1977)**

How about the next term, $O(\phi^3)$? Another 70 years?

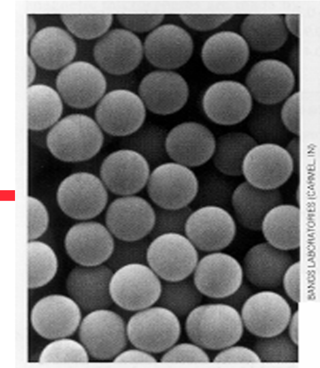


If you can do three, you can do *N*



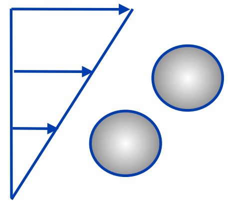
Stokesian Dynamics

Stokesian Dynamics (*Re* << 1)


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

Particle Motion:

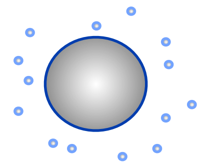
$$m \cdot \frac{dU}{dt} = F^H + F^B + F^P$$



Hydrodynamic:

$$F^H = -R(x) \cdot \left(U - U^\infty\right)$$

Stokes drag



$$\tau_p \sim O(m / 6\pi\eta a)$$
$$\approx 10^{-8} s$$

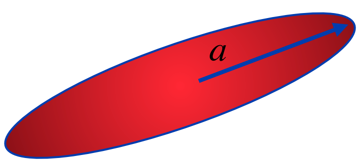
Brownian:

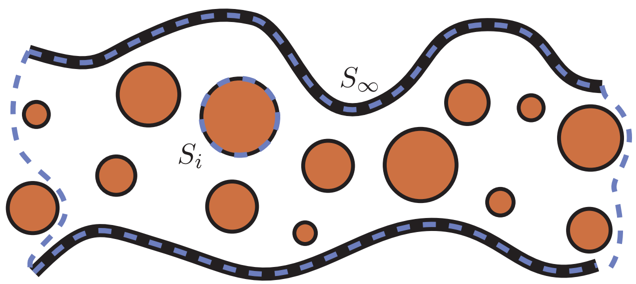
$$\overline{F^B} = 0 \quad , \quad \overline{F^B(0) F^B(t)} = 2kT R(x) \delta(t) \qquad O(10^{-13} s)$$

Interparticle/ external:

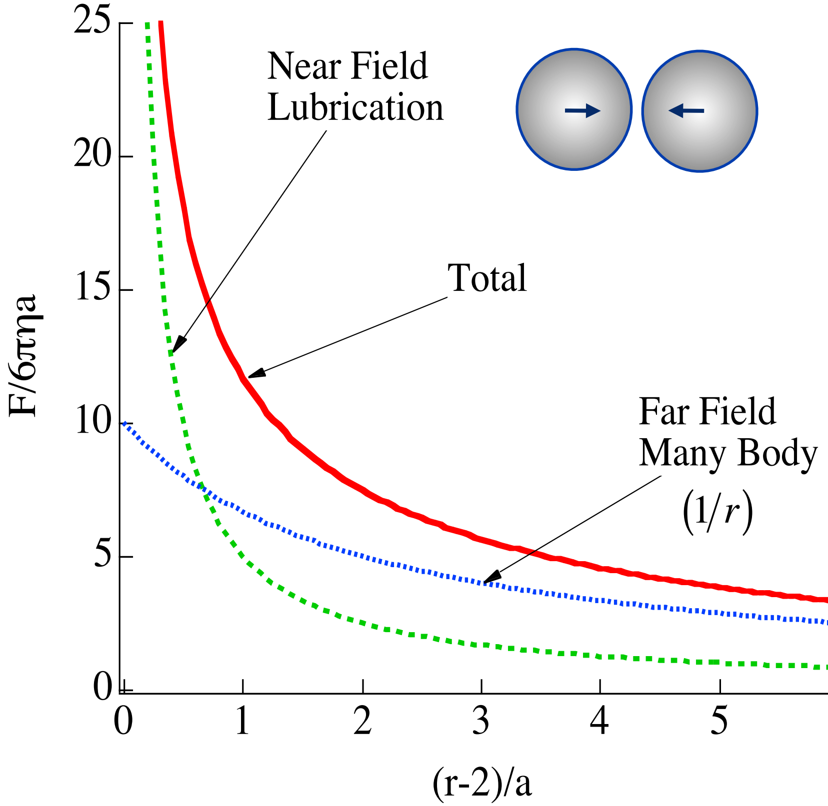
$$F^P = \Delta \rho V_p g \text{ , electrostatic, etc.}$$

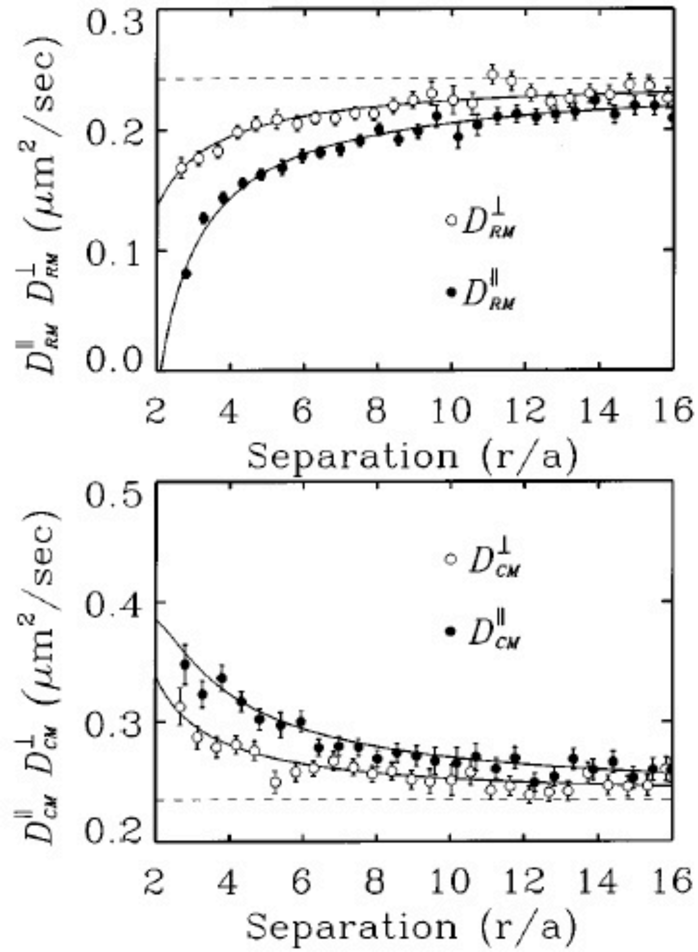
Shape, multiparticle, bounded, etc.





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





Measurement of the hydrodynamic corrections to the Brownian motion of two colloidal spheres

John C. Crocker
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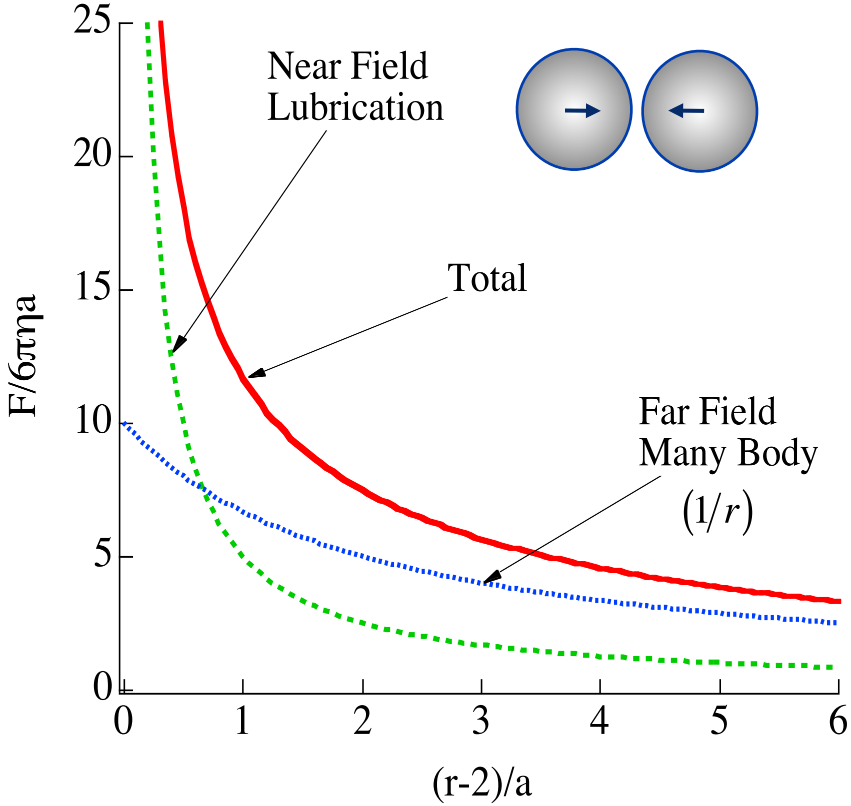
(Received 25 July 1996; accepted 14 November 1996)

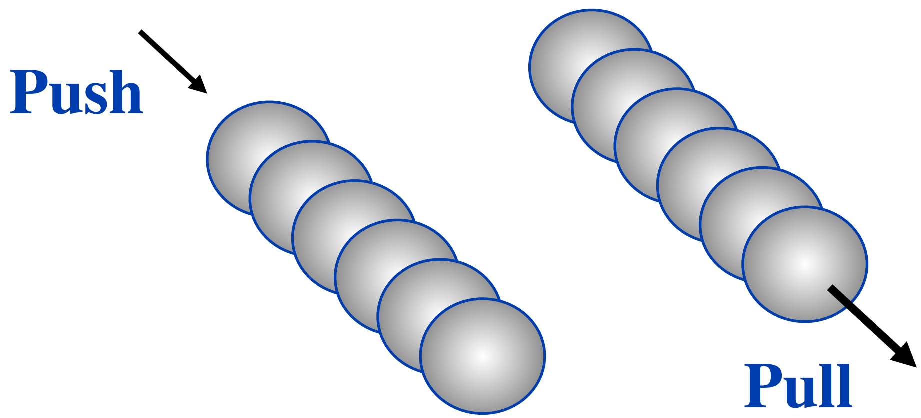
The hydrodynamic coupling between two isolated 0.97 μm diameter polystyrene spheres is measured by reconstructing their Brownian motion using digital video microscopy. Blinking optical tweezers are used to facilitate data collection by positioning the spheres in the microscope's focal

FIG. 1. The measured relative (top) and center of mass (bottom) diffusion coefficients for a pair of colloidal spheres of diameter $2a = 0.966$ μm as a function of dimensionless separation ρ. The solid curves indicate the theoretical prediction given by Eqs. (2)–(5). The dashed line indicates the asymptotic diffusivity $D_0/2$ (top) and $D_0'/2$ (bottom).

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

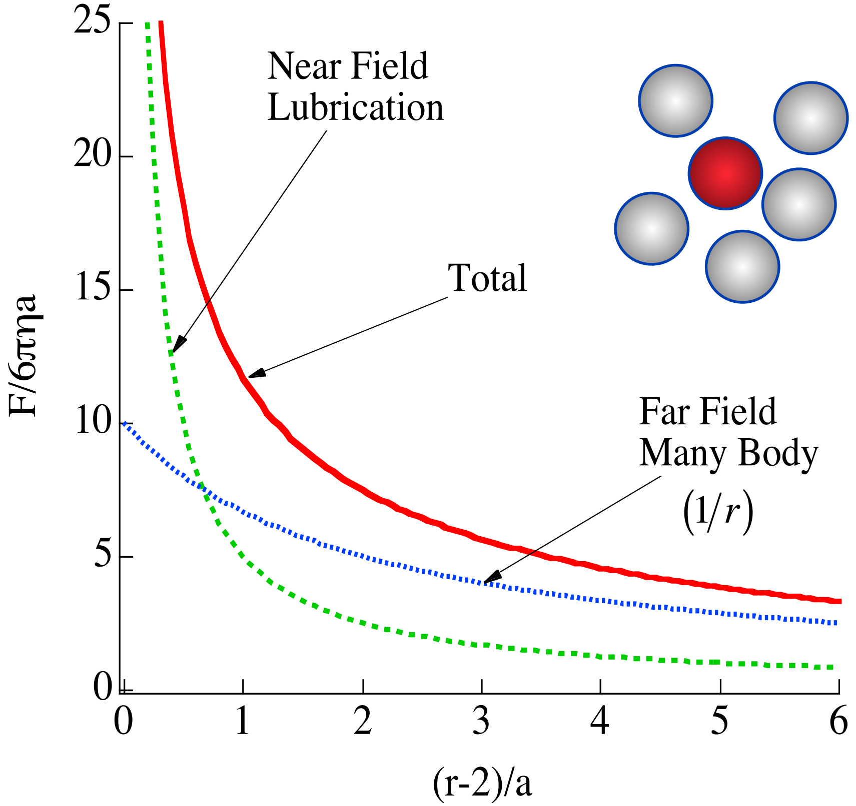


<u>Lubrication</u>: closely spaced particles move as a single (rigid) rod, whether you push or pull.

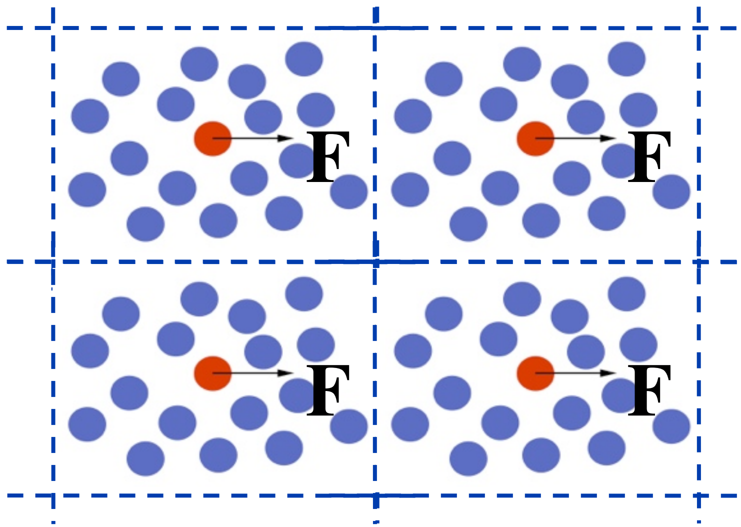


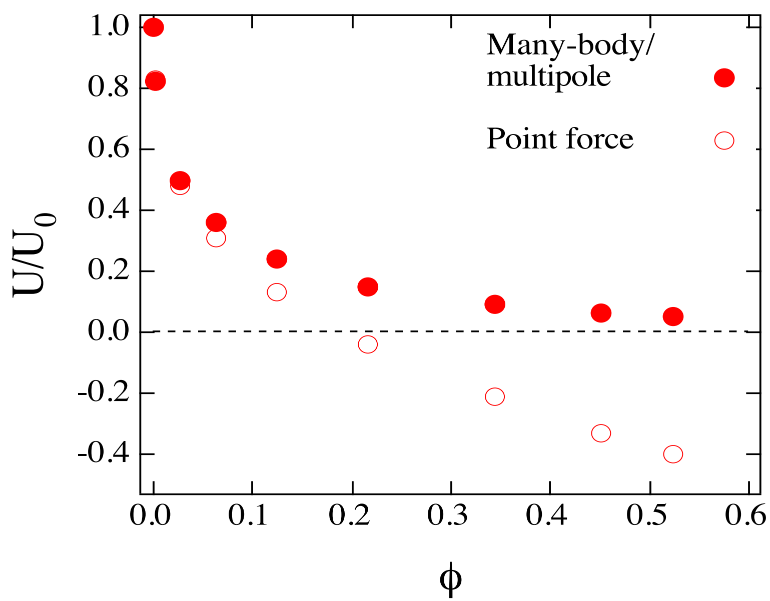
Lubrication: near-field, two-body problem

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



Periodic Boundaries

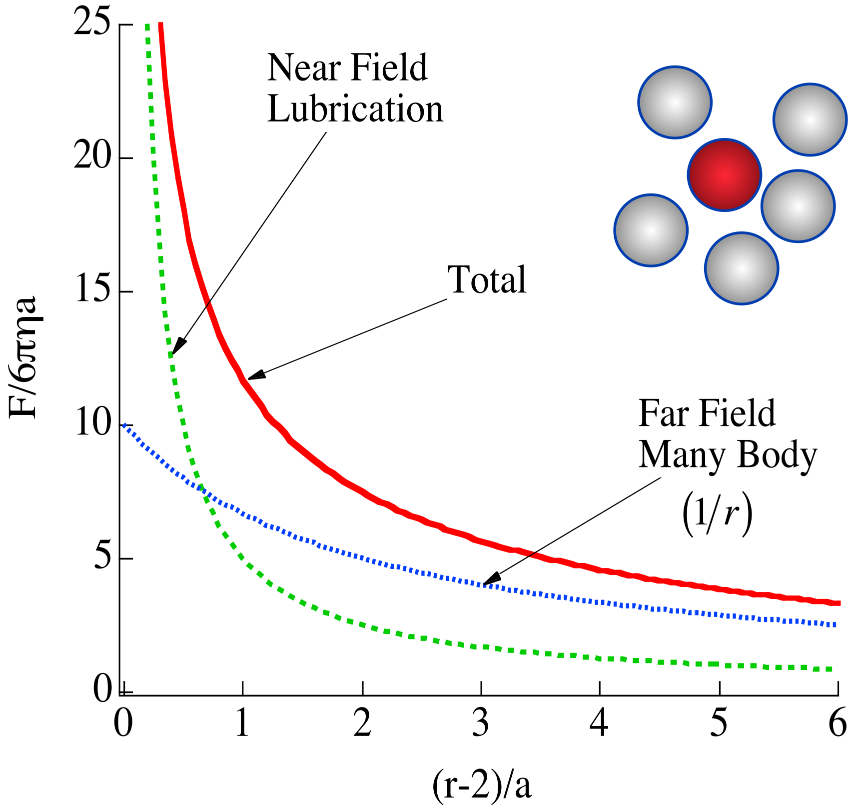




Far-field, many-body problem

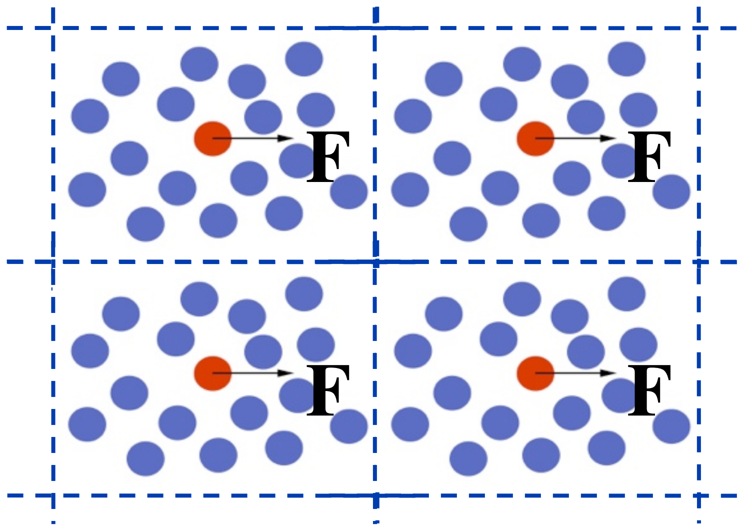
$$\boldsymbol{F}^H = -\boldsymbol{R}^*(\boldsymbol{x}) \cdot \boldsymbol{U}$$

Stokesian Dynamics: $F^H = -R(x) \cdot U$



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

Periodic Boundaries

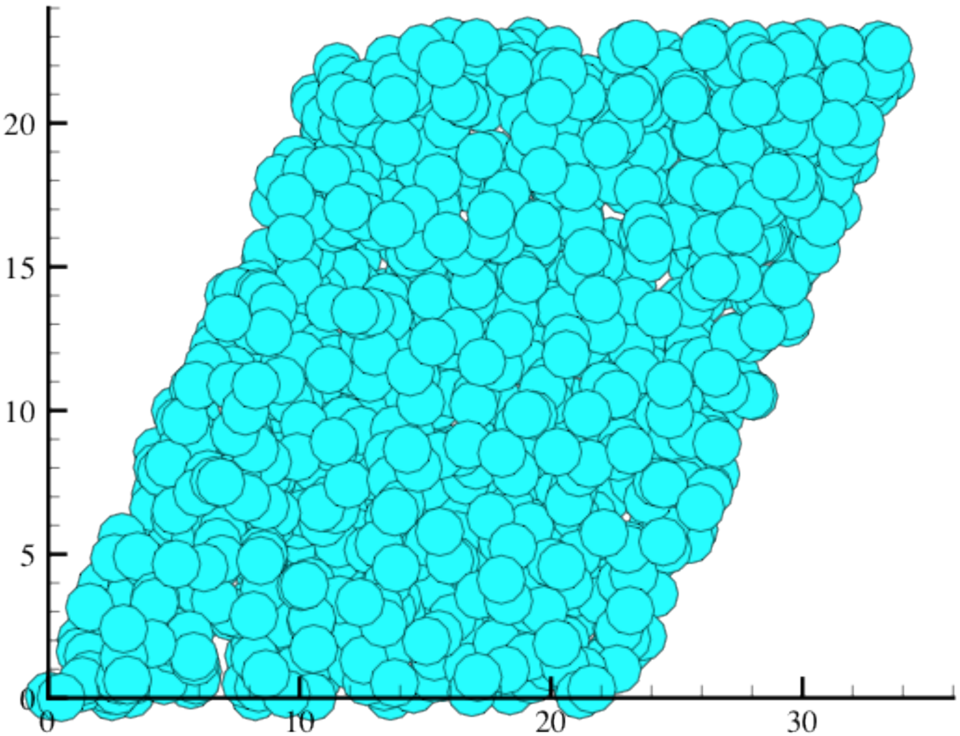


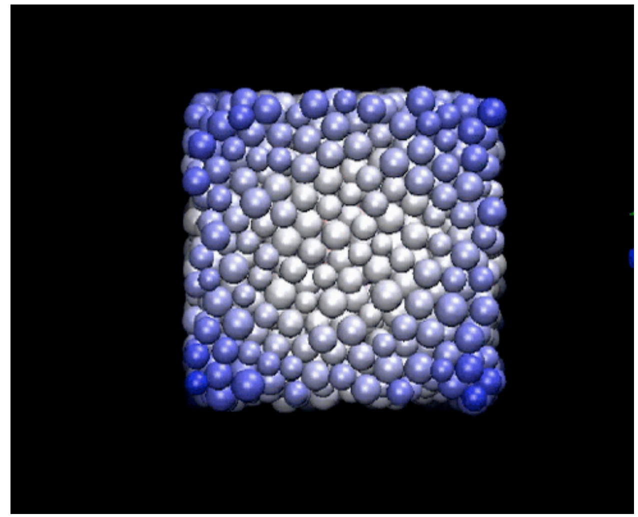
Implement matched asymptotic expansions dynamically for thousands of particles in $O(N \ln N)$ operations for millions of time steps.

$$\frac{d\boldsymbol{x}}{dt} = \boldsymbol{U} = (\boldsymbol{R}^*(\boldsymbol{x}))^{-1} \cdot \boldsymbol{F}^{other}$$

The amazing rheology of spheres

Three dimensional unbounded flow -- periodic boundary conditions

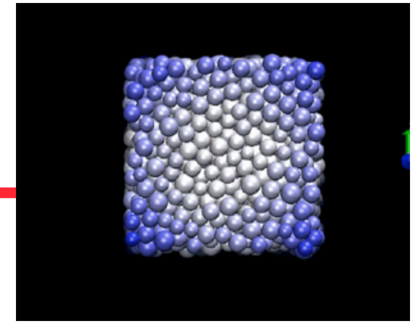


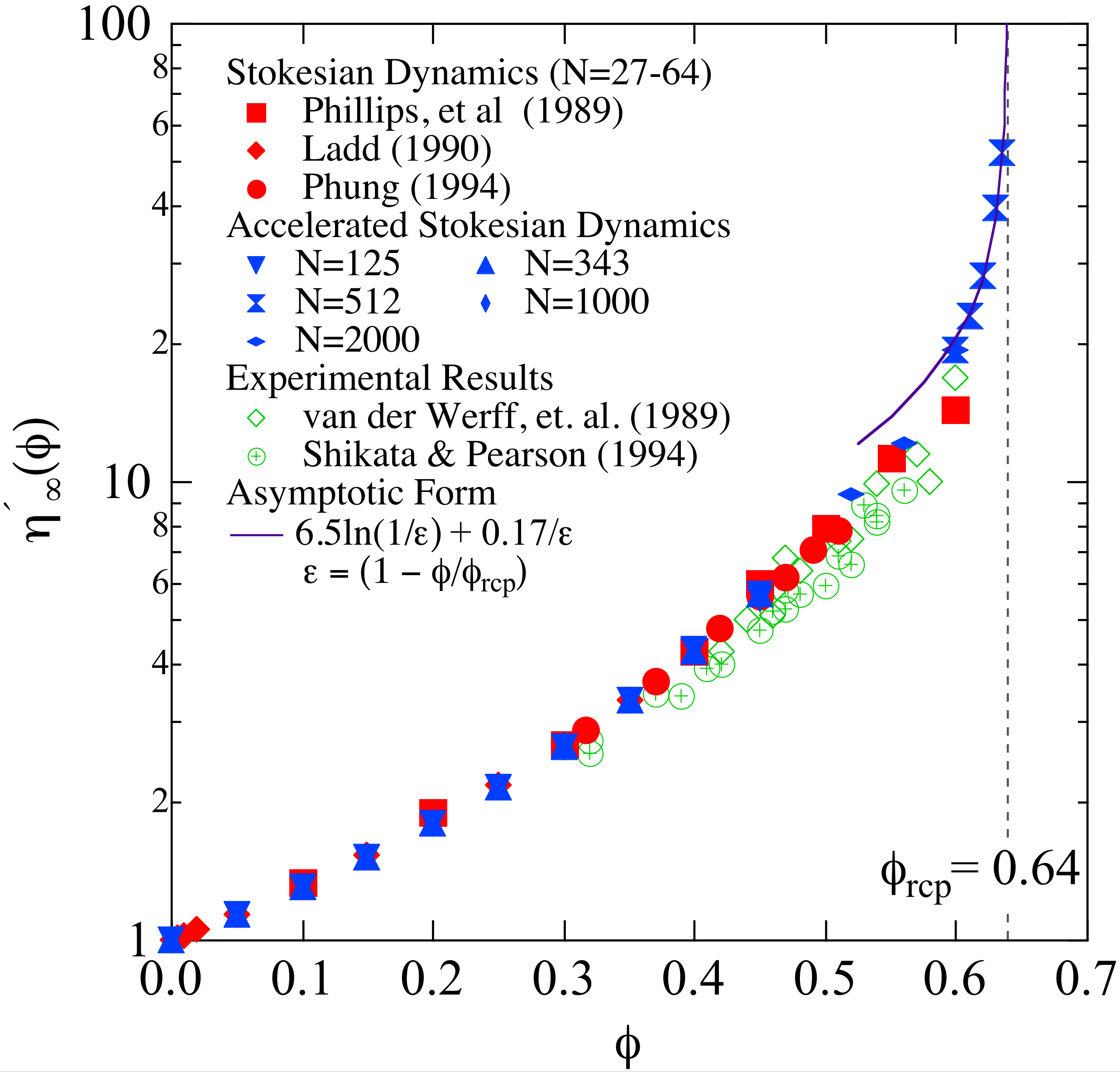


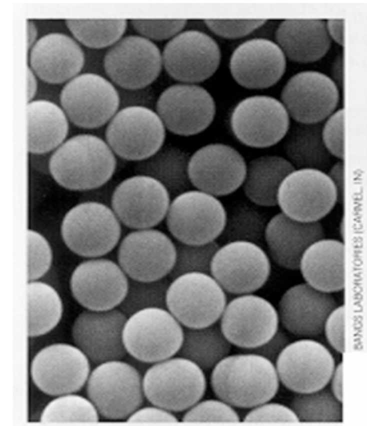
Hydrodynamics
Brownian Motion

$$Pe = \dot{\gamma} a^2 / D = 6\pi\eta a^3 \dot{\gamma} / kT$$

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







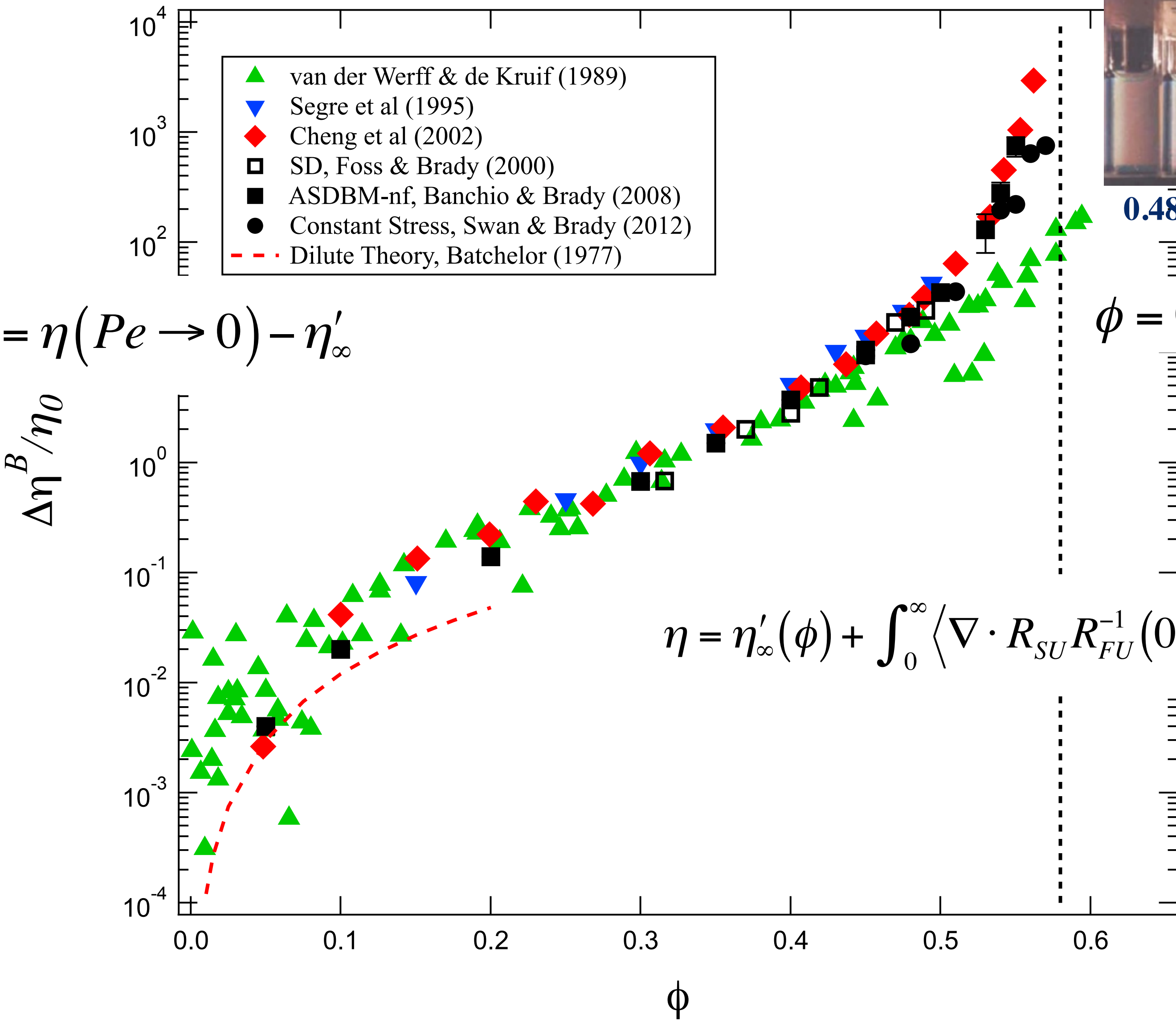
Uniform silica microspheres (1 μm diam., × 10,000).

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

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

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

$$\Delta\eta^B = \eta(Pe \to 0) - \eta'_\infty$$



0.48 0.50 -- 0.55 ----- 0.58 ---- 0.61

Pusey & van Megen (1986)

$$\phi = 0.58$$

$$\eta = \eta'_\infty(\phi) + \int_0^\infty \left\langle \nabla \cdot R_{SU} R_{FU}^{-1}(0) \nabla \cdot R_{SU} R_{FU}^{-1}(t) \right\rangle dt$$

(Banchio & Brady 2003)

Sheared 'Hard-Sphere' Suspensions

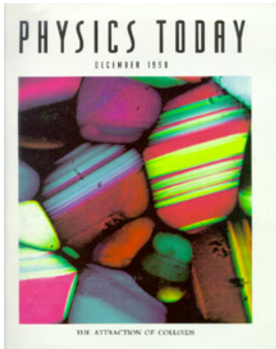
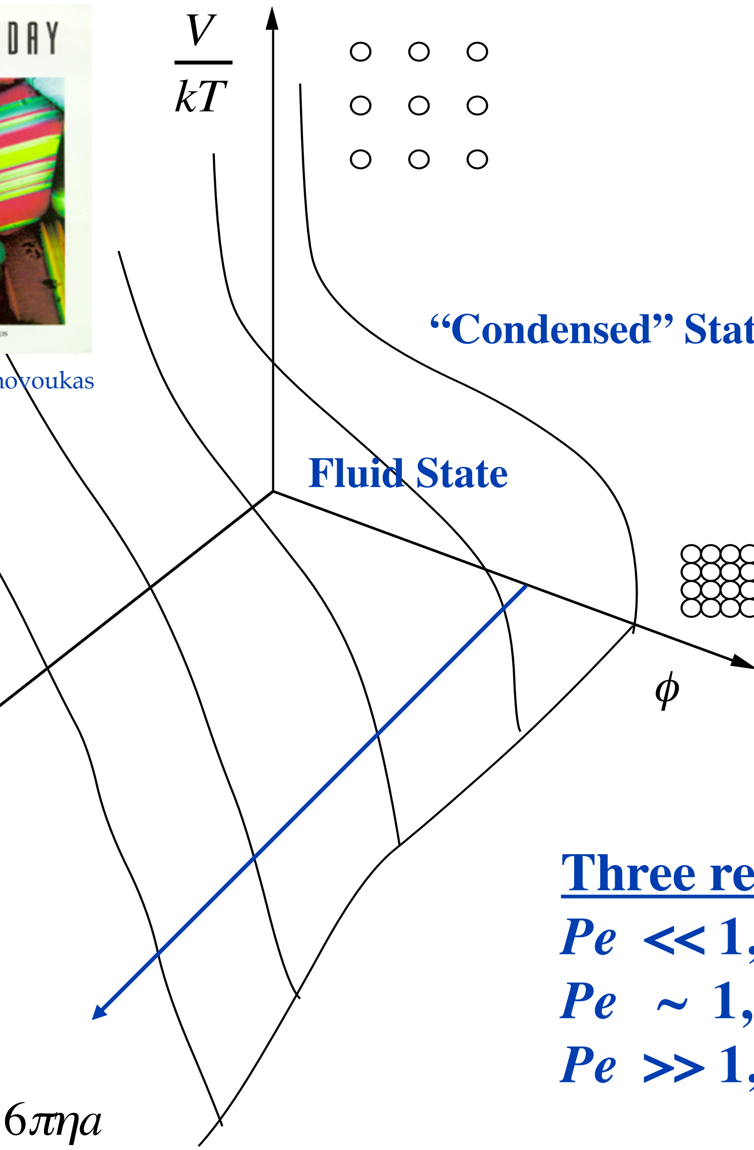
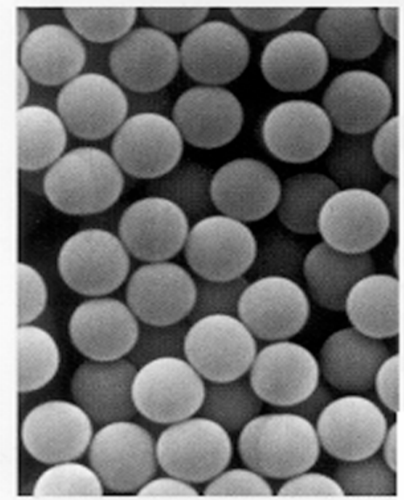


Photo by Y. Monovoukas





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

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

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

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

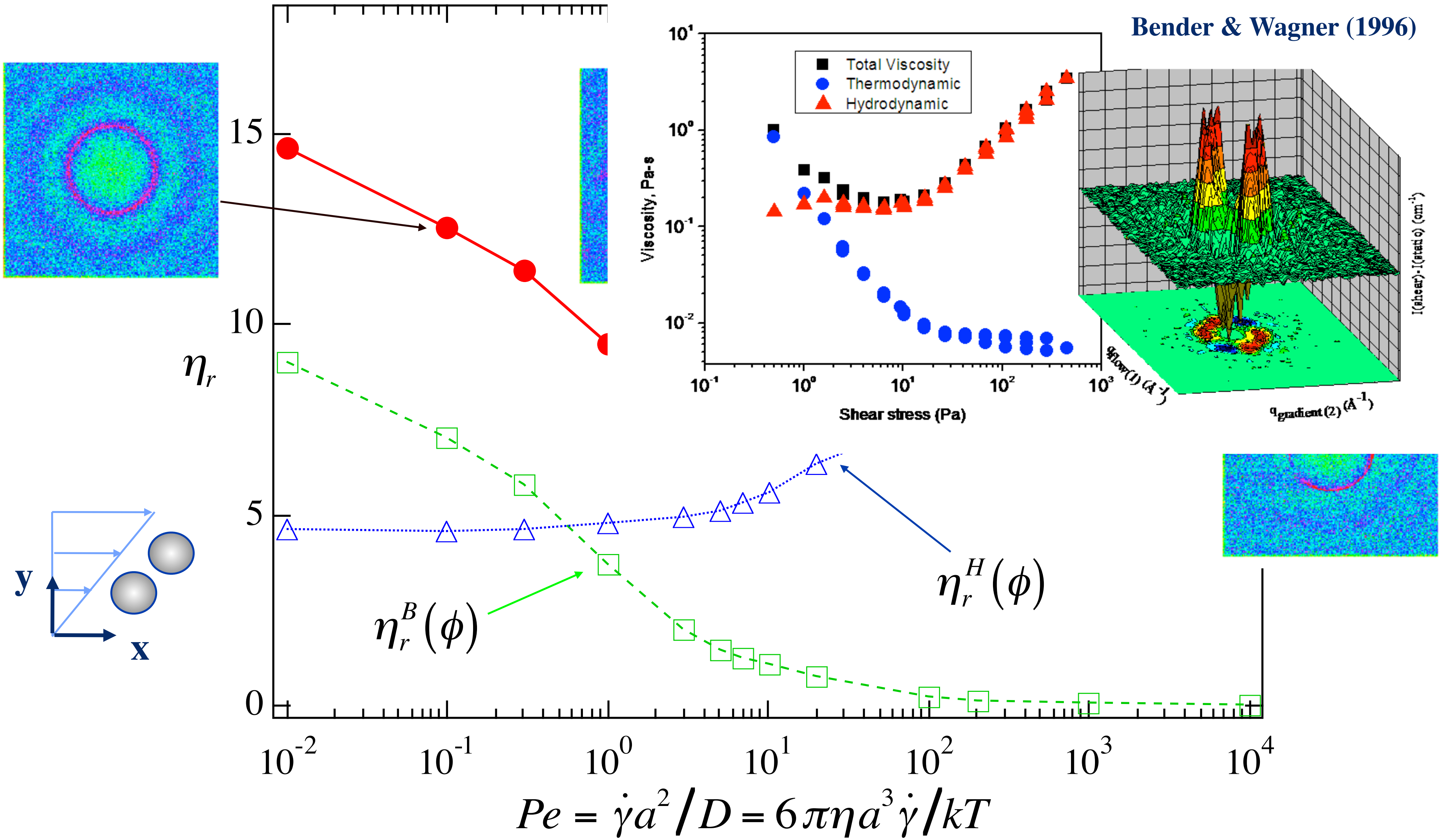
Three regimes:

***Pe* $\ll 1$, Brownian dominated**

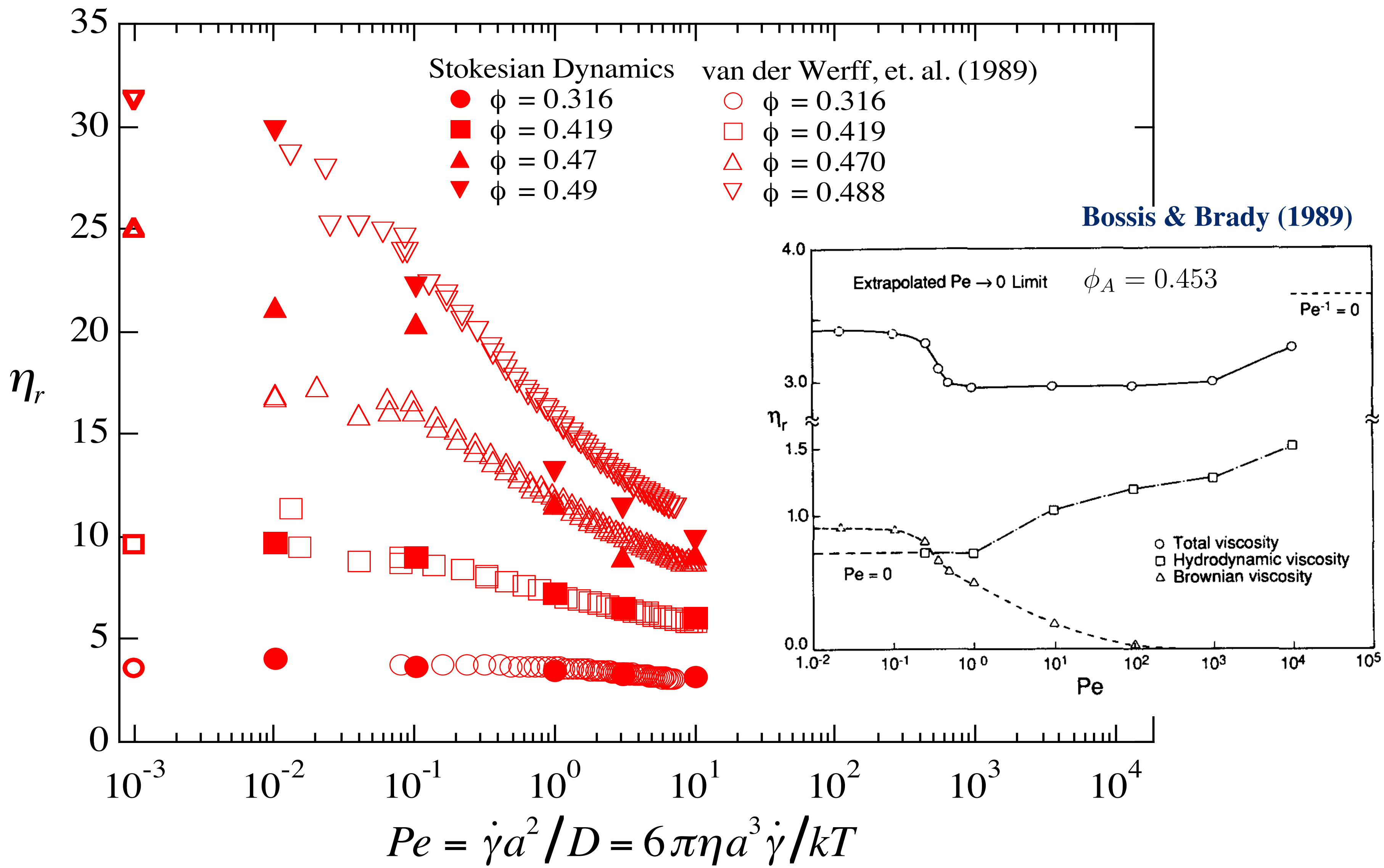
***Pe* ~ 1, Balance**

***Pe* $\gg 1$, Hydrodynamic dominated**

Brownian & hydrodynamic contributions to stress

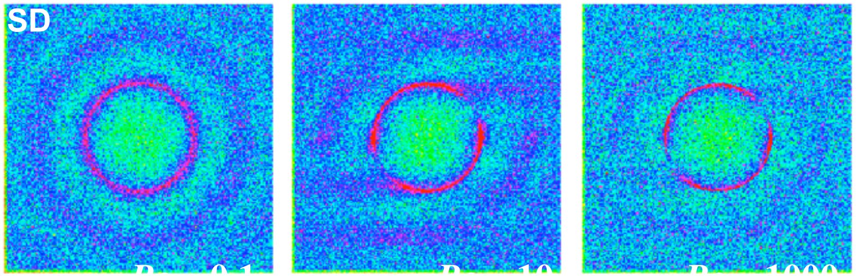


Rheology: Simulation vs. Experiment

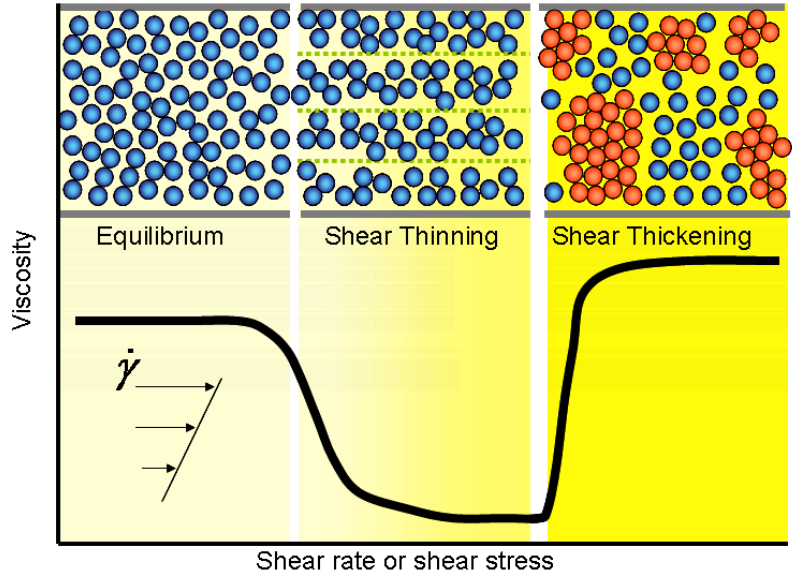


Mechanism of shear thickening: hydroclusters

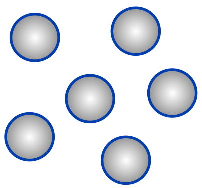
g(x,y)



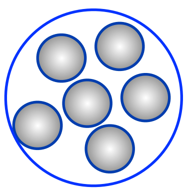
Wagner & Brady (*Phys. Today* 2009)



Hydrodynamic stress: $S^H \sim \eta\,\dot{\gamma}\,a^3$

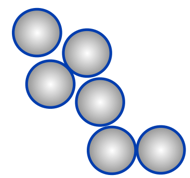


$$\eta^H \sim \eta\,a^3\,N/V$$



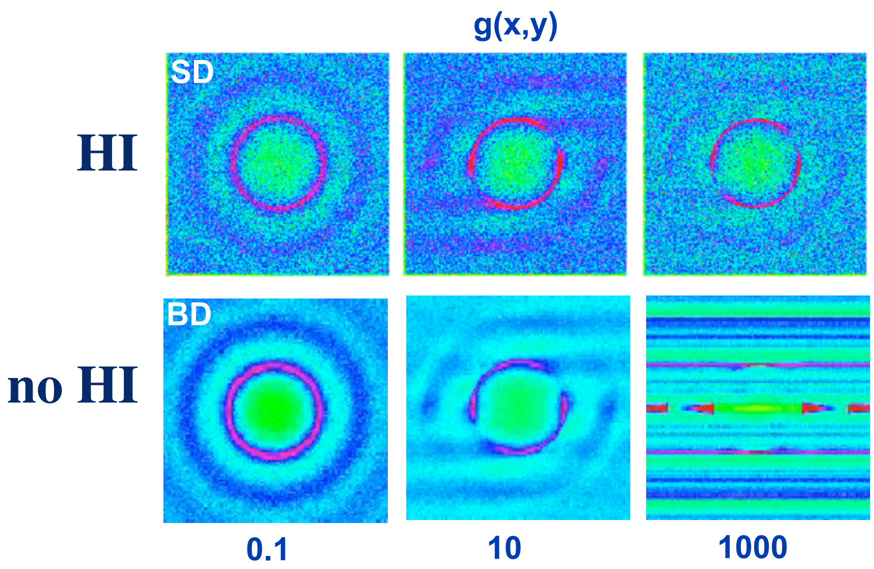
$b \sim N^{1/3}a$

$$\eta^H \sim \eta\,b^3\,1/V \sim \eta\,a^3\,N/V$$

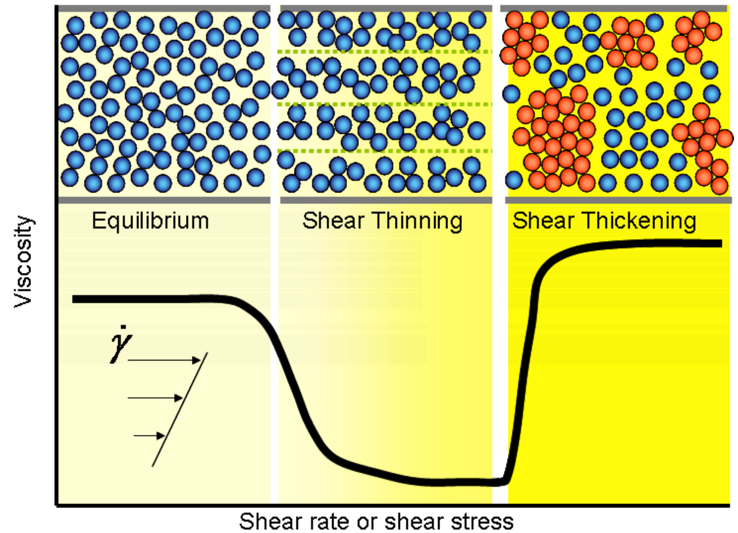


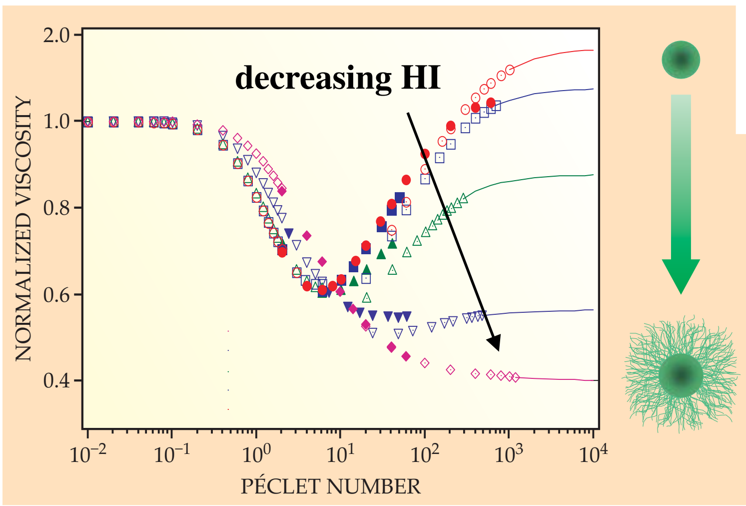
cluster due to hydrodynamic lubrication forces

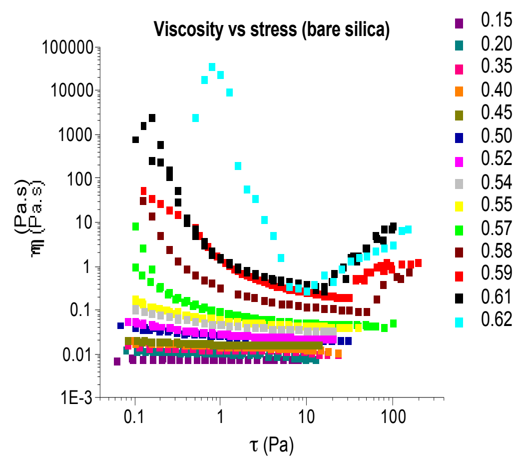
Mechanism of shear thickening: hydroclusters

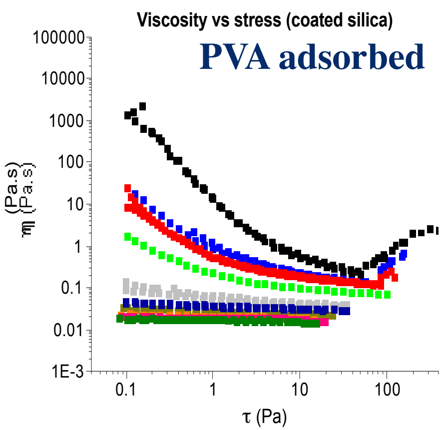


Wagner & Brady (*Phys. Today* 2009)

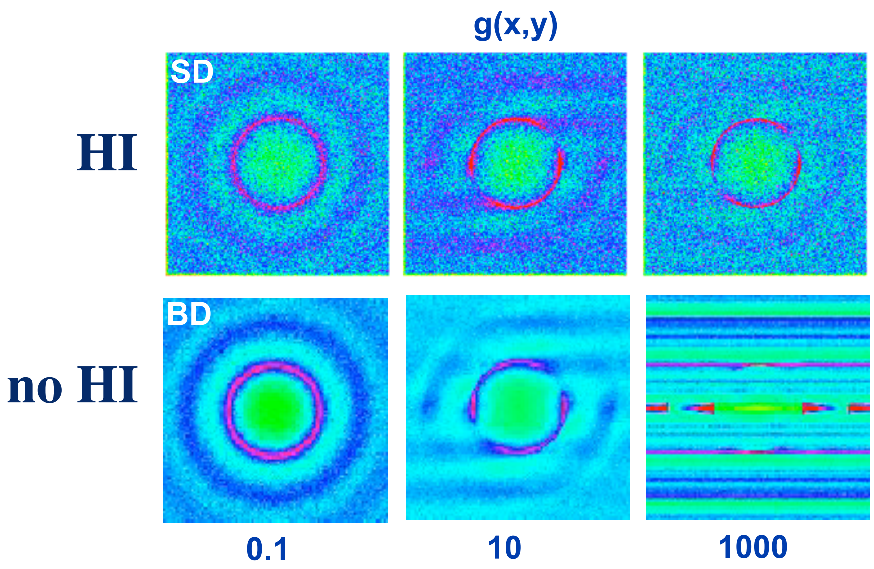




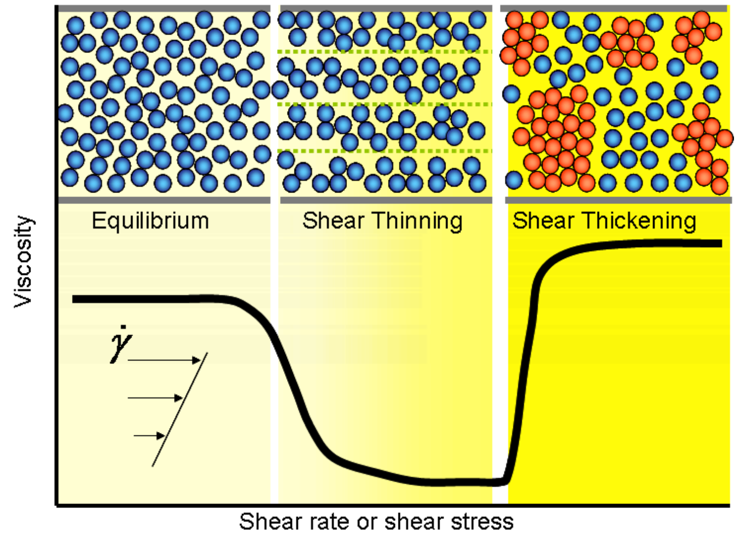


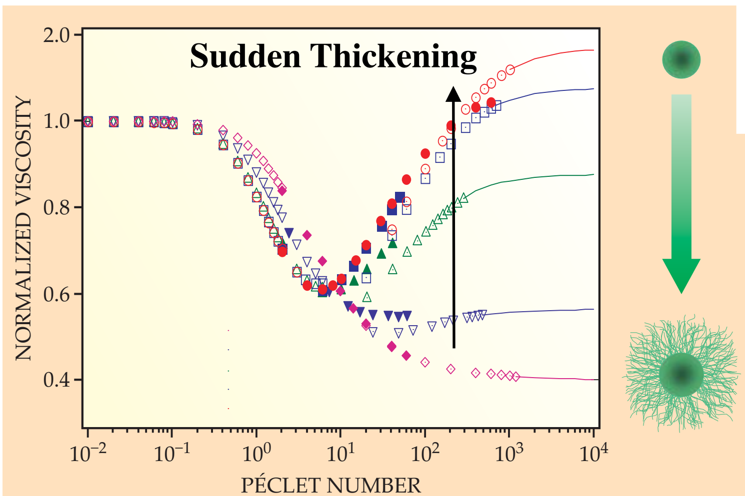


Mechanism of shear thickening: hydroclusters

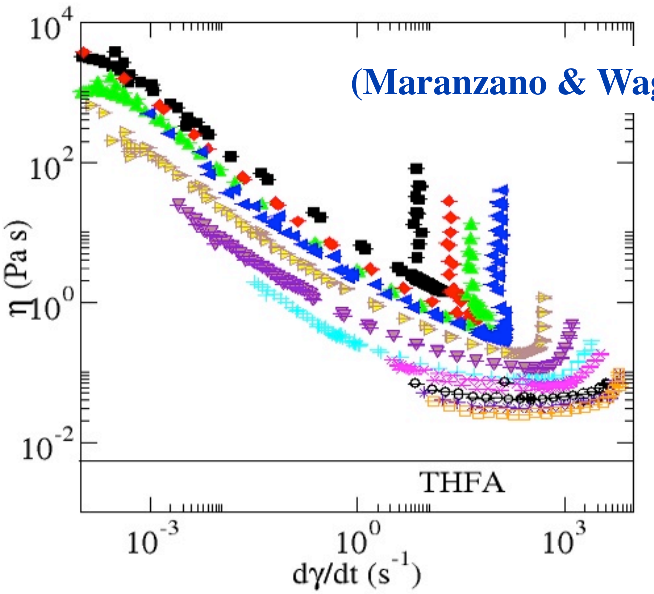


Wagner & Brady (*Phys. Today* 2009)





(Maranzano & Wagner 2001)



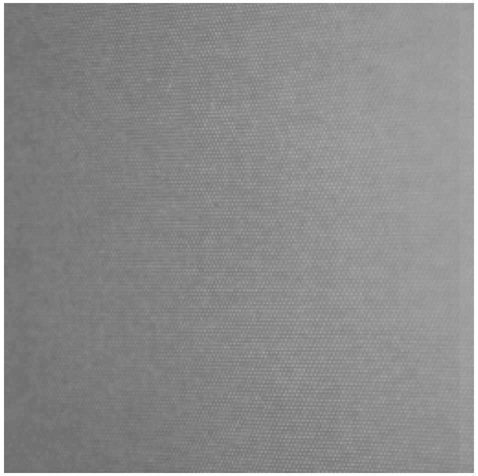
Shear thickening (the amazing part!)

Walking on water

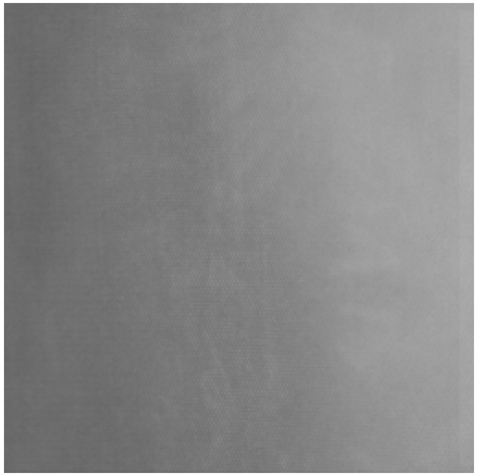
Cornstarch in water
also known as 'oobleck'

A bullet-proof vest

Neat
Kevlar



STF
Kevlar



'Liquid Armor'
(Wagner)

Outline

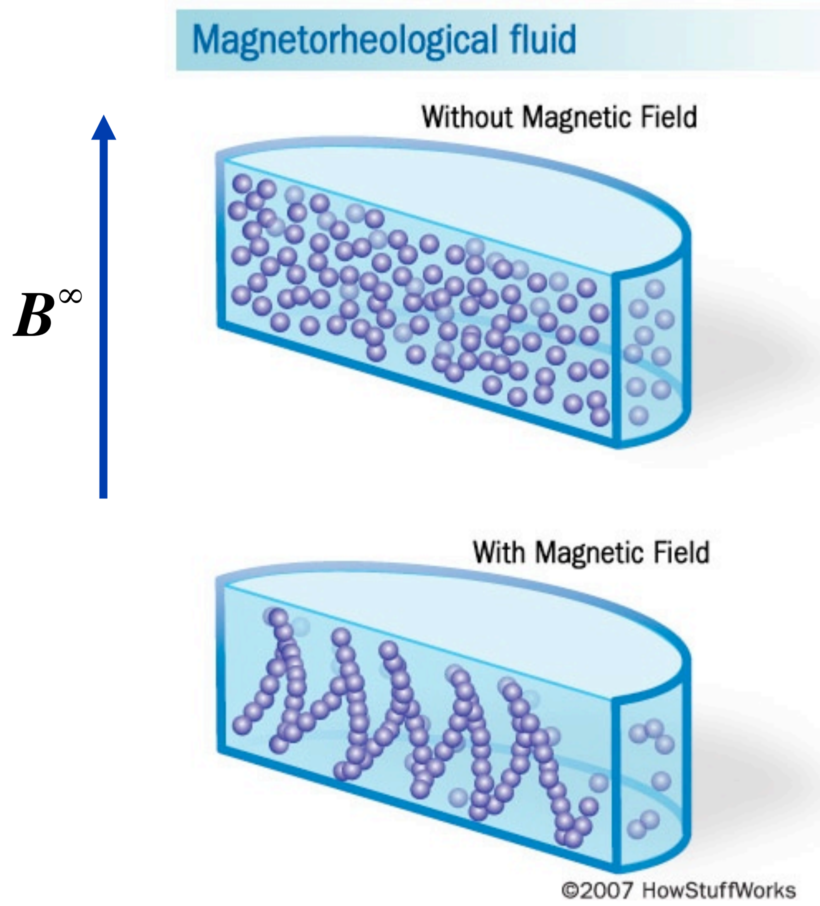
- What's a colloid and why do we care?
- How did the field start?
- The amazing rheology of spheres. (Or how to walk on water and make a bullet-proof vest.)
- How does random diffusion de-mix a suspension?
- **What can we do with active matter?**
- Conclusions

Active Matter: External fields

Particles with a dielectric mismatch with the solvent will chain up when an external field is applied (Winslow 1940).

'Magnetorheological Fluid'

The material can be changed from a low to high viscosity fluid (and even to a solid!) reversibly in a mille-second.



Active Matter: External fields

Magnetorheological Fluid

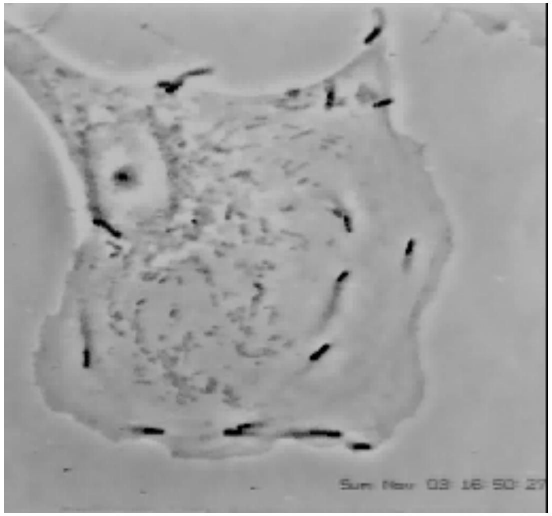
GM's Magnetic Ride Control is a complete, stand-alone vehicle suspension control system that uses innovative magneto-rheological fluid-based actuators, four wheel-to-body displacement sensors, and an onboard computer to provide real-time, continuous control of vehicle suspension damping.

Cadillac Seville STS 2002

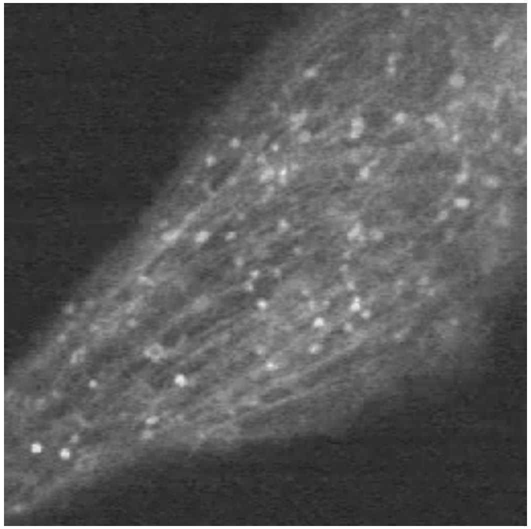
Active Matter: Internal activity

Paramecium

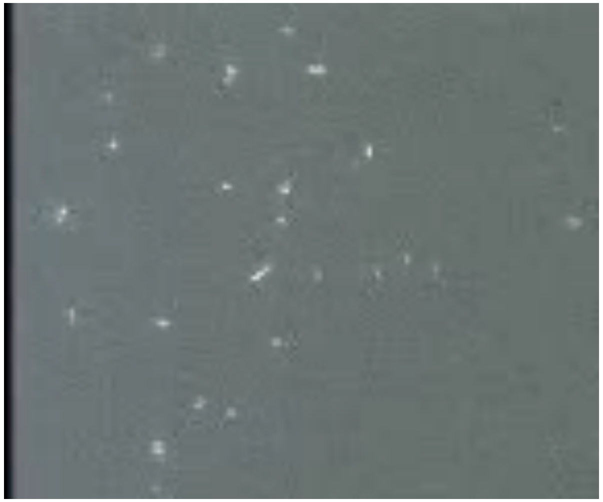
Listeria Bacteria



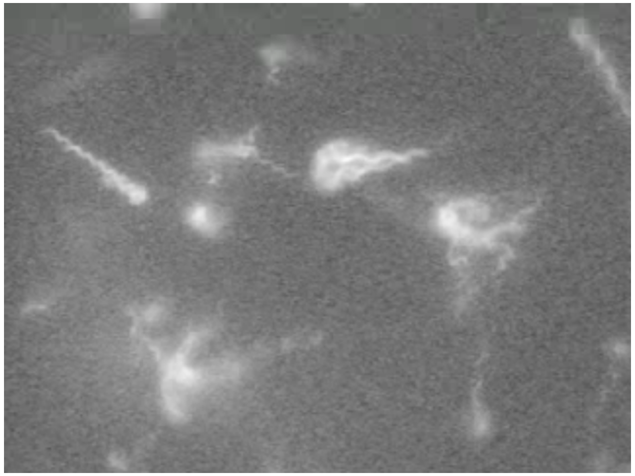
Kinesin Motors



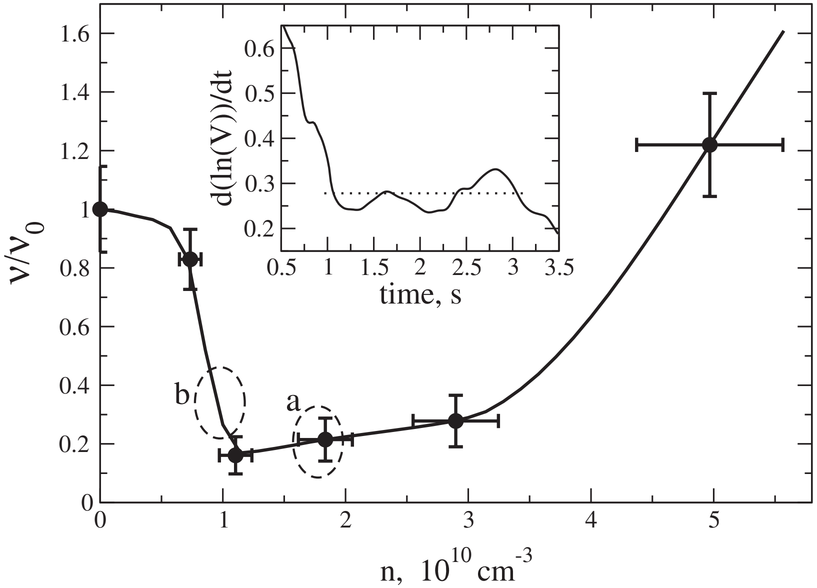
Catalytic Nanomotors



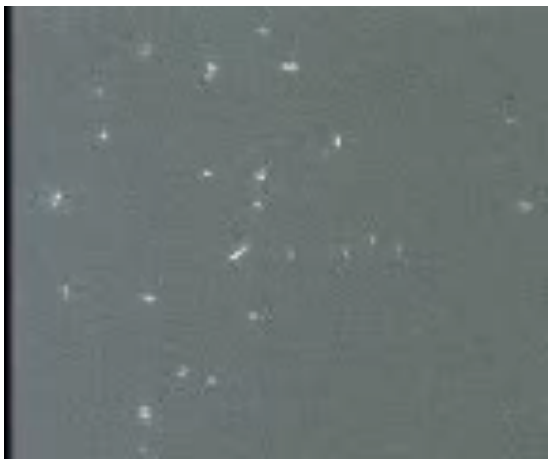
Active Matter: Internal activity



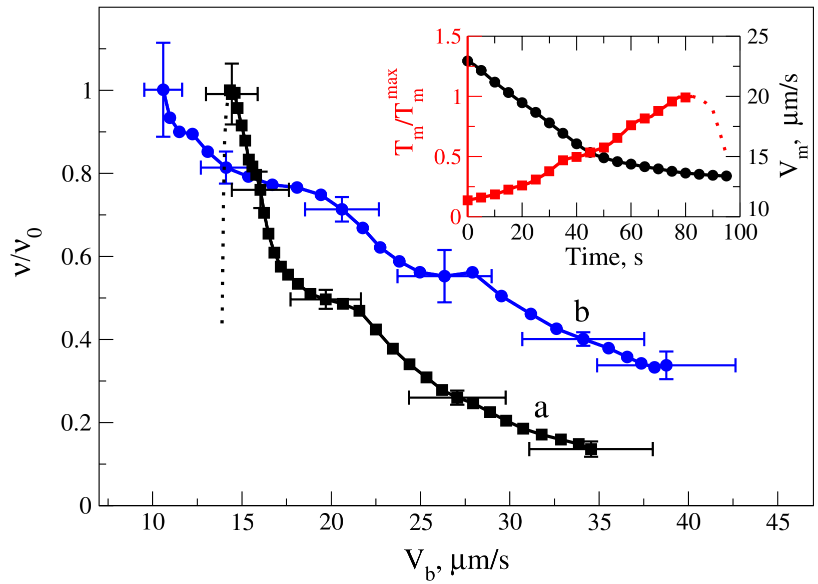
Berg (Harvard)



Solokov & Aranson *PRL* (2009)



Paxton et al (Penn State)



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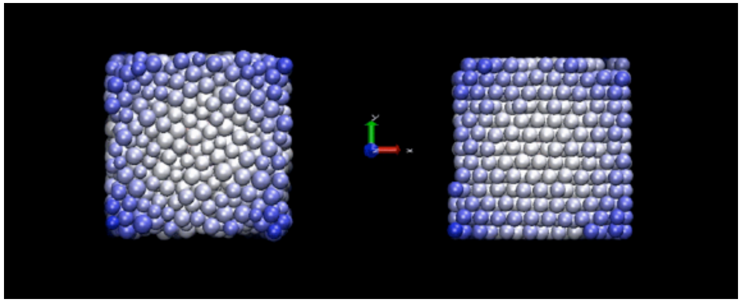
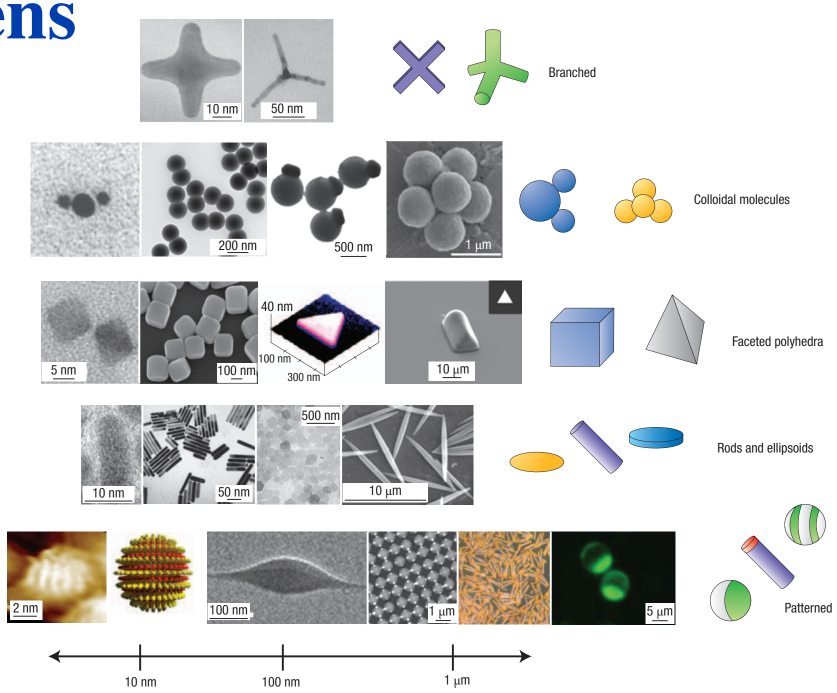
Conclusions

- Hydrodynamics plays a fundamental role in the behavior of colloids
- Stokesian Dynamics is a general molecular-dynamics-like method for studying colloids
- Even the humble sphere has a rich rheology - shear thins and shear thickens
- The fun has just begun!





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The End