The Micromechanics of Colloidal Dispersions

John F. Brady

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

With help from: My students and postdocs
And backed by: NSF, NASA, ONR, PRF

ICI Distinguished Lecture
University of Alberta
19 September 2013
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.

Why do we care?

How did the field start?

The answer is Einstein.

Brownian Motion

Einstein (circa 1905)

Stokes-Einstein Relation

\[ D = kT M \left( = \frac{kT}{6\pi\eta a} \right) \]

\[ F^H = -6\pi\eta a U \]

\[ Re = \frac{\rho U a}{\eta} \ll 1 \]

Brown (circa 1827)

Stokes (circa 1851)
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 \( \eta \). Then the resistance \( F \) to its motion is given by Stokes's formula

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

* A theorem attributed to Weber. See Gray and Matthews' 'Bessel's Functions,' p. 238.
† See 'Theory of Sound,' § 203, equations (14), (18).
‡ Communicated by the Author.


782 Mr. W. Sutherland on a Dynamical Theory

where \( \beta \) 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

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

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

\[
D = \frac{RT}{6\pi \eta a C} \frac{1 + 3\eta/\beta a}{1 + 2\eta/\beta a} \quad \ldots \ldots \quad (3)
\]
How did the field start?

Brownian Motion

Einstein (circa 1905)

Stokes (circa 1851)

Sutherland (circa 1879)

Stokes-Einstein-Sutherland Relation

\[ D = kT M \left( = \frac{kT}{6\pi \eta a} \right) \]

\[ F^H = -6\pi \eta a U \]

\[ Re = \frac{\rho U a}{\eta} \ll 1 \]
Einstein and the effective viscosity

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

\[ \eta_{\text{eff}} = \eta \left(1 + \frac{5}{2} \phi\right), \quad \phi = \frac{4}{3} \pi a^3 n \]
Einstein and Avagadro’s Number

Stokes-Einstein-Sutherland Relation:

\[ D = \frac{RT}{6\pi \eta} \frac{1}{N_A a} \]

For a sugar molecule:

\[ N_A = 6.56 \times 10^{23} \]

\[ a = 4.9 \text{ Å} \]
Jean B. Perrin (1926 Nobel Prize)

Definitive proof of the atomic nature of matter
‘Generalized’ Stokes-Einstein-Sutherland Relation

Rotational Diffusivity:

\[ D_{\text{rot}} = kT M_{\text{rot}} = \frac{kT}{8\pi\eta a^3} \]

- Separation of length and time scales between the motion of the ‘particle’ and that of a solvent molecule: \( a/b \gg 1 \)
  - Particle/solvent time:
    \[ \frac{\tau_p}{\tau_s} \sim (a/b)^2 \]
  - # 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].

Characteristic Scales: A Simple Example

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

Particle Size: \( a = \frac{1}{2} \mu m \)

Fall Speed: \( U = \frac{1}{2} \mu m/s \)

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

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

Peclet Number: \( Pe = \frac{1}{2} \)

Stokes - Einstein - Sutherland Relation: \( D = \frac{kT}{6\pi \eta a} \)
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
The amazing rheology of spheres

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

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

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

1) Long-range interactions

\[ u' \sim \frac{1}{r^2}, \quad S \sim \frac{1}{r^3} \]

2) Microstructure

\[ g(r) \]

3) Brownian contribution to stress

\[ S^B \]

\[ \Delta \eta^H = 5.0 \phi^2 \]

\[ \Delta \eta^B = 1.2 \phi^2 \]
The amazing rheology of spheres

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

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 ($Re << 1$)

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

Hydrodynamic:
\[ F^H = -R(x) \cdot (U - U^\infty) \]
Stokes drag

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

Interparicle/external:
\[ F^P = \Delta \rho V_p g, \text{ electrostatic, etc.} \]

Shape, multiparticle, bounded, etc.
Nature of Hydrodynamic Forces: \( F^H = - R(x) \cdot U \)

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

John C. Crocker
James Franck Institute and Department of Physics, University of Chicago, Chicago, Illinois 60637
(Received 25 July 1996; accepted 14 November 1996)

The hydrodynamic coupling between two isolated 0.97 \( \mu \)m diameter polystyrene spheres is measured by reconstructing their Brownian motion using digital video microscopy. Blanking 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 \( 2a = 0.966 \) \( \mu \)m as a function of dimensionless separation \( \rho \). The solid curves indicate the theoretical prediction given by Eqs. (2)–(5). The dashed line indicates the asymptotic diffusivity \( D_0/2 \) (top) and \( D_i/2 \) (bottom).
Nature of Hydrodynamic Forces: $F^H = -R(x)\cdot U$

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

**Lubrication**: near-field, two-body problem
Nature of Hydrodynamic Forces: $F^H = -R(x) \cdot U$

Far-field, many-body problem

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

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

\[
\frac{d\mathbf{x}}{dt} = \mathbf{U} = (\mathbf{R}^*(\mathbf{x}))^{-1} \cdot \mathbf{F}^{\text{other}}
\]
The amazing rheology of spheres

Three dimensional unbounded flow -- periodic boundary conditions

Hydrodynamics
Brownian Motion

\[ Pe = \frac{\dot{\gamma} a^2}{D} = 6\pi \eta a^3 \dot{\gamma} / kT \]
Near Equilibrium Behavior: $\omega \to \infty$

Stokesian Dynamics (N=27-64)
- Ladd (1990)
- Phung (1994)

Accelerated Stokesian Dynamics
- N=125
- N=343
- N=512
- N=1000
- N=2000

Experimental Results
- van der Werff, et. al. (1989)
- Shikata & Pearson (1994)

Asymptotic Form
$$\eta'_{\infty} \sim 1 + \frac{5}{2} \phi + 5\phi^2 \quad \text{as} \quad \phi \to 0$$
$$\eta'_{\infty} \sim \ln(1 - \phi / \phi_m)^{-1} \quad \text{as} \quad \phi \to \phi_m$$

$\phi_{rcp} = 0.64$
Zero-shear Brownian viscosity \((Pe = 0)\)

\[
\Delta \eta^B = \eta(Pe \rightarrow 0) - \eta'_{\infty}
\]

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

\(\phi = 0.58\)

(Banchio & Brady 2003)
Sheared ‘Hard-Sphere’ Suspensions

Three regimes:

- \( Pe \ll 1 \), Brownian dominated
- \( Pe \sim 1 \), Balance
- \( Pe \gg 1 \), Hydrodynamic dominated

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

\[ = \frac{\text{Brownian Time}}{\text{Flow Time}} \]

\[ = \frac{a^2 / D}{1 / \dot{\gamma}}, \quad D = \frac{kT}{6\pi\eta a} \]
Brownian & hydrodynamic contributions to stress

\[ \eta_r(\phi) \]

\[ \eta_r^B(\phi) \]

\[ \eta_r^H(\phi) \]

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

Bender & Wagner (1996)
Rheology: Simulation vs. Experiment

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

Stokesian Dynamics
- \( \phi = 0.316 \)
- \( \phi = 0.419 \)
- \( \phi = 0.47 \)
- \( \phi = 0.49 \)

van derWerff, et al. (1989)
- \( \phi = 0.316 \)
- \( \phi = 0.419 \)
- \( \phi = 0.470 \)
- \( \phi = 0.488 \)

Bossis & Brady (1989)

Extrapolated \( Pe \to 0 \) Limit
- \( \phi_A = 0.453 \)
Mechanism of shear thickening: hydroclusters

Hydrodynamic stress: \( S^H \sim \eta \dot{\gamma} a^3 \)

\( \eta^H \sim \eta a^3 N/V \)

\( \eta^H \sim \eta b^3 1/V \sim \eta a^3 N/V \)

\( b \sim N^{1/3} a \)

Wagner & Brady (Phys. Today 2009)
Mechanism of shear thickening: hydroclusters

**Mechanism of shear thickening**

Hydroclusters

www.physicstoday.org October 2009  Physics Today

Model dispersions experimentally confirm the predictions of processes or applications. Simulating a dispersion that behaves as needed for specific applications requires understanding the interparticle forces, which dominate the viscosity at low shear and in environments of the suspending medium. All aspects of the shear-thickening state are affected by the properties of the suspending medium—particle size, shape, surface chemistry, and ionic strength. Changes in the viscosity are significant: 1 Pa·s at a low shear stress and again at one more volume fraction.

**Figure 3.** The measured viscosity of a latex dispersion whose volume fraction $\phi = 0.50$ produces a latex dispersion whose viscosity is 1 Pa·s at a low shear stress and again at one more volume fraction. Referring back to figure 1, one can see that a colloidal suspension with lower viscosity. Moreover, even very high processing rates but could increase the suspension's viscosity. Manipulating those nanoscale forces, the particles' approach is predicted to be on the order of nanometers for typical interparticle forces at play. Fluid slip, adsorbed ions, surface tension, and properties of the suspending medium can prevent the particles from getting too close together. With the right selection of stabilizing forces, the suspension will not shear at any higher rate. Rather, shear thickening can be suppressed.

**Controlling shear thickening**

As shown in figure 3, rheo-optical measurements on colloidal suspensions are understood, many aspects of the fast-shear processing rate, and the shear-thickening state or a shear-thinning one. The Péclet number (a measure of shear rate) leads to a discontinuous shear thickening whereby the shear thickening is suppressed by imposing a purely repulsive force field—akin to the effect of a polymer brush—around the particles. This effect is evident experimentally when a polymer graft density, molecular weight, and solvent, the onset of shear thickening is generally reversible, though, so re-confining and complex fluids remain active research problems.

**Figure 4.** Shear thickening can be suppressed by imposing a purely repulsive force field—akin to the effect of a polymer brush—around the particles: The dis-tribution of graft density, molecular weight, and solvent, the onset of shear thickening is generally reversible, though, so re-confining and complex fluids remain active research problems.

**Figure 5.** Changes in the shear-thickening state are affected by the properties of the suspending medium—particle size, shape, surface chemistry, and ionic strength. Changes in the viscosity are significant: 1 Pa·s at a low shear stress and again at one more volume fraction.

**Figure 6.** Rheo-optical measurements on colloidal suspensions are understood, many aspects of the fast-shear processing rate, and the shear-thickening state or a shear-thinning one. The Péclet number (a measure of shear rate) leads to a discontinuous shear thickening whereby the shear thickening is suppressed by imposing a purely repulsive force field—akin to the effect of a polymer brush—around the particles.
Mechanism of shear thickening: hydroclusters

HI

no HI

Sudden Thickening

Wagner & Brady (Phys. Today 2009)

Equilibrium
Shear Thinning
Shear Thickening

(Sudden Thickening)

(Maranzano & Wagner 2001)
Shear thickening (the amazing part!)

Walking on water

Cornstarch in water
also known as ‘oobleck’

‘Liquid Armor’
(Wagner)

A bullet-proof vest

Neat Kevlar

STF Kevlar
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 magnetorheological 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)

Paxton et al (Penn State)

Solokov & Aranson

*PRL* (2009)
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
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!
Acknowledgements

**PhD Students**

Lou Durlofsky  
Ron Phillips  
Julia Lester  
Thanh Phung  
Jeff Morris  
Mike Vicic  
David Foss  
Asimina Sierou  
Jim Swan  
Roseanna Zia

**Postdocs**

Johan Bergenholtz  
Aldolfo Banchio

**Funding**

NSF  
NASA  
ONR  
PRF  
IFPRI

**Collaborators**

Georges Bossis  
Norm Wagner  
George Petekidis
The End