From Proteins to Peas: Diffusion Across Scales

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KITP Granular Physics
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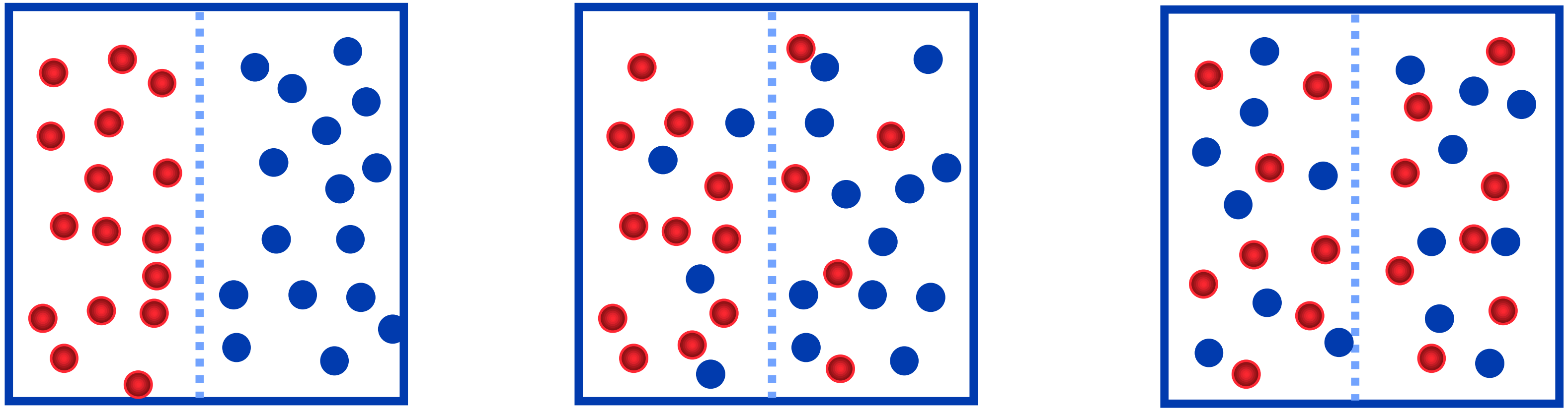
CALIFORNIA INSTITUTE OF TECHNOLOGY 1891

COMPLEX FLUIDS

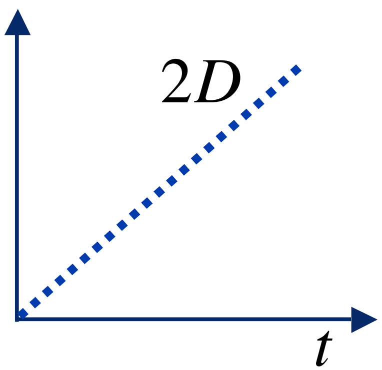
Diffusion: D (m²/s)



increasing time

$$t_{\text{mix}} \sim \frac{(\text{length})^2}{\text{diffusivity}} \sim \frac{L^2}{D}$$

Mean-square displacement $\langle x^2 \rangle$

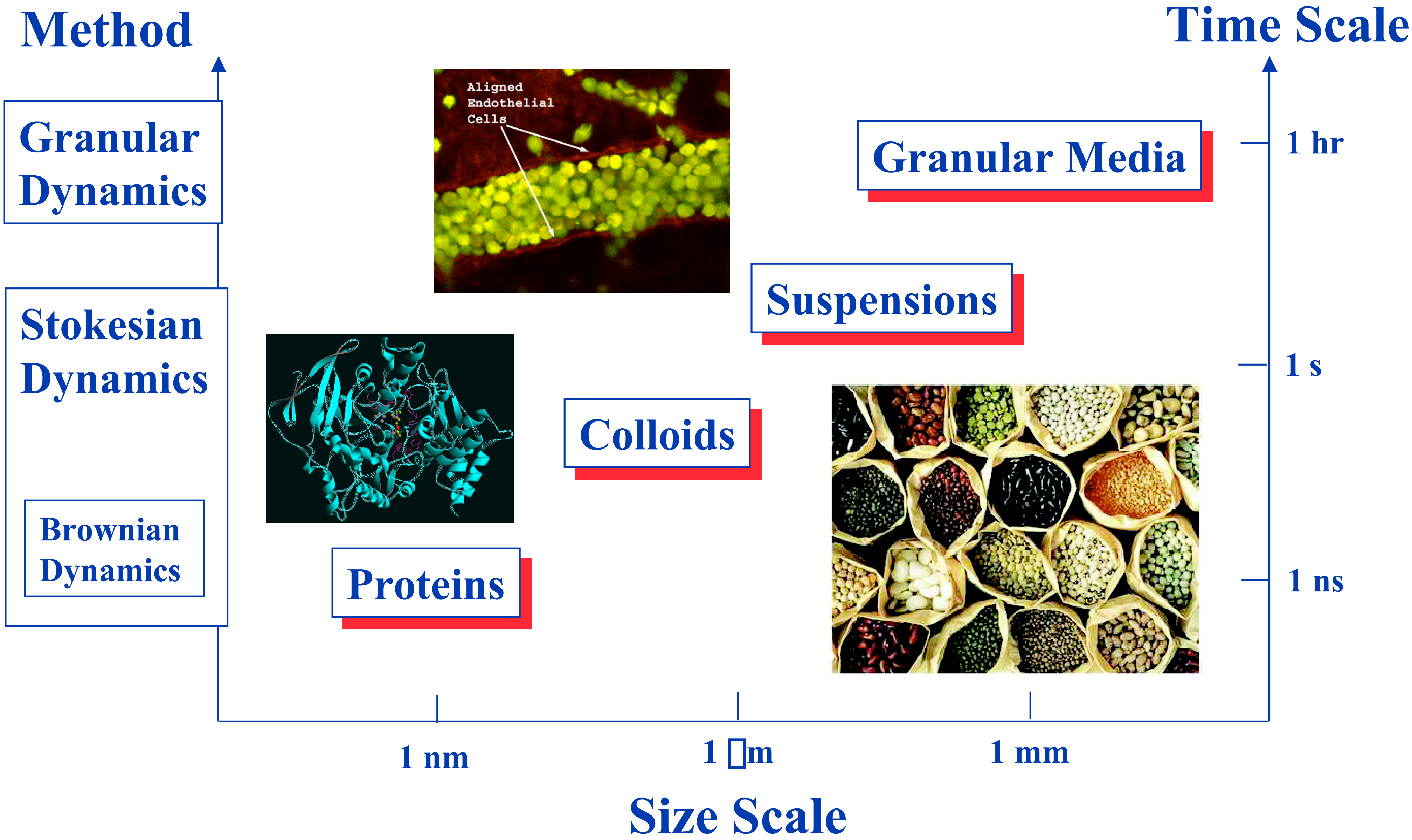


Fick's Law:

$$j_x = \square D \frac{\partial c}{\partial x}$$

particle flux   concentration gradient

Diffusion Across Scales

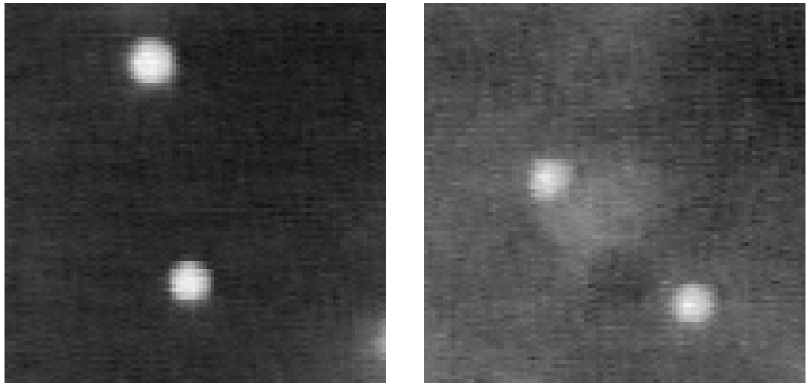


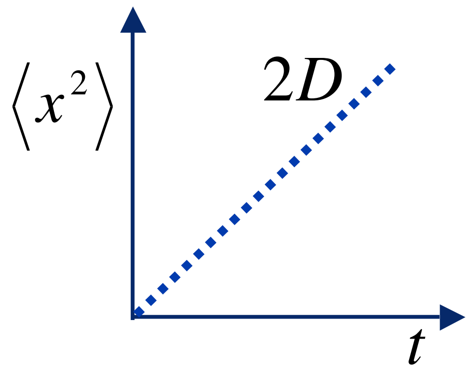
Einstein & Brownian Motion (1905)

Brown's microscope

Einstein (circa 1905)

Brownian motion of 2 μm particles, Weitz lab (Harvard).





Mean-square displacement

$$D = kTM = \frac{kT}{6\pi\eta a}$$

Stokes-Einstein Relation

Stokes (circa 1851)

W. Sutherland (1905)

(1859-1911)

(age 20)

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 $\mathrm{RT}dc/dx$, if c is the concentration of the solute at x and R is the gas constant. Hence

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

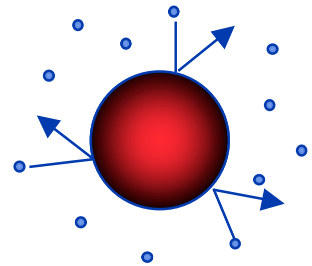
and the required formula for the coefficient of diffusion with C for the number of molecules in a gramme-molecule is

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

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

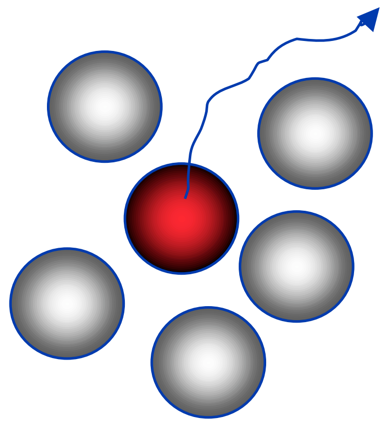
- **Brownian motion (Stokes-Einstein-Sutherland)**

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

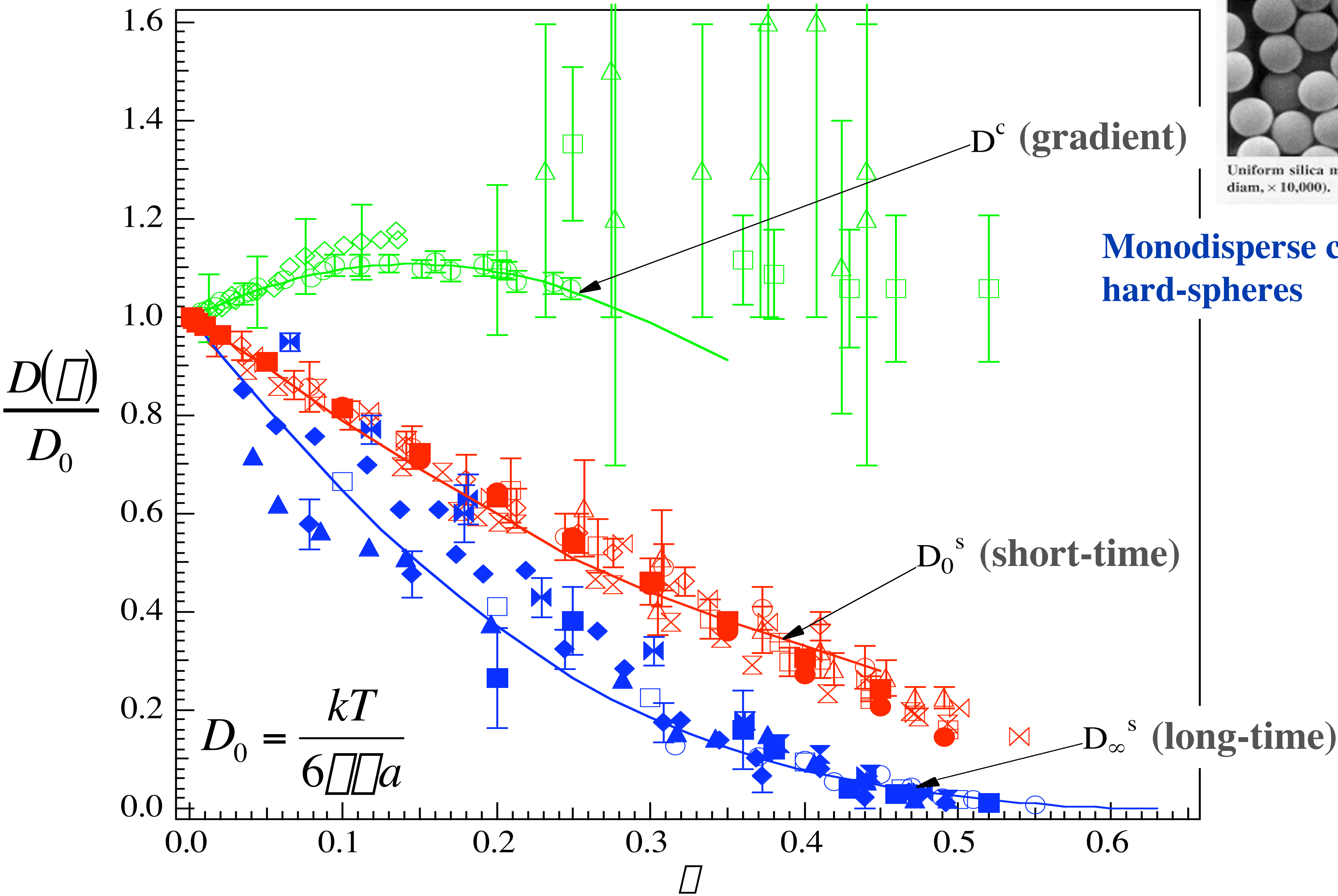


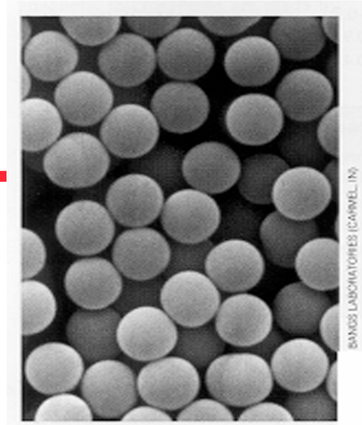
- **Time to diffuse the order of the particle size**

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



Brownian Self- and Gradient-Diffusivities

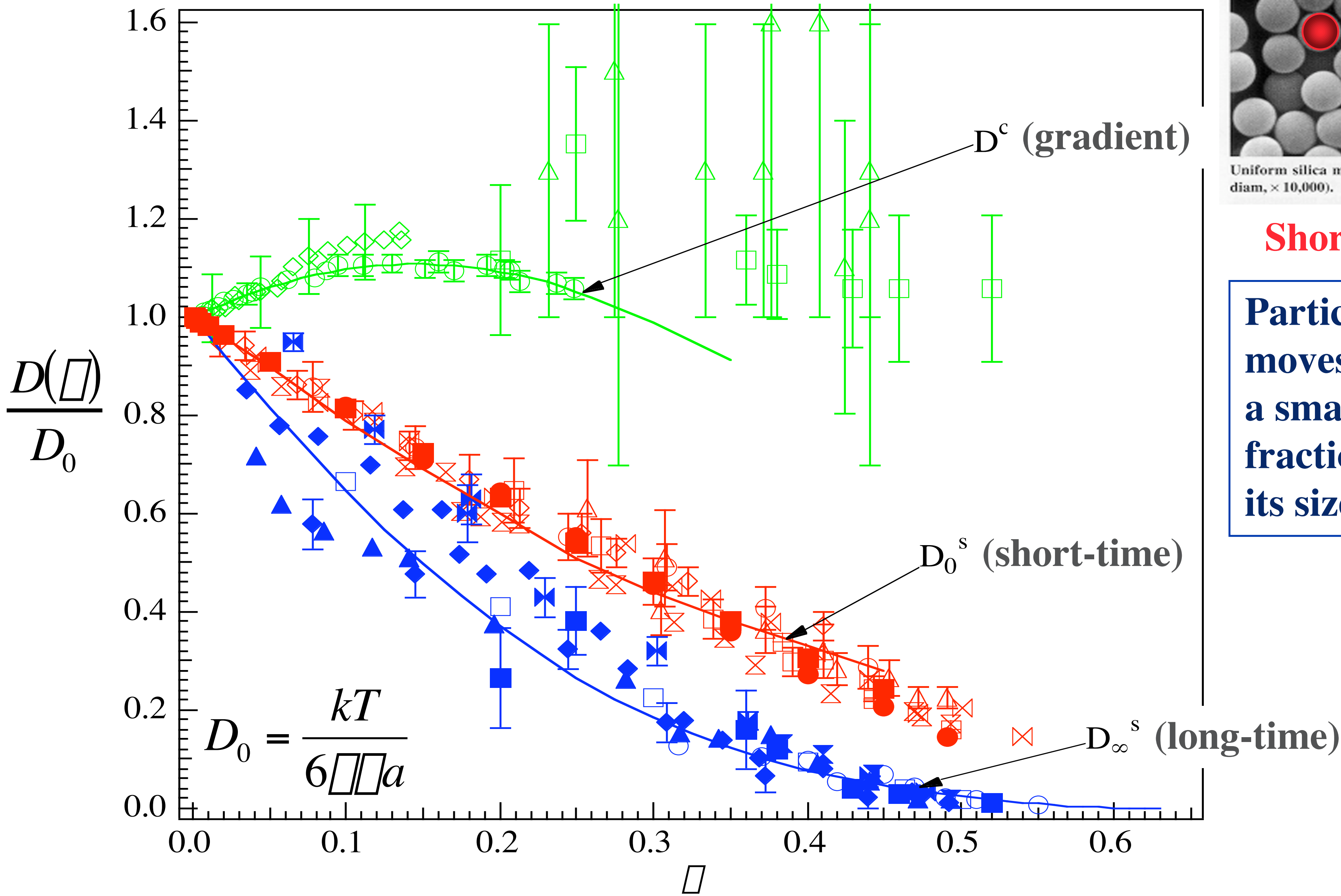


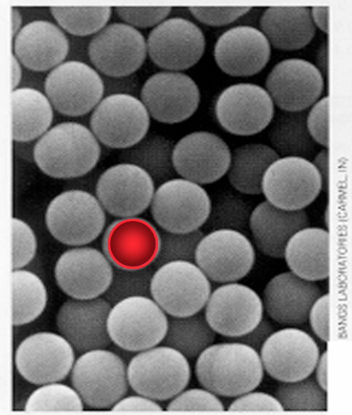


Uniform silica microspheres (1 μm diam, × 10,000).

Monodisperse colloidal hard-spheres

Brownian Self- and Gradient-Diffusivities



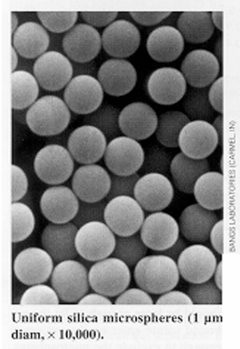


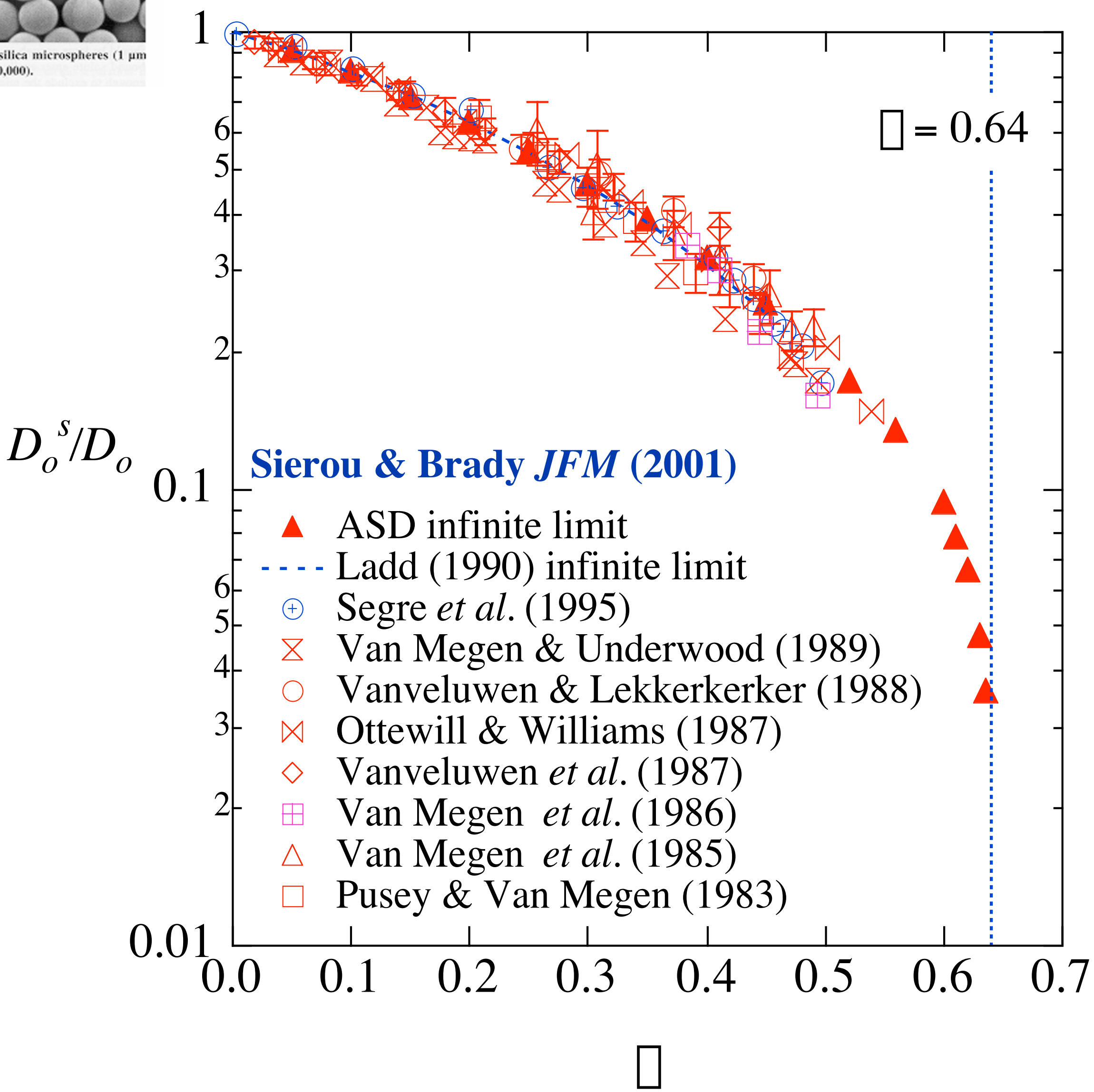
Uniform silica microspheres (1 µm diam, × 10,000).

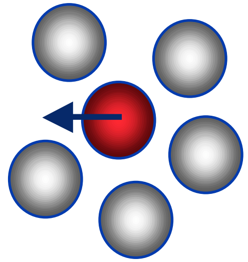
Short-time

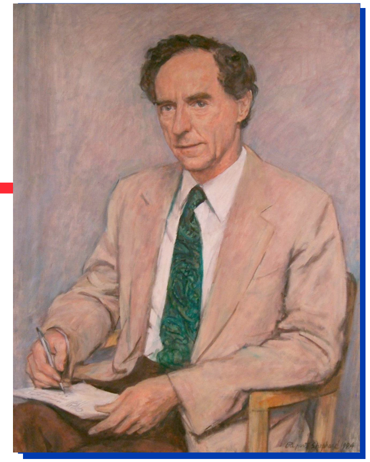
Particle moves only a small fraction of its size

Short-time self-diffusivity









Batchelor (1976)

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

Dilute limit : $\phi \to 0$

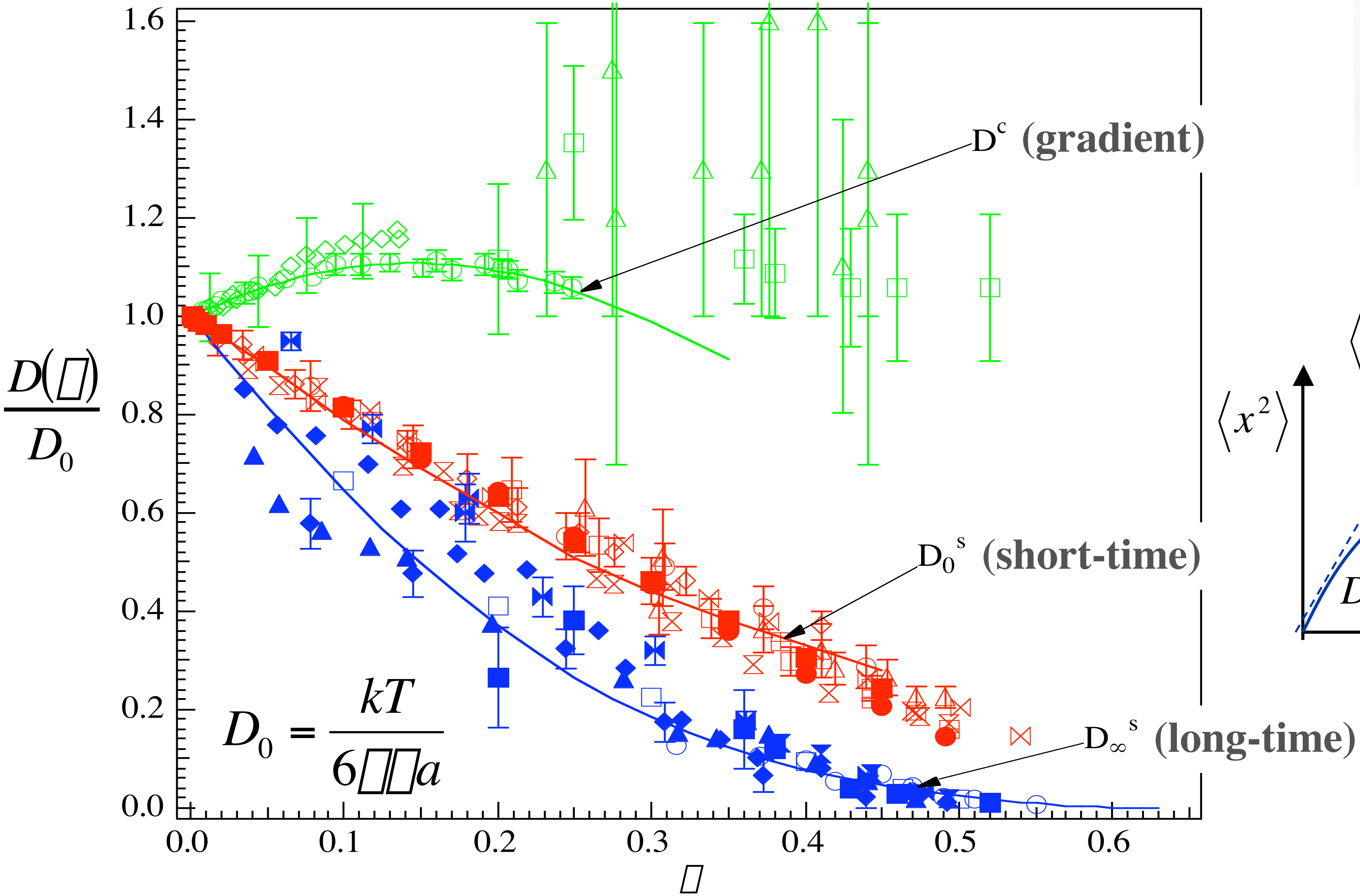
$$D_0^s(\phi) \sim D_0(1-1.83\phi)$$

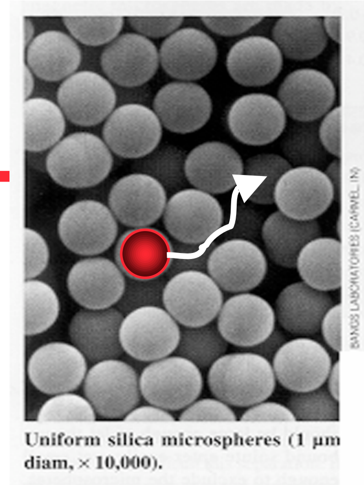
Close packing :

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

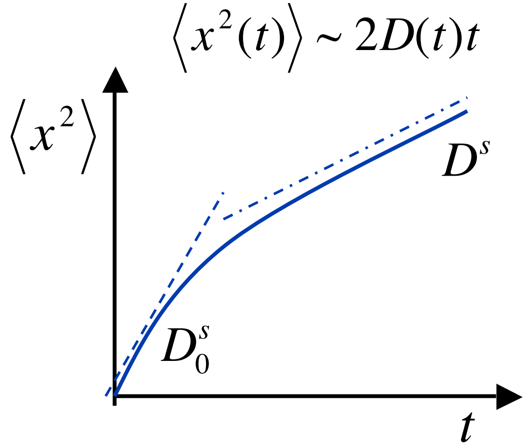
$$D_0^s(\phi) \sim D_0/\ln(1/\epsilon)$$

Brownian Self- and Gradient-Diffusivities

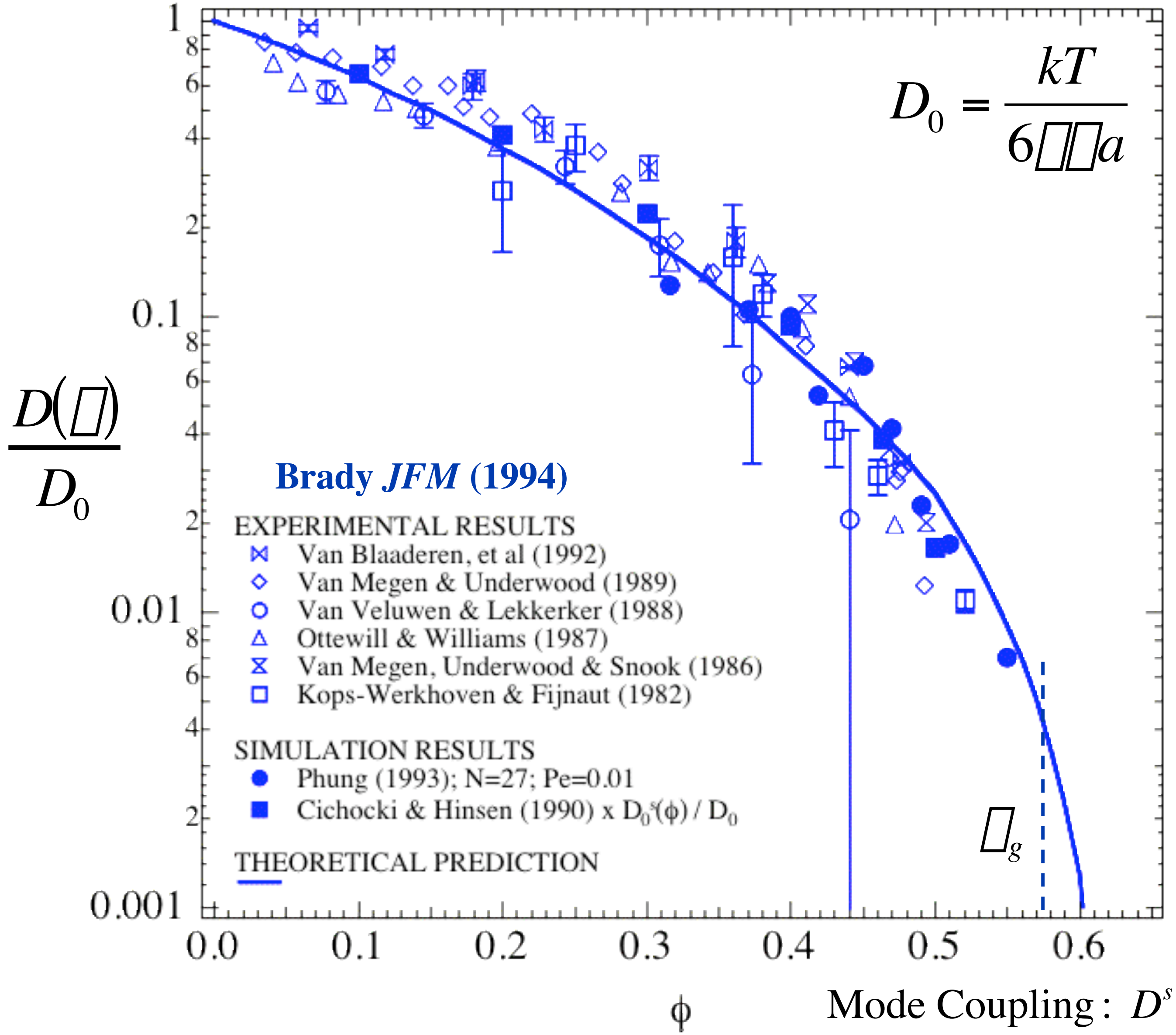




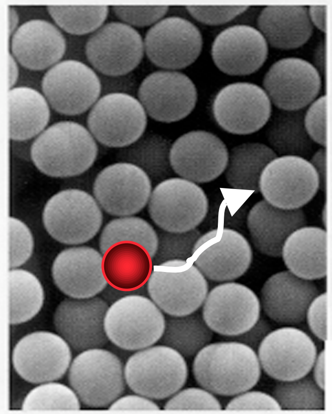
Long-time



Brownian Self-Diffusivity (long-time)



$$D_0 = \frac{kT}{6\pi\eta a}$$



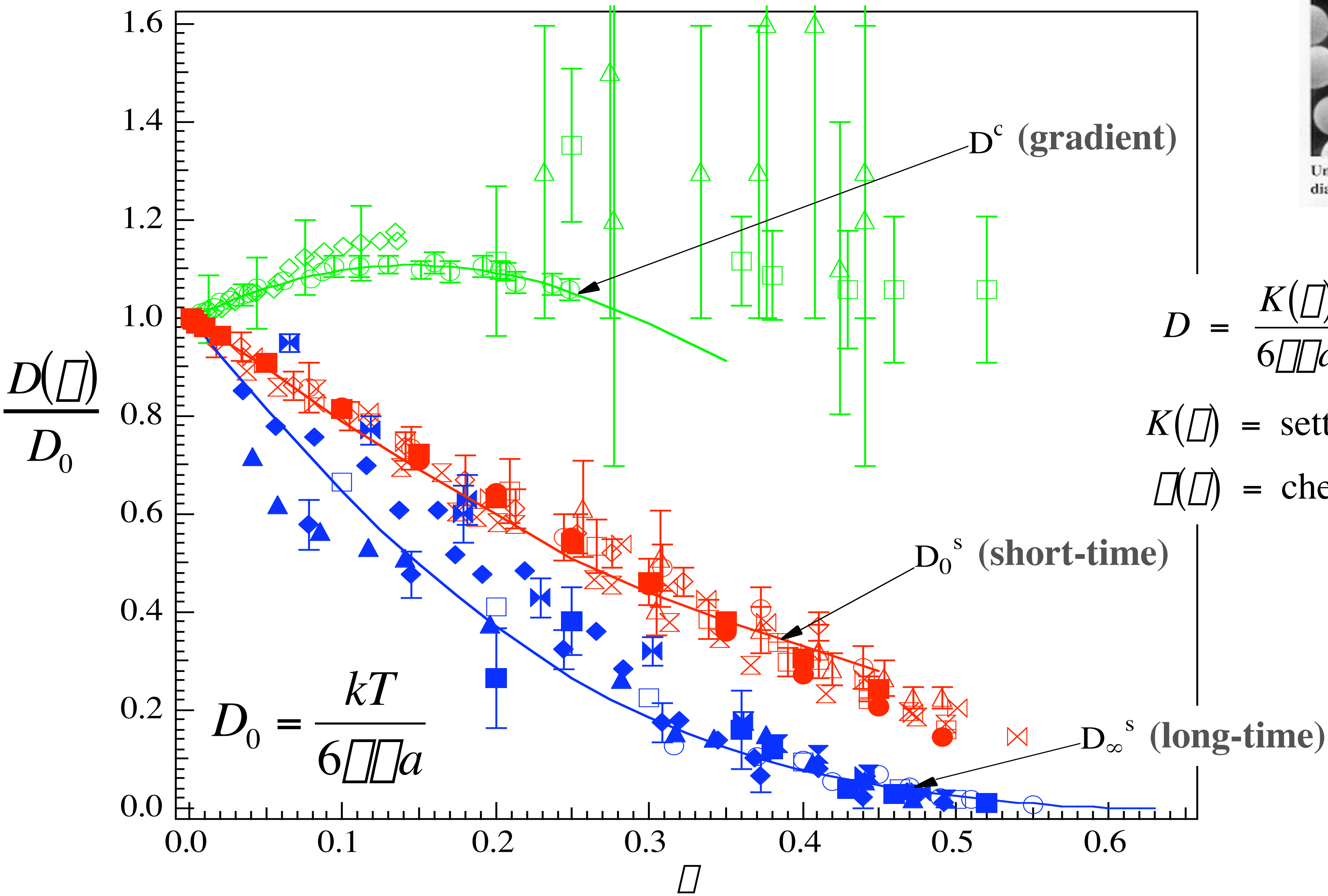
Uniform silica microspheres (1 μm diam, × 10,000).

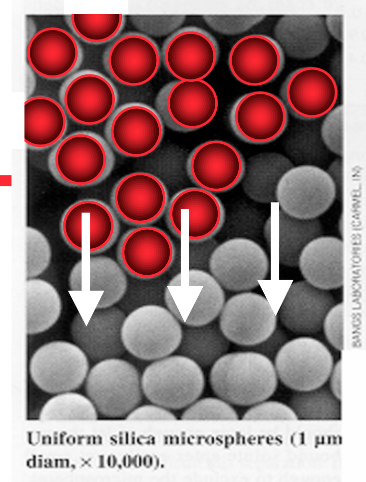
The self-diffusivity decreases with increasing concentration as the diffusing particle must push past its neighbors to move.

Fuchs *et al* (1992)

$$\text{Mode Coupling}: \; D^s(\phi) \sim D_0^s(\phi_g - \phi)^{2.62}$$

Brownian Self- and Gradient-Diffusivities





Gradient

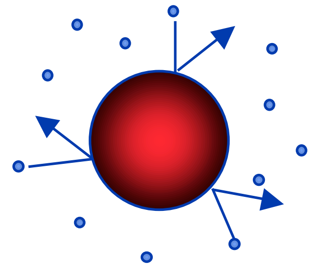
$$D = \frac{K(\phi)}{6\pi\eta a}\frac{\phi}{1-\phi}\left(\frac{\partial\mu}{\partial\phi}\right)_{p,T}$$

$K(\phi)$ = settling function

$\mu(\phi)$ = chemical potential

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

- **Brownian motion (Stokes-Einstein-Sutherland)**



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

$$t_a \sim \frac{a^2}{D} \sim \frac{2\pi\eta a^3}{kT}$$

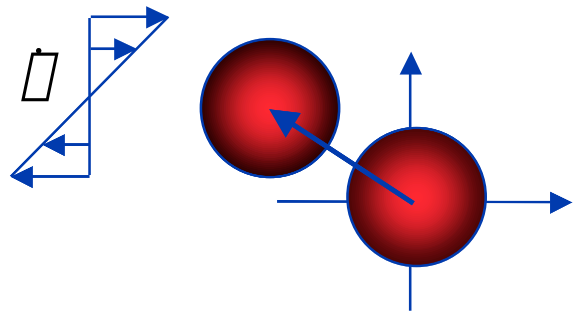
$\approx 1s$ for $a = 0.5\mu m$

$\approx 1000s$ for $a = 5\mu m$

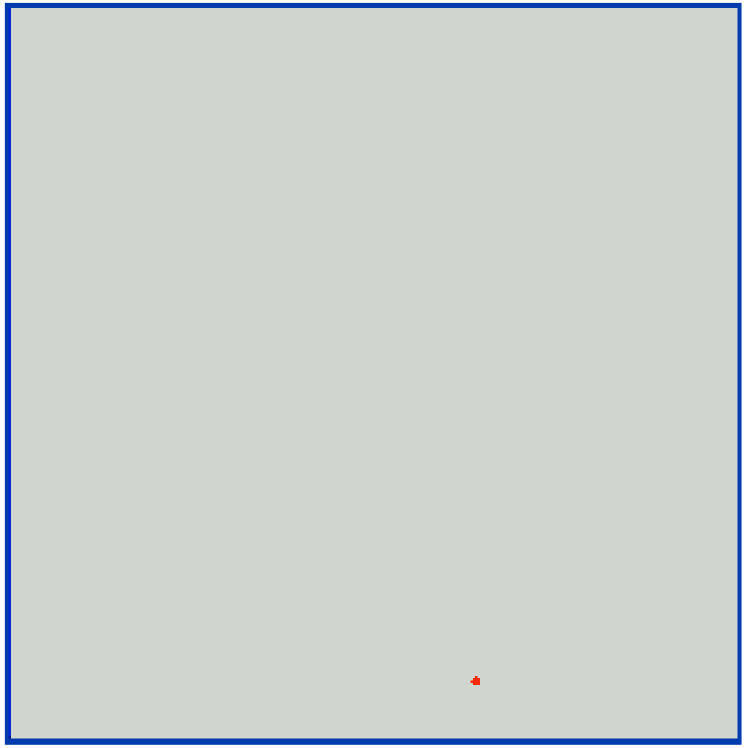
$\approx 10^9 s \sim 30 yrs$ for $a = 500\mu m$

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

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



Does shear-induced diffusion exist? You Judge!



Run A

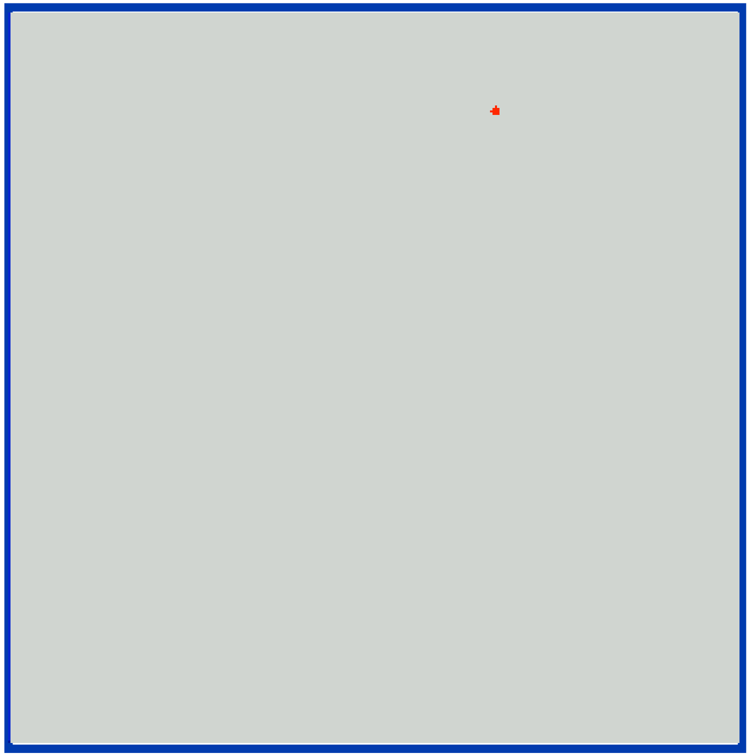
View is in the velocity-gradient -- vorticity plane

Simple Shear Flow

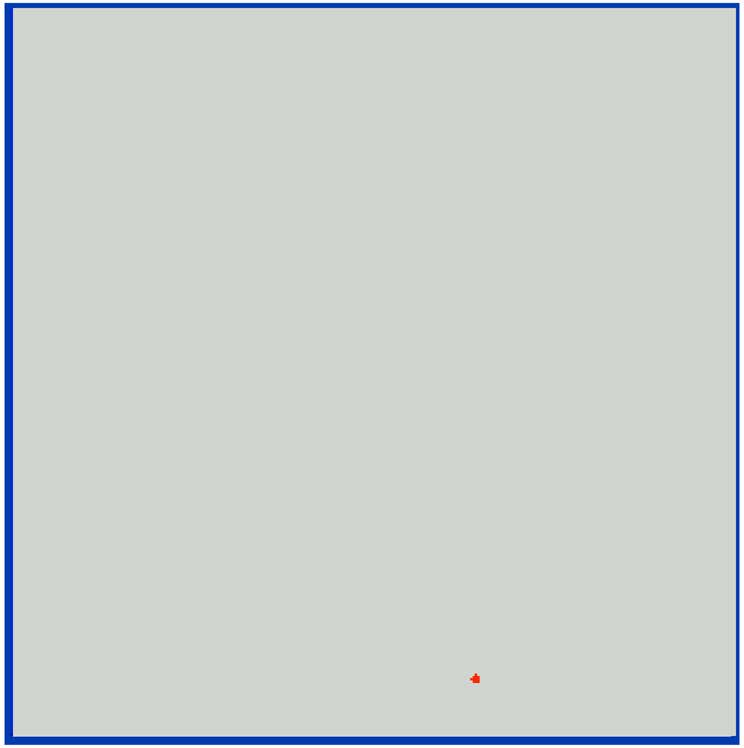
□ = 0.35, *Re* << 1

***Pe* = 0,**

Run B



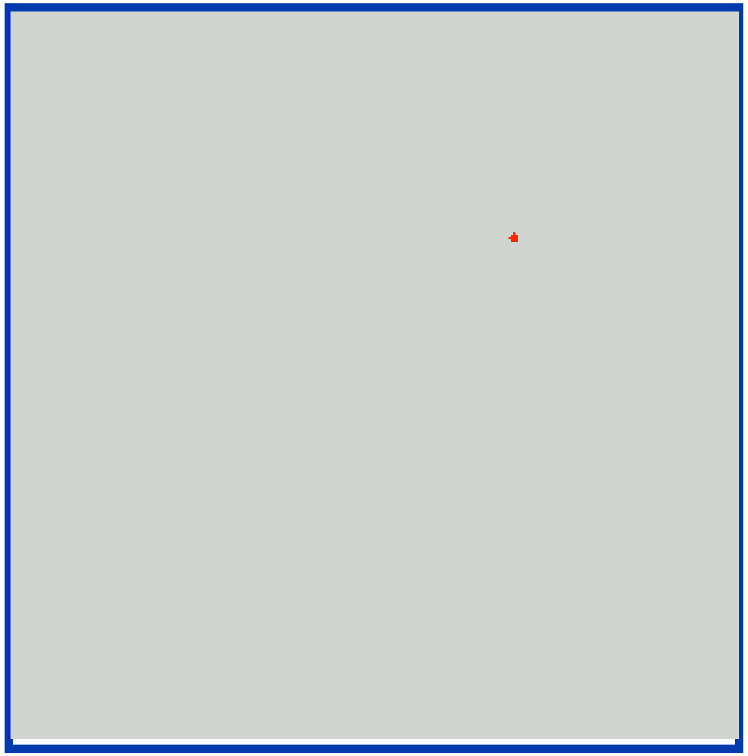
Which one is which?



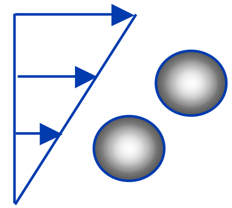
Run C

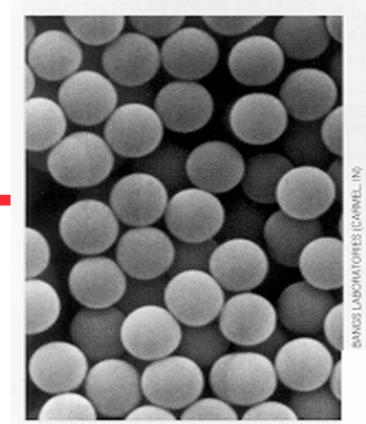
Same as previous runs, but at a finer time scale

Run D



Micromechanics: Stokes Flow ($Re = 0$)



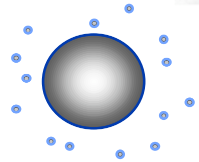


Uniform silica microspheres (1 μm diam, × 10,000).

Particle Motion: $\boldsymbol{m} \cdot \frac{d\boldsymbol{U}}{dt} = \boldsymbol{F}^H + \boldsymbol{F}^B + \boldsymbol{F}^P$ (the inertia term $m \cdot dU/dt$ is crossed out)

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

Stokes drag



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

$\approx 10^{-8} s$

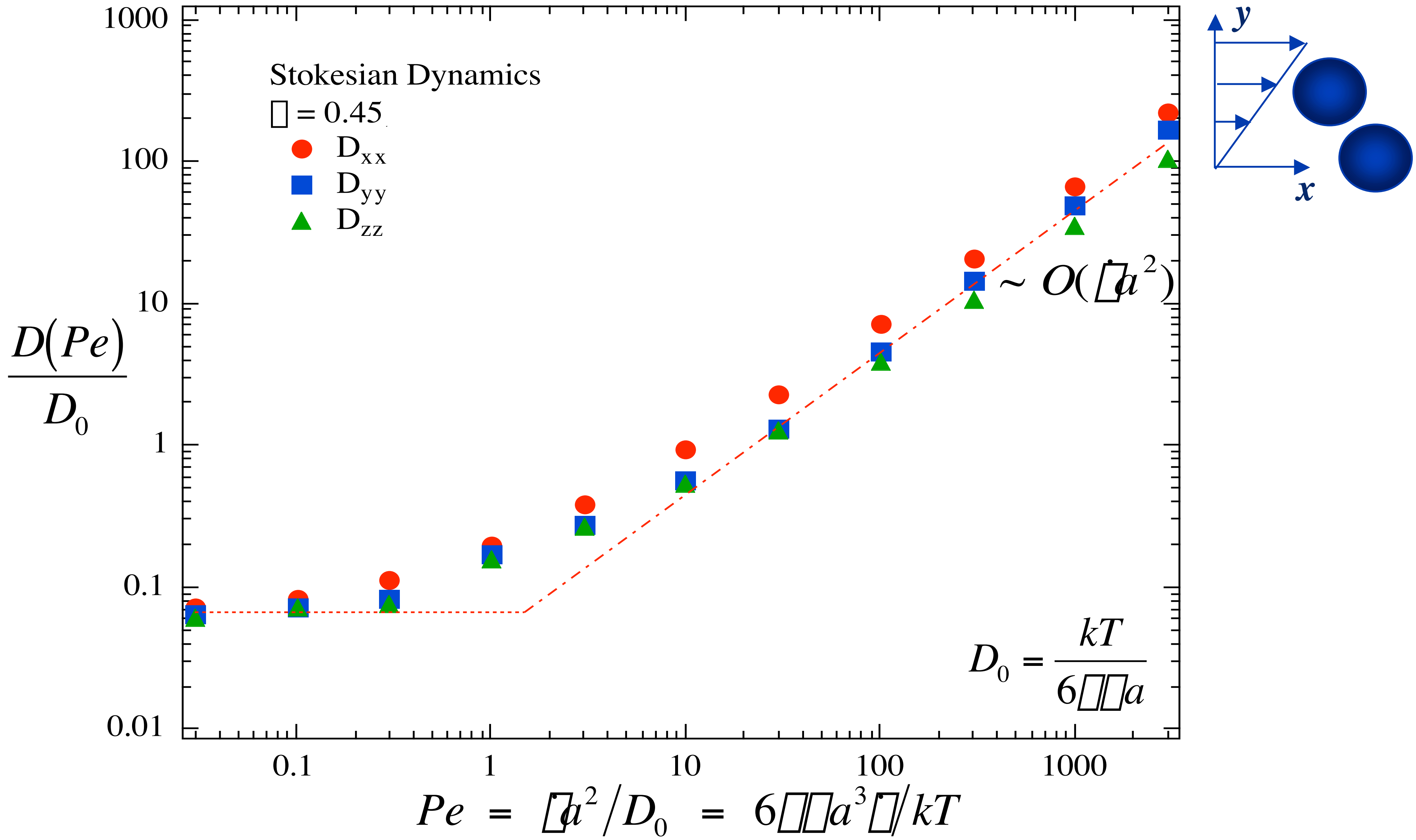
Brownian: $\overline{\boldsymbol{F}^B} = 0 \; , \; \overline{\boldsymbol{F}^B(0)\boldsymbol{F}^B(t)} = 2kT\boldsymbol{R}(\boldsymbol{x})\delta(t)$

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

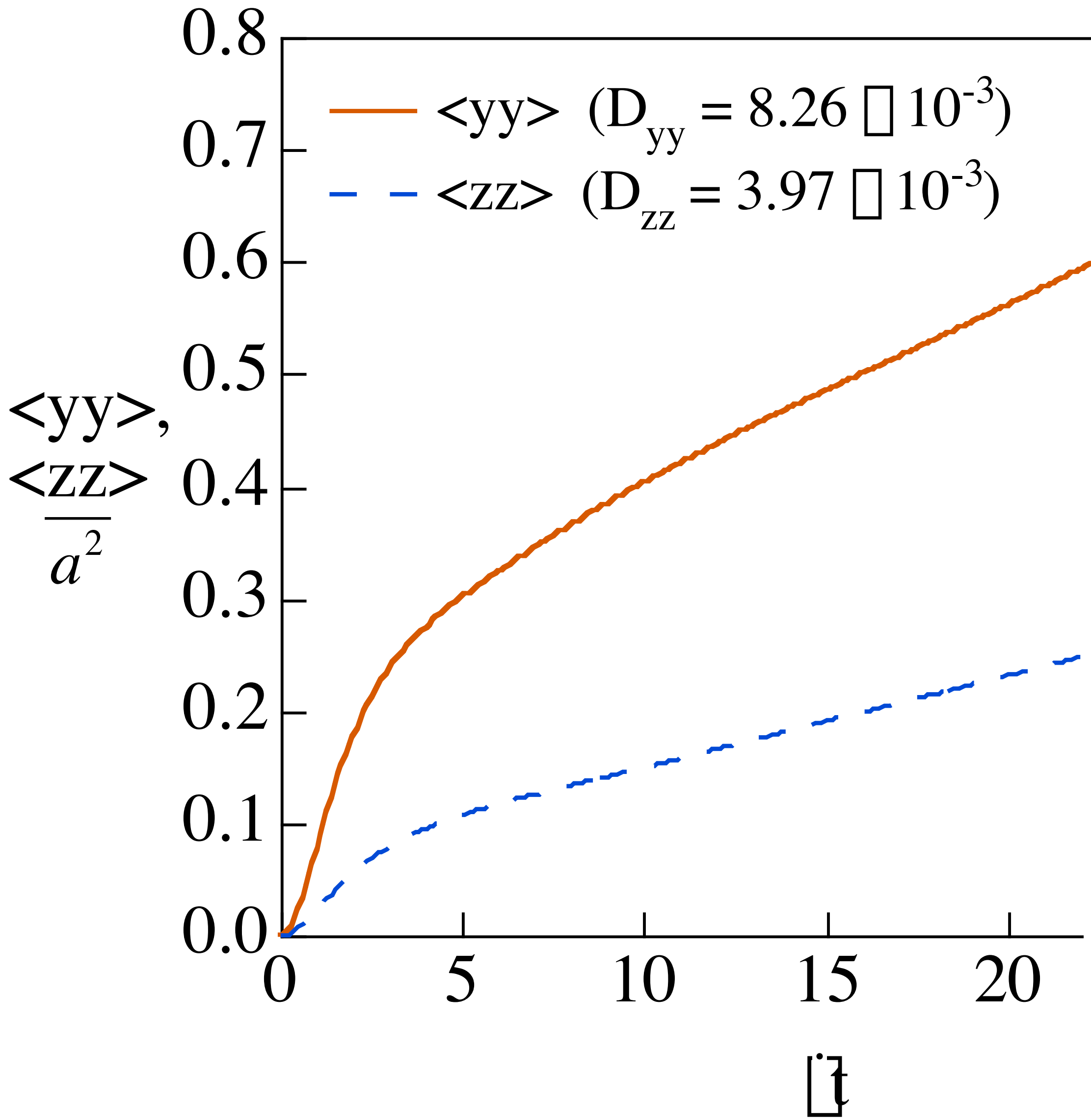
Interparicle/ external: $\boldsymbol{F}^P =$ Hard-sphere collisions

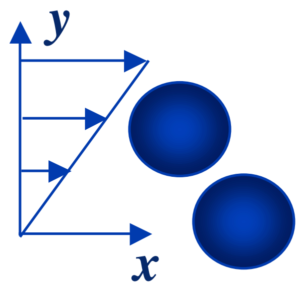
$$Pe = \tau_B \dot{\gamma} = a^2 \dot{\gamma} / D_B = 6\pi\eta a^3 \dot{\gamma} / kT$$

Shear-Induced Diffusivity

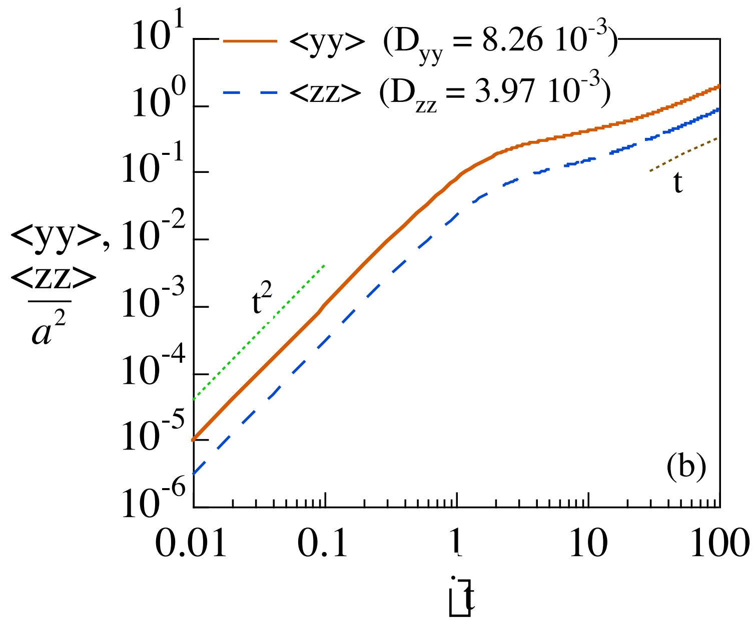


Mean-square displacements (Sierou & Brady 2004)

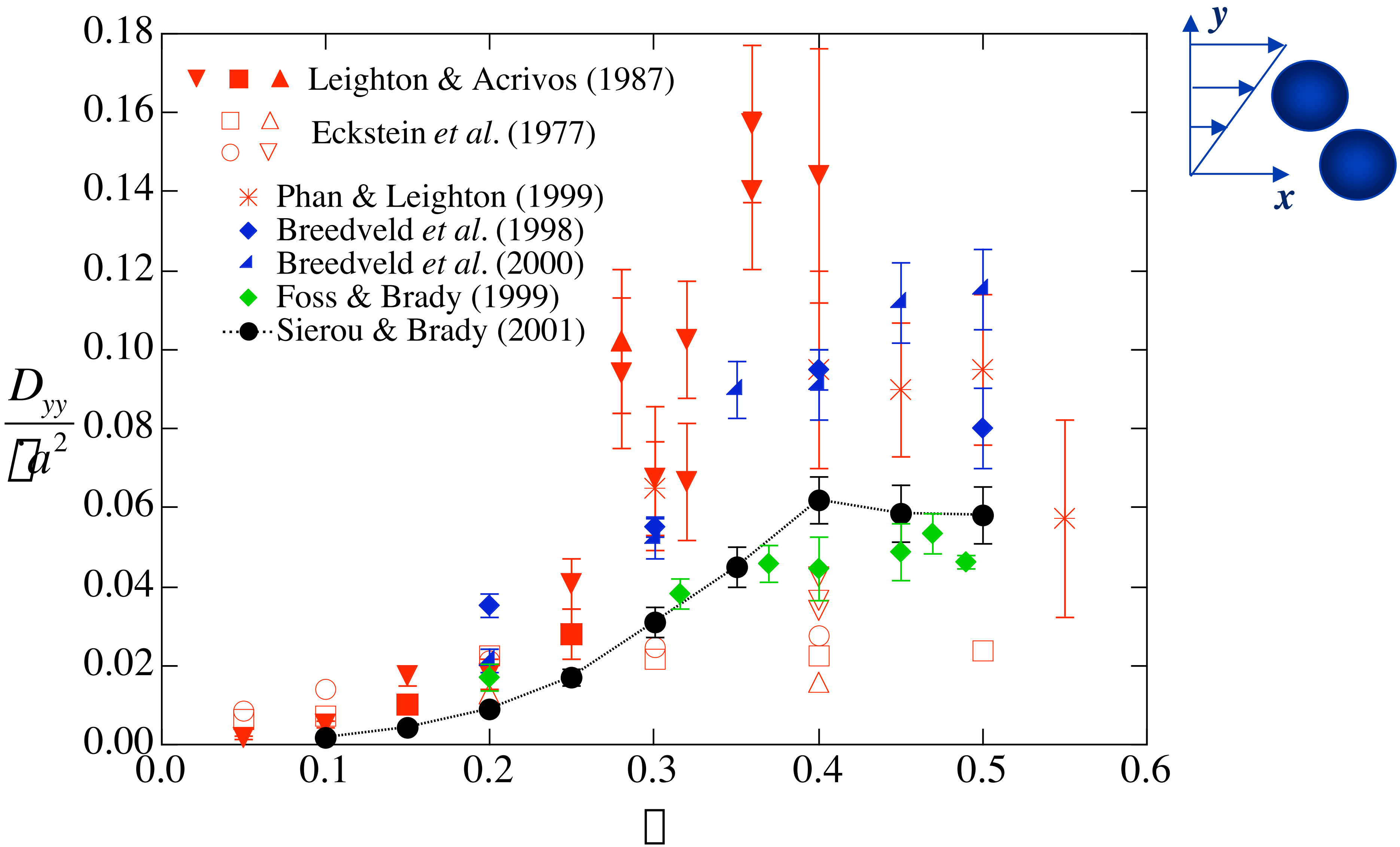




volume fraction:
= 0.2

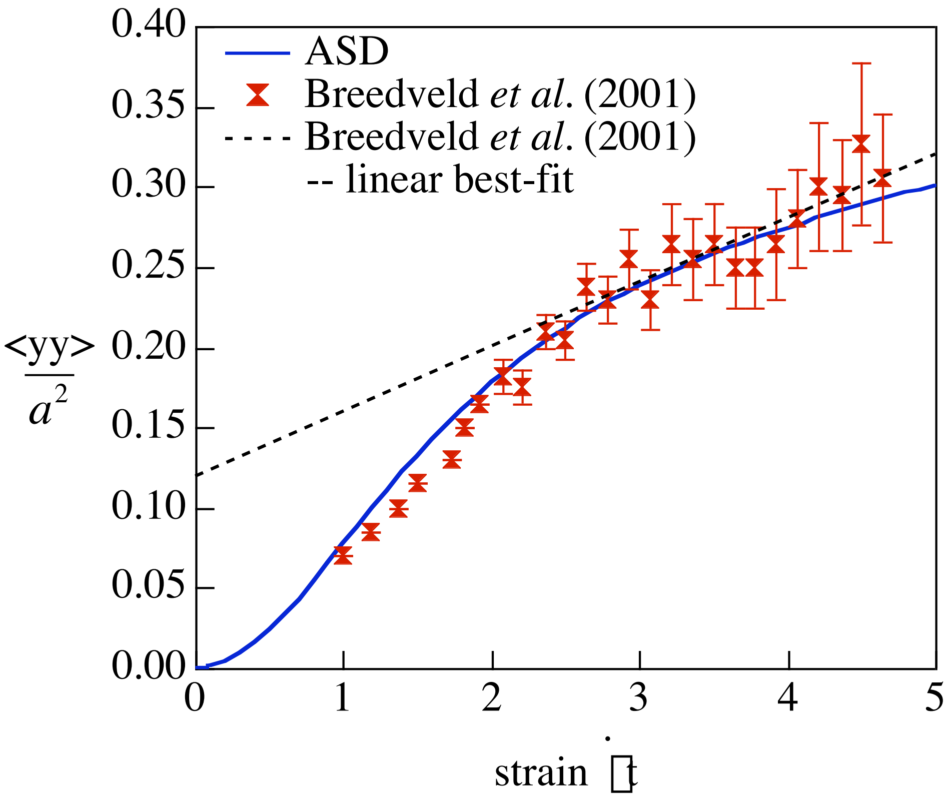


Shear-Induced Self-Diffusivity

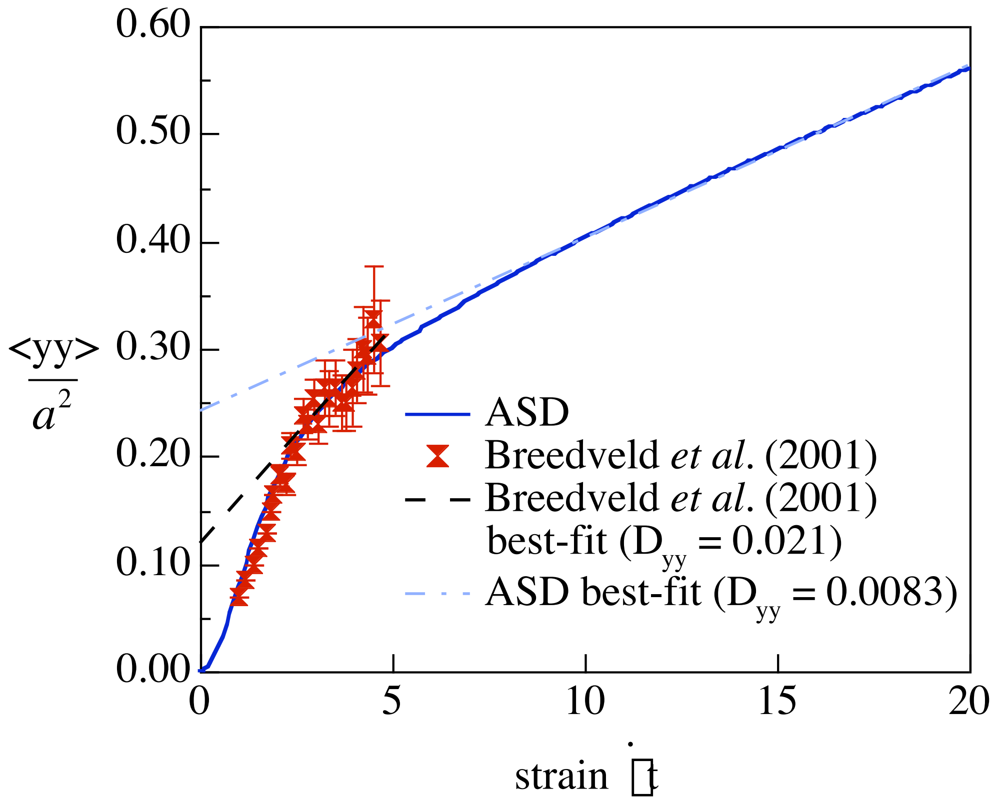


Long-time Asymptote?

□ = 0.2

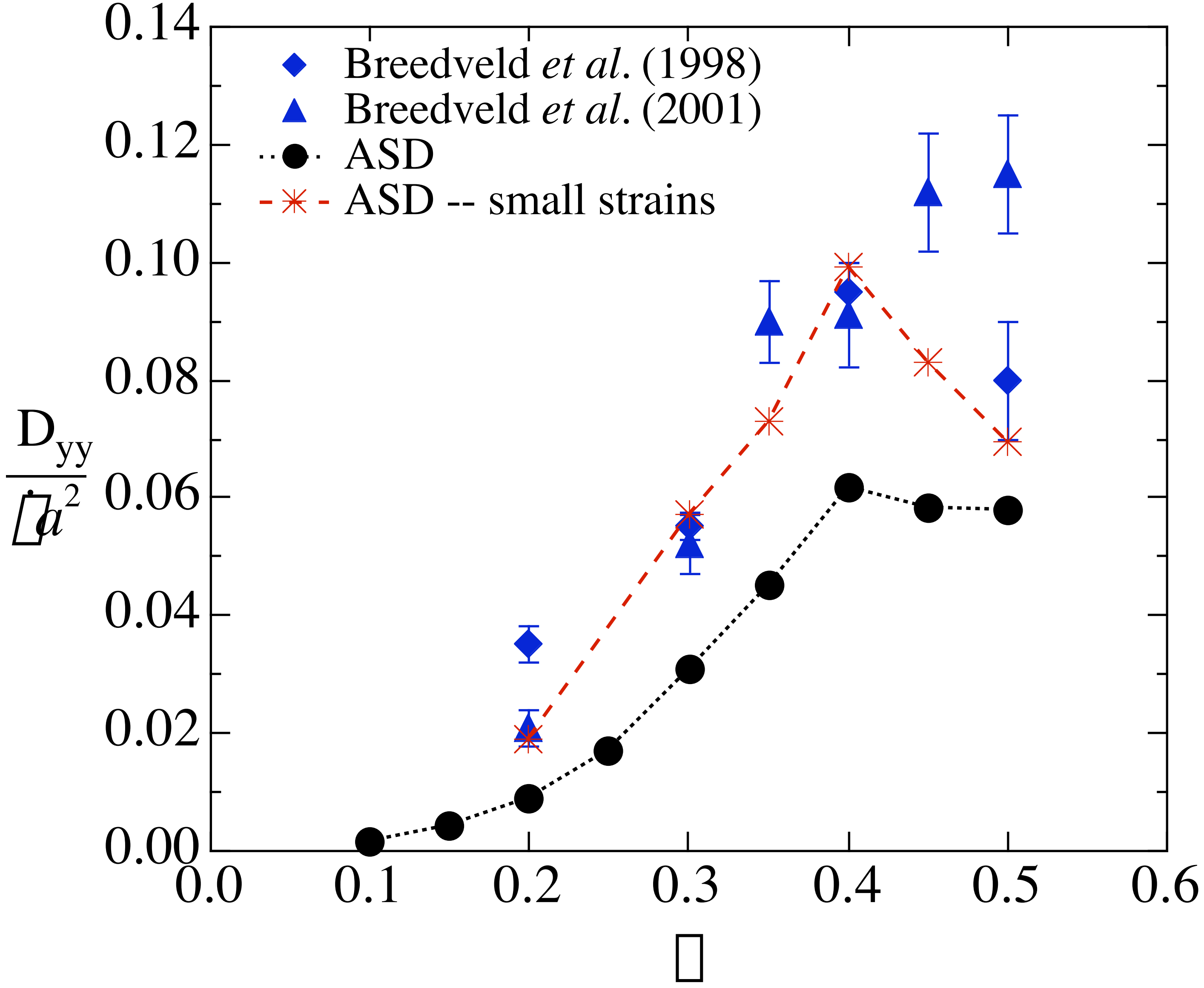


Short times

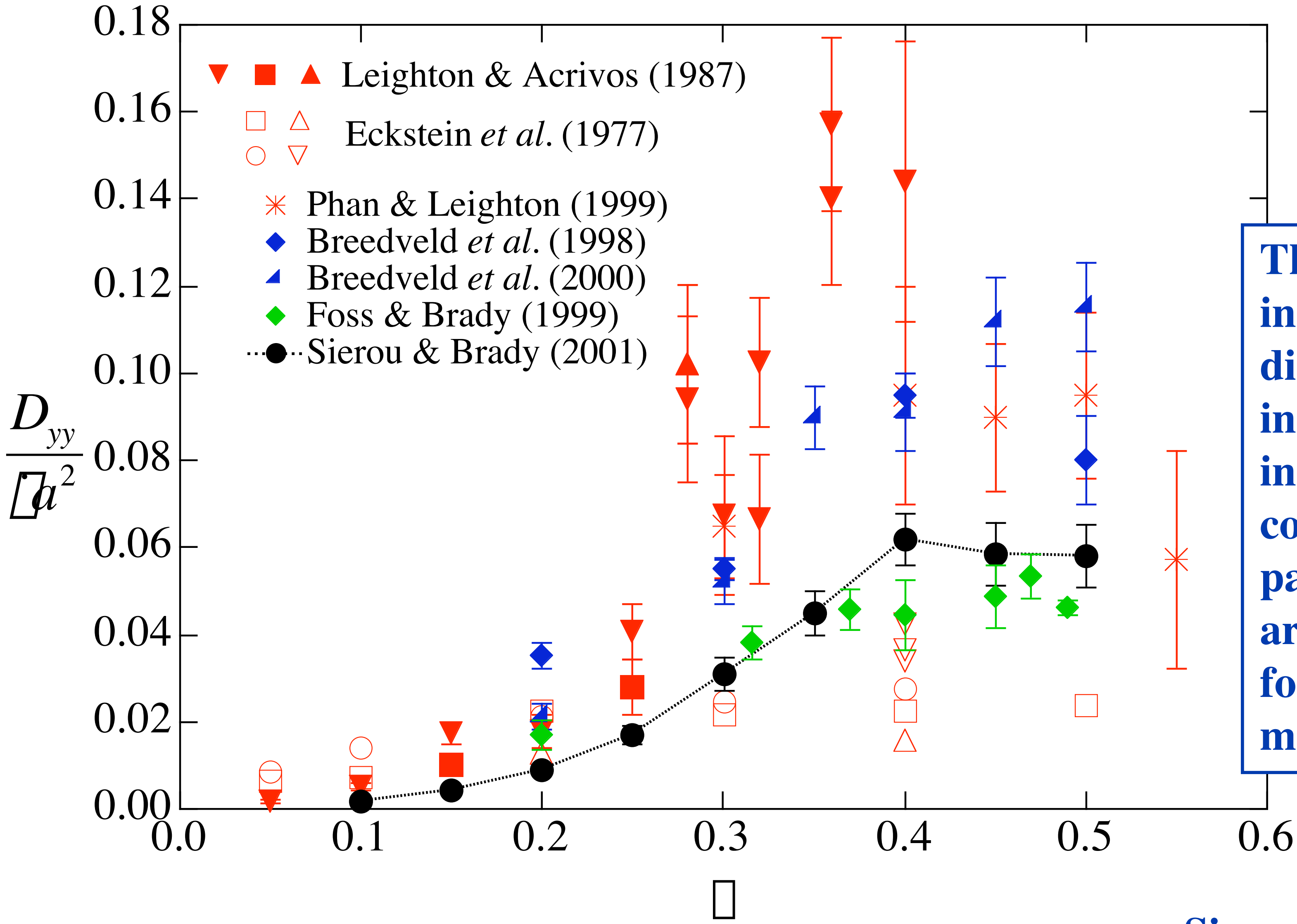


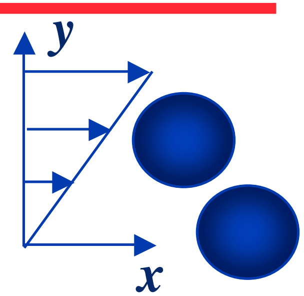
Long times

Simulation vs. Experiment (small strains)



Shear-Induced Self-Diffusivity

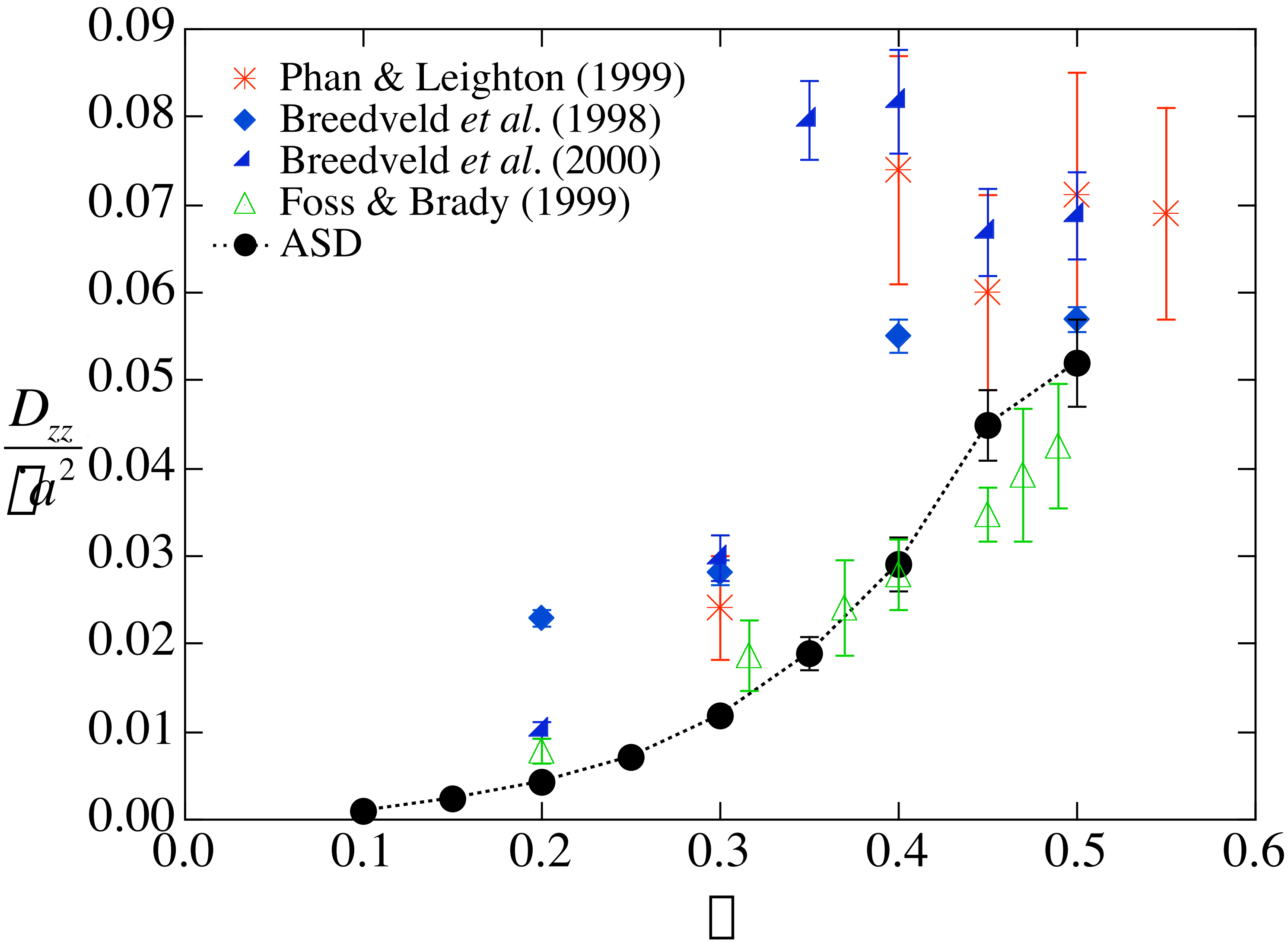


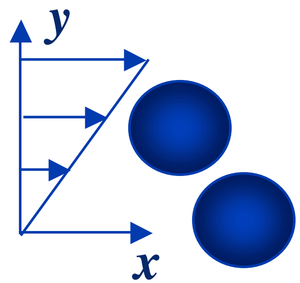


The shear-induced self-diffusivity increases with increasing concentration as particle collisions are responsible for the diffusive motion.

Sierou & Brady (2004)

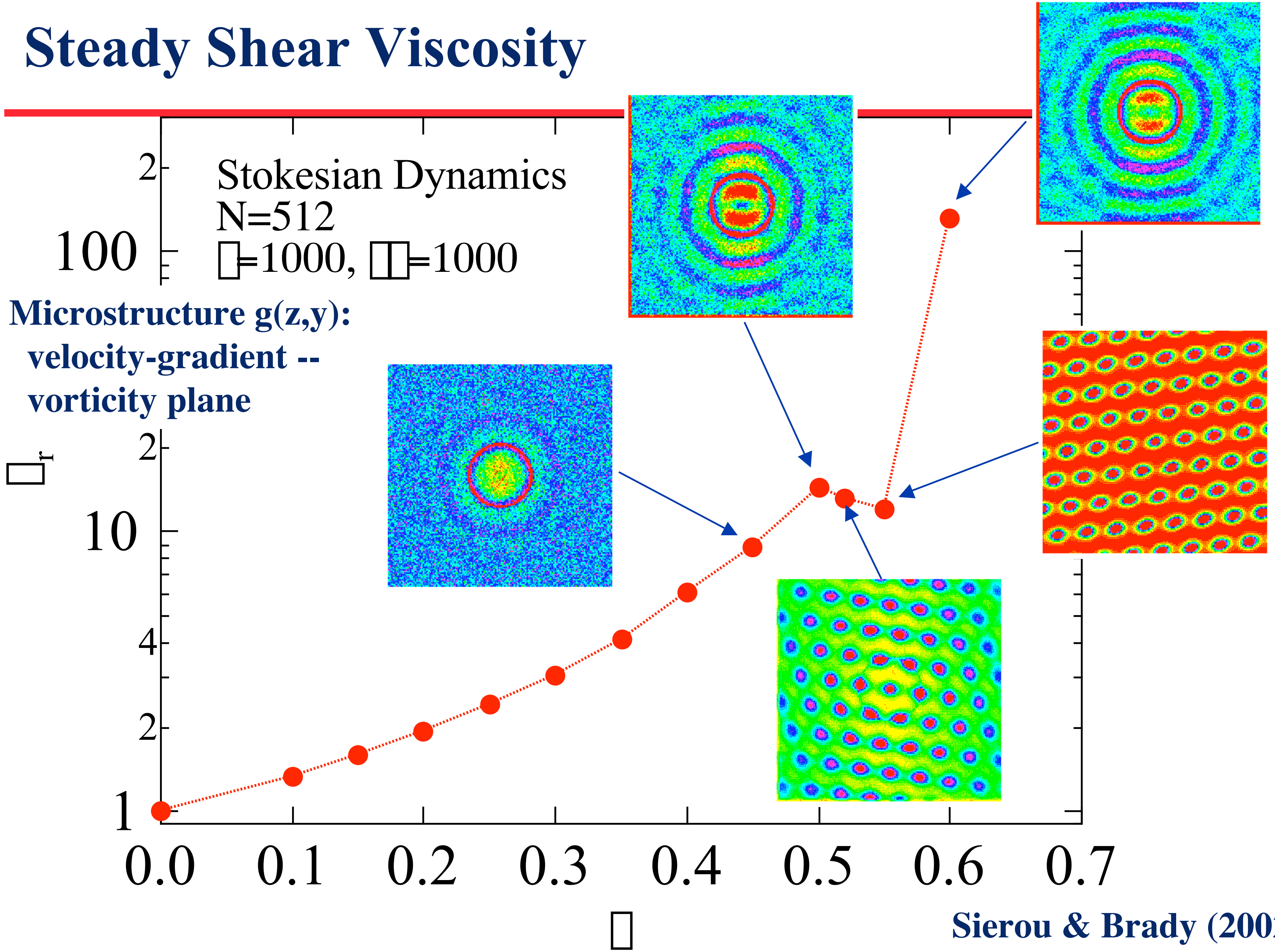
Shear-Induced Self-Diffusivity





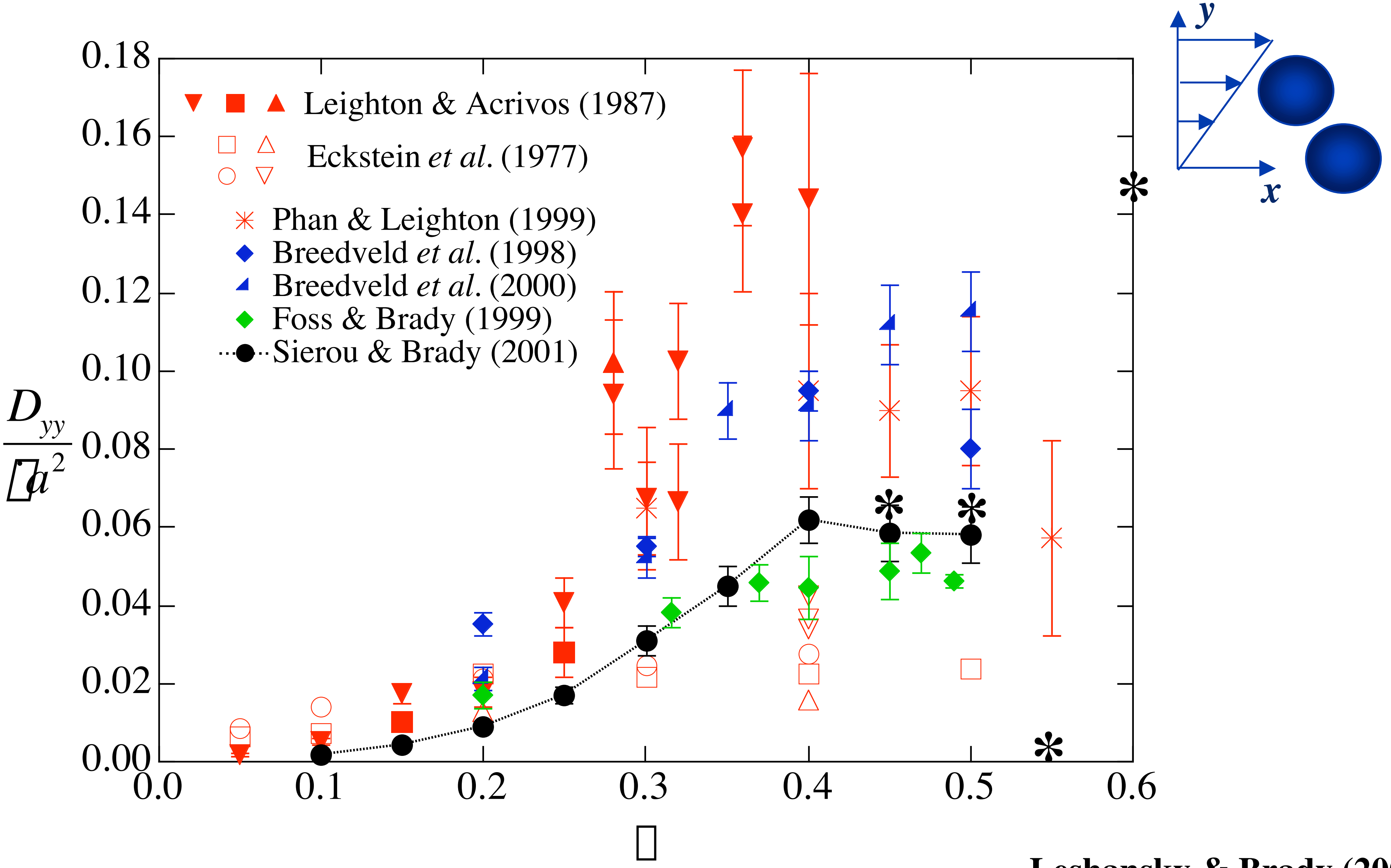
Sierou & Brady (2004)

Steady Shear Viscosity



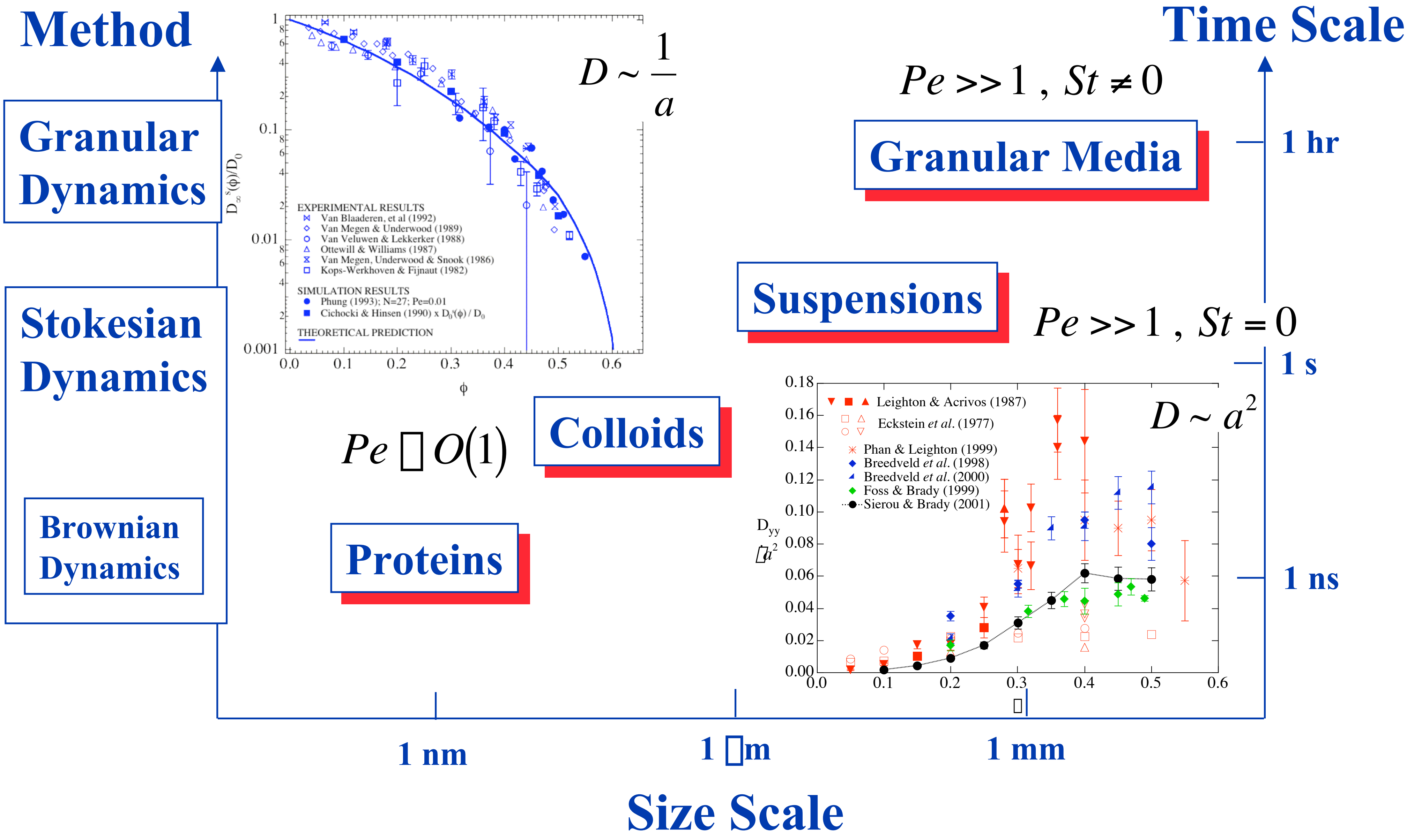
Sierou & Brady (2002)

Shear-Induced Self-Diffusivity



Leshansky & Brady (2005)

Diffusion Across Scales

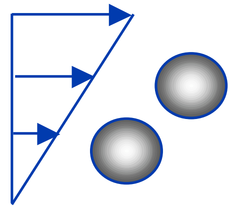


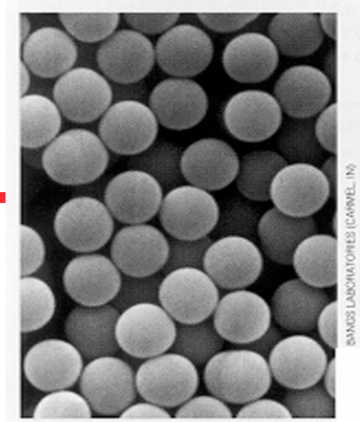
Micromechanics: Particle Inertia ($St \neq 0$)

Particle Motion:

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

(the F^B term is crossed out)





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

Hydrodynamic:

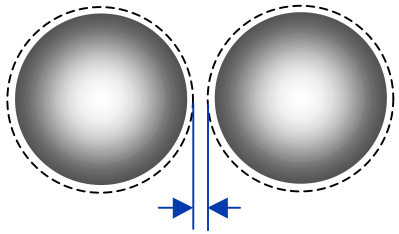
$$F^H = -R(x) \cdot \left(U - U^{\infty}\right)$$

Stokes drag

Dissipation: e, μ

Interparicle/ external:

$$F^P = \text{Hard-sphere collisions}$$

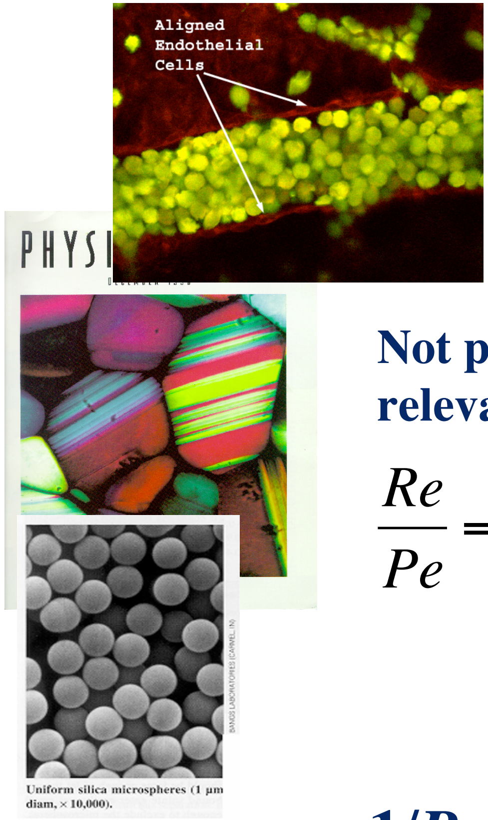


$\delta = 10^{-3}a$

$$St = \tau_p \dot{\gamma} = m\dot{\gamma}/6\pi\eta a \sim \rho_p \dot{\gamma} a^2/\eta$$

$$Re = \frac{\rho_f}{\rho_p} St << 1$$

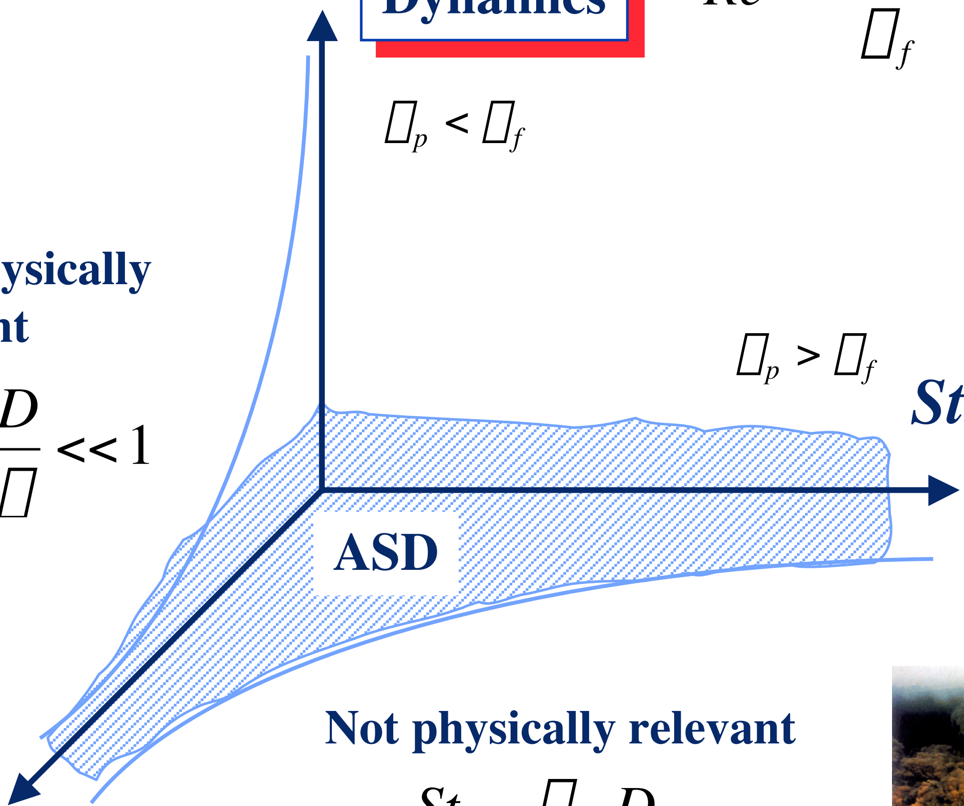
Stokesian (Brownian) Dynamics to Granular Dynamics



Not physically relevant

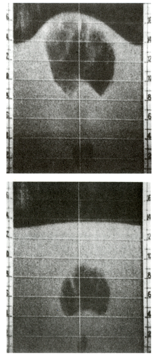
$$\frac{Re}{Pe} = \frac{D}{\nu} << 1$$

$$Pe = \frac{a^2\dot{\gamma}}{D}$$



Bubble Dynamics

$$Re = \frac{\rho_f a^2 \dot{\gamma}}{\mu_f}$$



$$St = \frac{\rho_p a^2 \dot{\gamma}}{\mu_f}$$

Granular Dynamics

Stokesian (Brownian) Dynamics

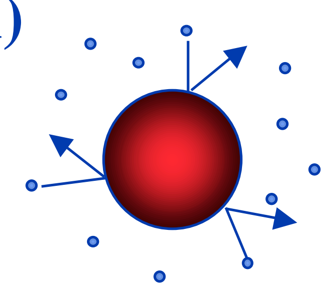
Not physically relevant

$$\frac{St}{Pe} = \frac{\rho_p}{\rho_f}\frac{D}{\nu} \ll 1$$

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

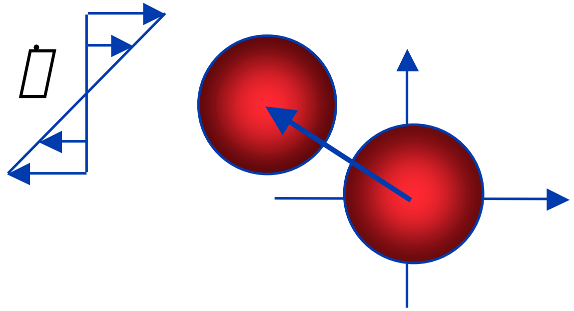
- **Brownian motion (Stokes-Einstein-Sutherland)**

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



- **Shear-induced**

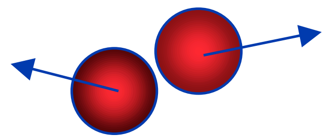
$$(v')^2 \sim (\dot{\gamma} a)^2, \quad \tau \sim \dot{\gamma}^{-1}, \quad D \sim \dot{\gamma} a^2$$



- **Granular Gas (Kinetic Theory)**

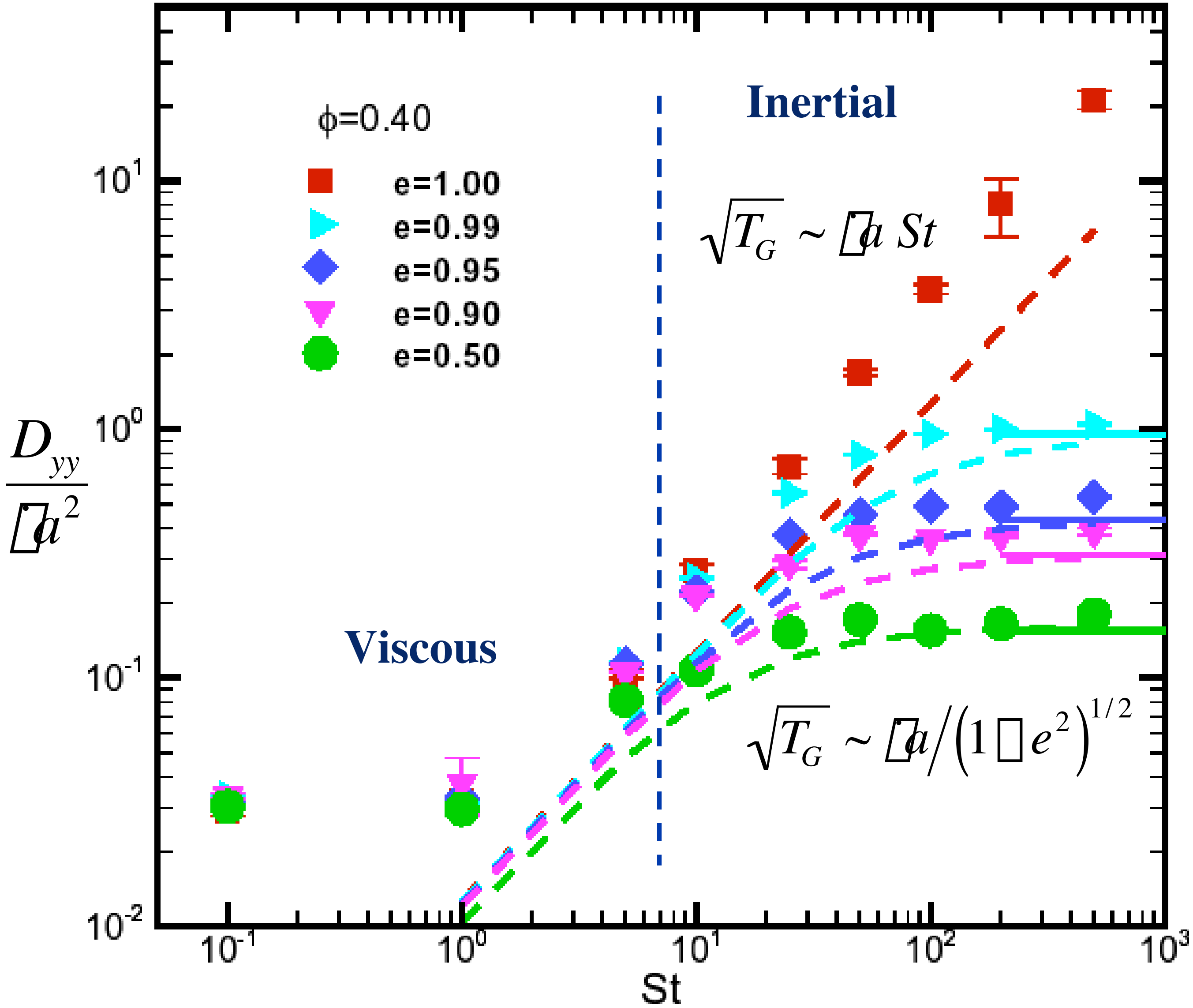
$$(v')^2 \sim T_G, \quad \tau \sim \frac{\lambda}{\sqrt{(v')^2}}, \quad D \sim \lambda\sqrt{T_G} \sim \dot{\gamma} a \lambda$$

$$T_G \sim (\dot{\gamma} a)^2$$



Self Diffusion vs. *St*

Savage & Dai (1993): $D = \dfrac{a\sqrt{\Box}\sqrt{T_G}}{4(1+e)\Box g_0(\Box)}$



Energy balance:
(Sangani *et al* 1996)

$\Box_s \dot{\Box}^2 = \dot{\Box}_{viscous} + \dot{\Box}_{inelastic}$

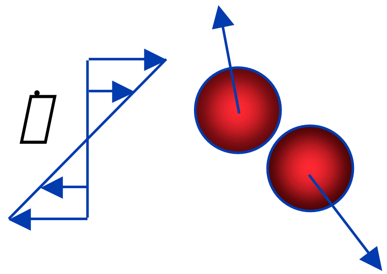
$\dot{\Box}_{viscous} \sim \Box a^{\Box 2} \Box T_G$

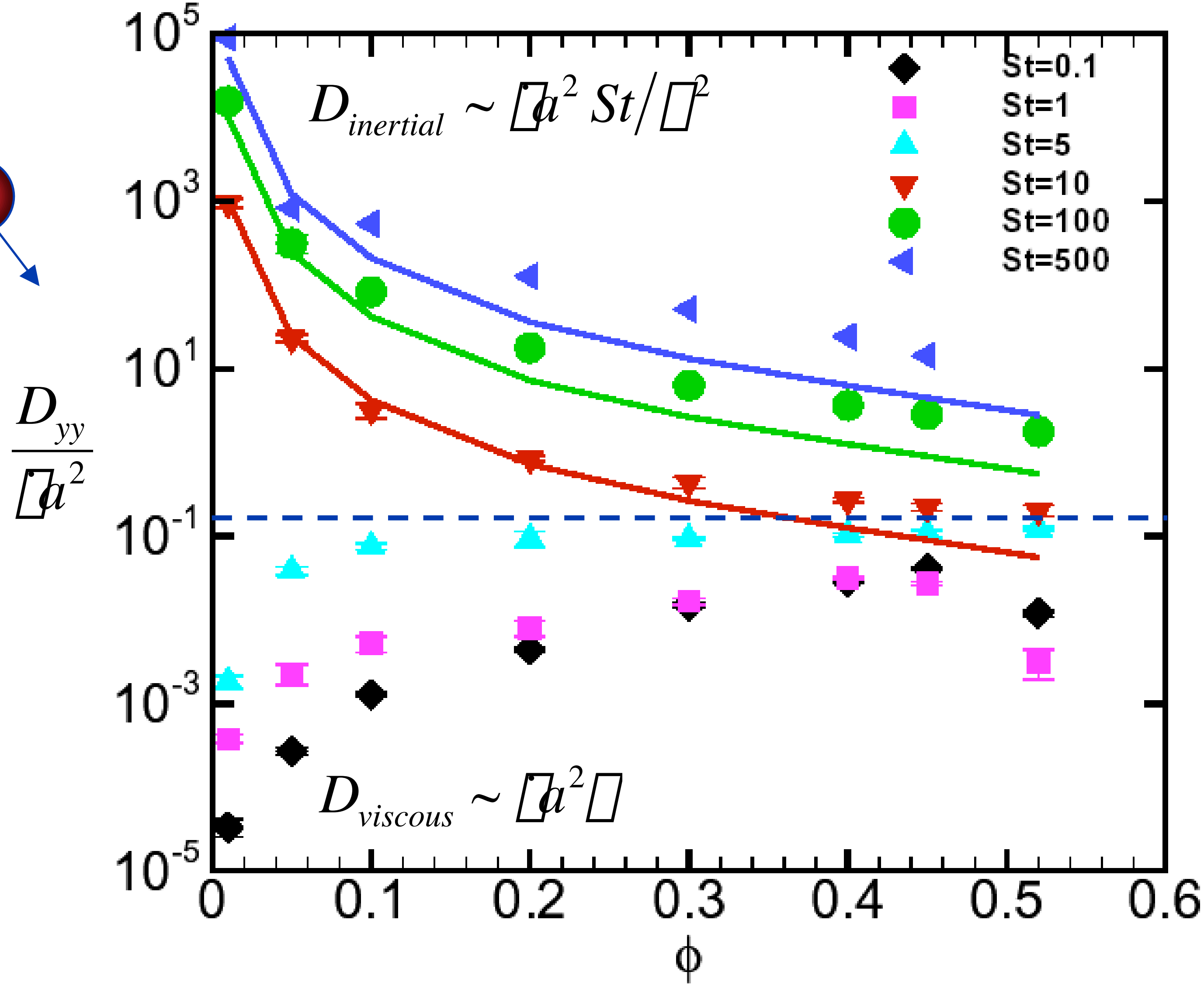
$\dot{\Box}_{inelastic} \sim$

$\Box_p a^{\Box 1}(1\Box e^2)\Box^3 T_G^{3/2}$

$\Box_s \sim \Box_p a\sqrt{T_G}$

Self Diffusion at finite *St*





Summary and Remarks

- **Particle Diffusion:**

Proteins

a ↓

Peas

$$\text{Brownian}: \quad D \sim kT/\square a \qquad \square \quad \text{as} \quad \square \uparrow$$

$$\text{Viscous}: \quad D \sim \square a^2 \qquad \uparrow \quad \text{as} \quad \square \uparrow$$

$$\text{Inertial}: \quad D \sim \square\sqrt{T_G} \qquad \square \quad \text{as} \quad \square \uparrow \quad \text{for } St \geq 10$$

- **Implications:**

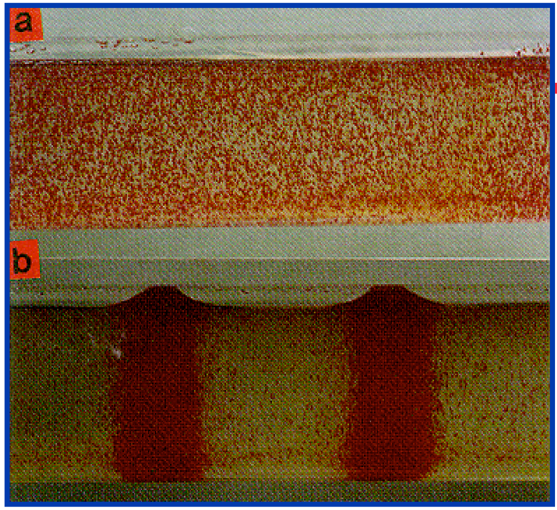
$$\text{Mesoscopic}: \qquad \frac{\partial c(\boldsymbol{r})}{\partial t} + \square\square \cdot \boldsymbol{U}(\boldsymbol{r})c(\boldsymbol{r}) = \square \cdot \boldsymbol{D}(\boldsymbol{r}) \cdot \square c(\boldsymbol{r}) \quad ?$$

$$Pe \sim O(1)$$

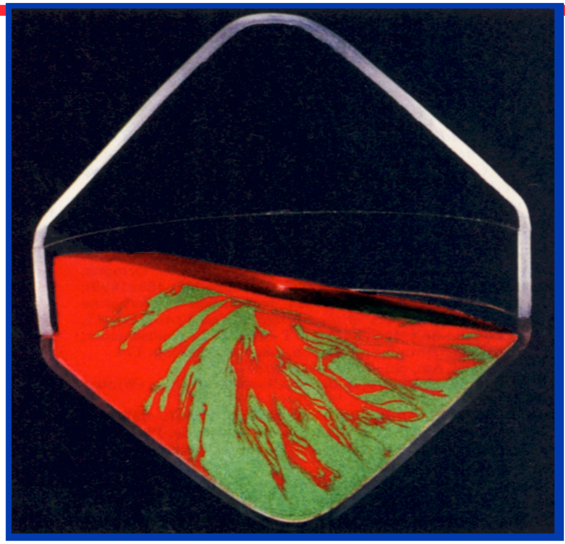
$$\text{Macroscopic}: \quad \text{when } \square \text{ varies spatially} \quad \square \quad \begin{cases} \text{particle migration} \\ \text{phase separation} \\ \text{pattern fomration} \end{cases}$$

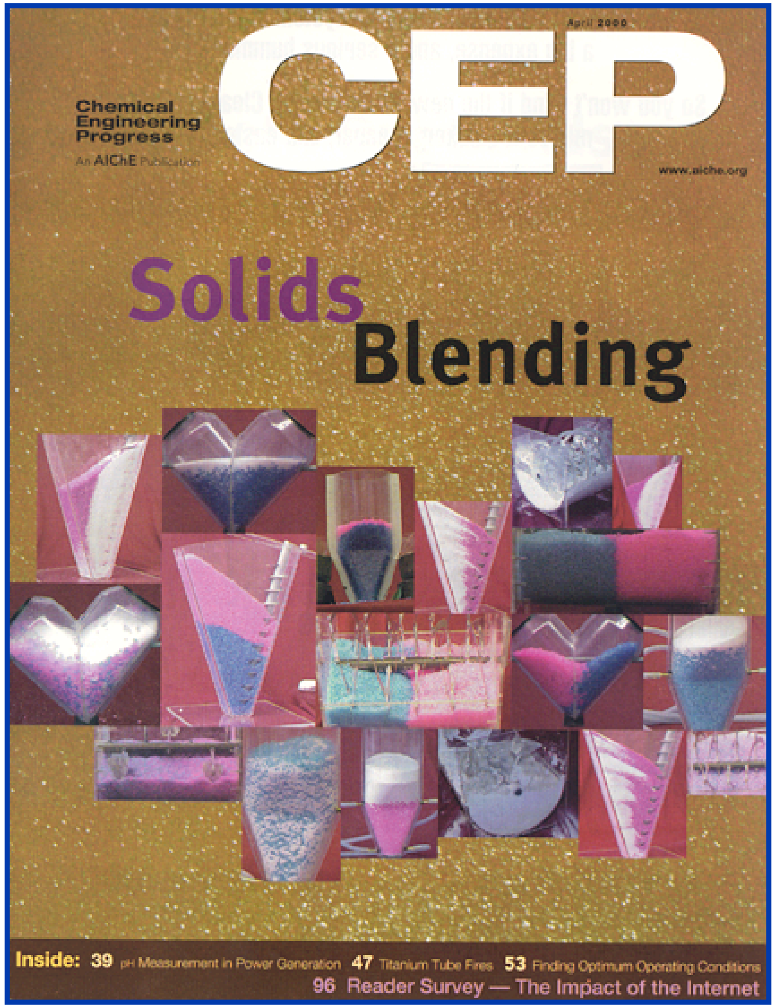
Pattern Formation

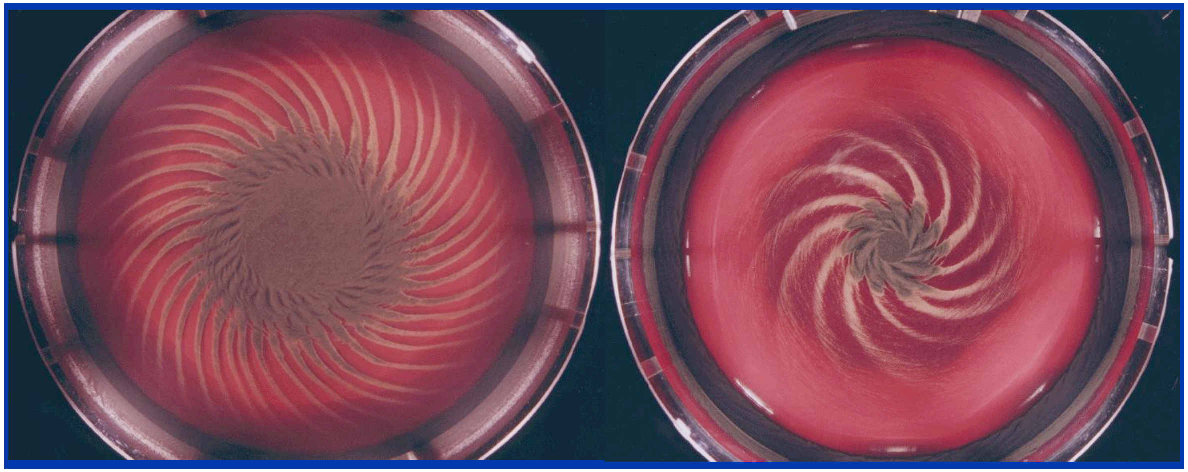
Tirumkudulu *et al* (1999)



Shinbrot & Muzzio (2000)







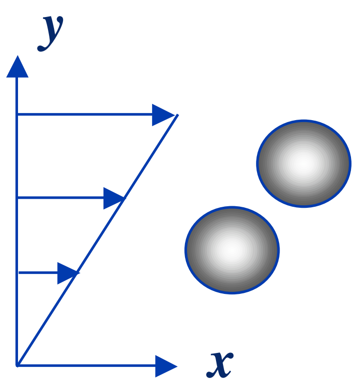
Zoueshtiagh & Thomas (2000)

The End

The full tensorial diffusivity

- But what about the general form of the self-diffusivity in a suspension undergoing flow?

- For simple shear flow:



$$\begin{bmatrix} D_{xx} & D_{xy} & 0 \\ D_{yx} & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{bmatrix}$$

Extracting diffusion from dispersion

At long times:

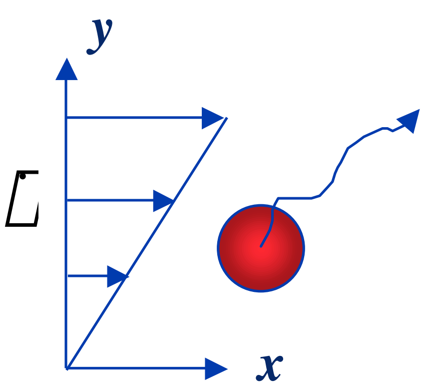
$$\langle x(t)x(t)\rangle \sim 2D_{xx}t + 2D_{xy}\dot{\gamma}t^2 + 2D_{yy}\tfrac{1}{3}\dot{\gamma}^2t^3$$

$$\langle x(t)y(t)\rangle \sim 2D_{xy}t + 2D_{yy}\tfrac{1}{2}\dot{\gamma}t^2$$

$$\langle y(t)y(t)\rangle \sim 2D_{yy}t$$

$$\langle z(t)z(t)\rangle \sim 2D_{zz}t$$

$$\langle x(t)z(t)\rangle = \langle y(t)z(t)\rangle = 0$$



Need to remove the affine shearing motion to reveal the underlying diffusive behavior.

Master or Fokker-Planck equation

Particle motion: $$\frac{d\boldsymbol{x}(t)}{dt} = \square y(t)\boldsymbol{e}_x + \boldsymbol{U}\square(t)$$ **Sierou & Brady (2004)**

$$\square$$

$$\frac{\partial P}{\partial t} + \square y \frac{\partial P}{\partial x} = D_{xx}(t)\frac{\partial^2 P}{\partial x^2} + D_{yy}(t)\frac{\partial^2 P}{\partial y^2} + D_{zz}(t)\frac{\partial^2 P}{\partial z^2} + 2D_{xy}(t)\frac{\partial^2 P}{\partial x \partial y}$$

$$D_{yy}(t) = \frac{1}{2}\frac{d}{dt}\langle y(t)y(t)\rangle$$

$$D_{zz}(t) = \frac{1}{2}\frac{d}{dt}\langle z(t)z(t)\rangle$$

$$D_{xy}(t) = \frac{1}{2}\frac{d}{dt}\langle x(t)y(t)\rangle \square \frac{1}{2}\square\langle y(t)y(t)\rangle$$

$$D_{xx}(t) = \frac{1}{2}\frac{d}{dt}\langle x(t)x(t)\rangle \square\square\langle x(t)y(t)\rangle$$

What does it mean to have a D_{xy} or cross diffusivity?

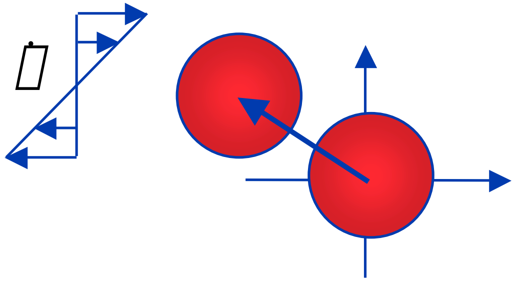
Relation between diffusion and stress

- **Chemical Potential & 'Osmotic Pressure'**

$$\boldsymbol{j} = -\boldsymbol{M} \cdot \nabla \mu = \boldsymbol{M} \cdot \nabla \cdot \boldsymbol{\Sigma}$$

particle flux = mobility x chemical potential ~ - 'osmotic pressure'

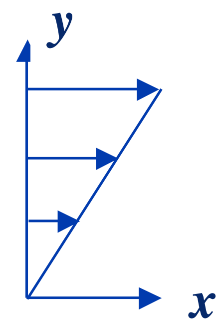
- **The particle flux in driven by *stress* gradients**



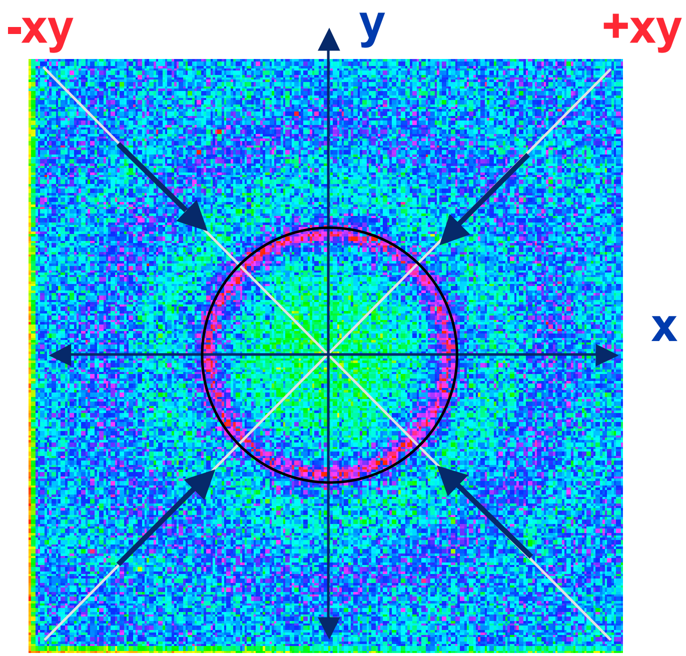
Out of equilibrium, the shear stress is non zero and so there should be an off-diagonal (negative) diffusivity.

Brady & Morris (1997)

Collision-induced *xy*-diffusivity

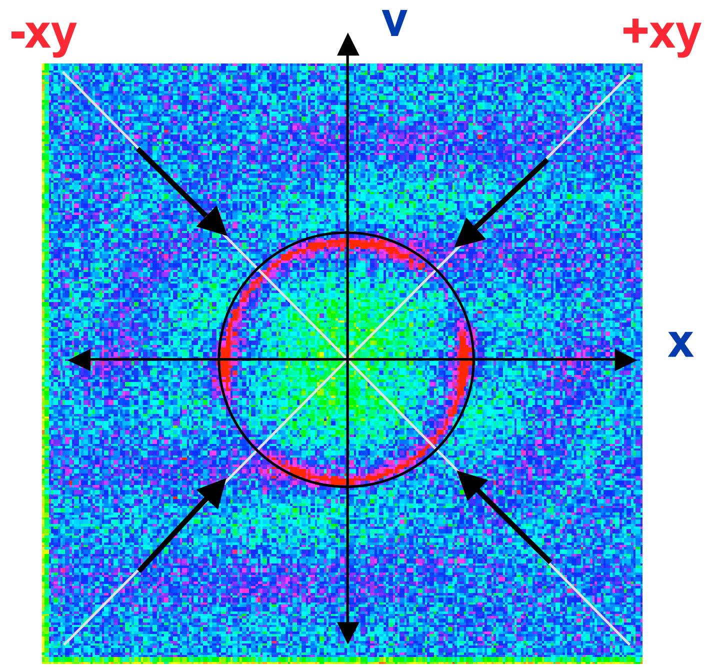


Equilibrium



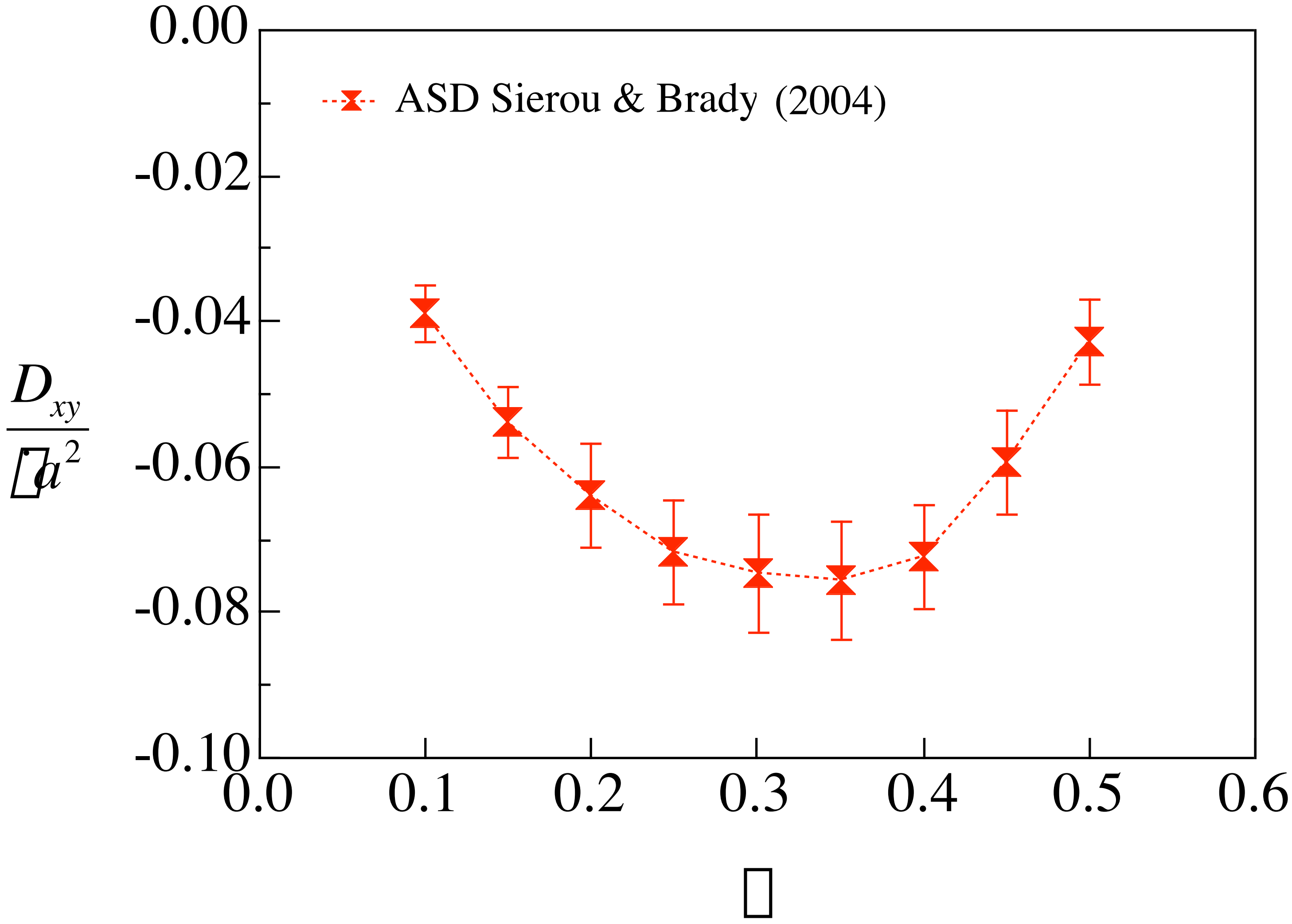
Motion of test particle resulting from collisions with a second particle

Shear Flow



Microstructure: g(x,y)
ASD, □ = 0.45

Off-Diagonal Self-Diffusivity

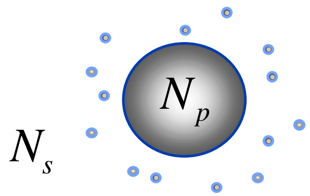


Particle Size Scale

Simulation Method

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

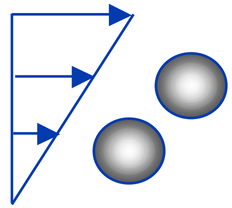
$$Re = \frac{\rho U a}{\eta} < 1 \quad , \quad St = \frac{\rho_p}{\rho_f} Re, \quad Pe = \frac{\nu}{D} Re \quad \text{arbitrary}$$

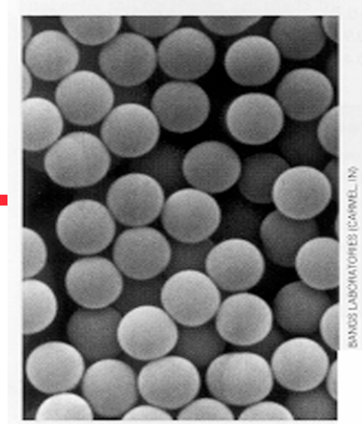


$$\frac{N_s}{N_p} \sim \left(\frac{a_p}{a_s}\right)^3 \quad , \quad \frac{\rho_p}{\rho_s} \sim \left(\frac{a_p}{a_s}\right)^3 \quad , \quad \text{CPU} \sim \left(\frac{a_p}{a_s}\right)^6 N_p$$

Brady & Bossis (1988)

Micromechanics





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

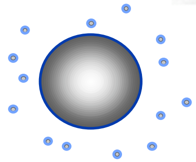
Particle Motion:

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

Hydrodynamic:

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

Stokes drag



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

$$\sim 10^{-8} s$$

Brownian:

$$\overline{F^B} = 0 \ , \ \overline{F^B(0) F^B(t)} = 2kTR(x)\delta(t)$$

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

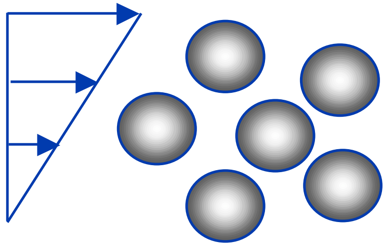
Interparicle/ external:

$$F^P = \Delta\rho V_p g \ , \ \textbf{DLVO}$$

Fluid Motion: Stokes Equations

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

$$\nabla \cdot u = 0$$



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

no slip at particle surfaces