Particle pressure and phase migration in suspensions: ***an osmotic approach***

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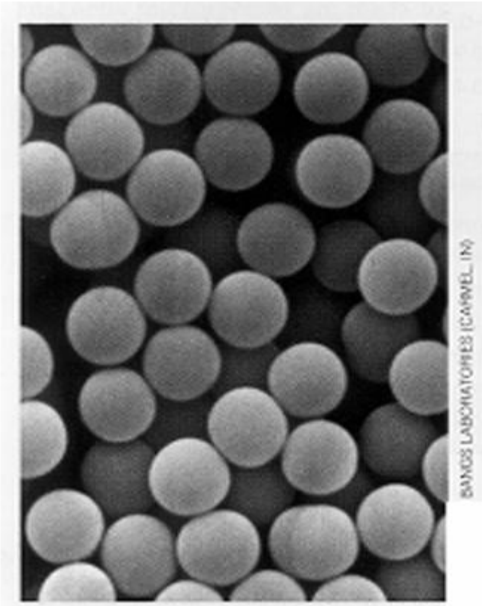
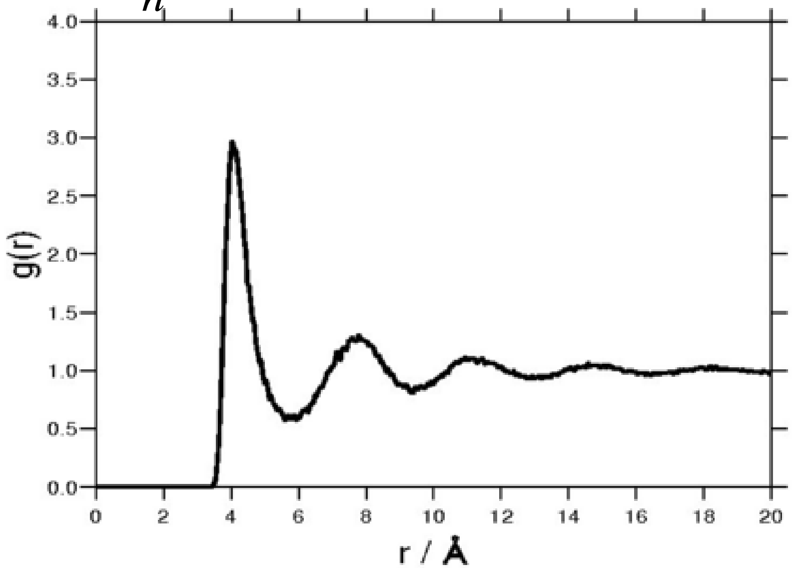
Complex Fluids:
Flow and microstructure are coupled

Hard-Sphere
Colloidal Dispersions:
Simplest Complex Fluids



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

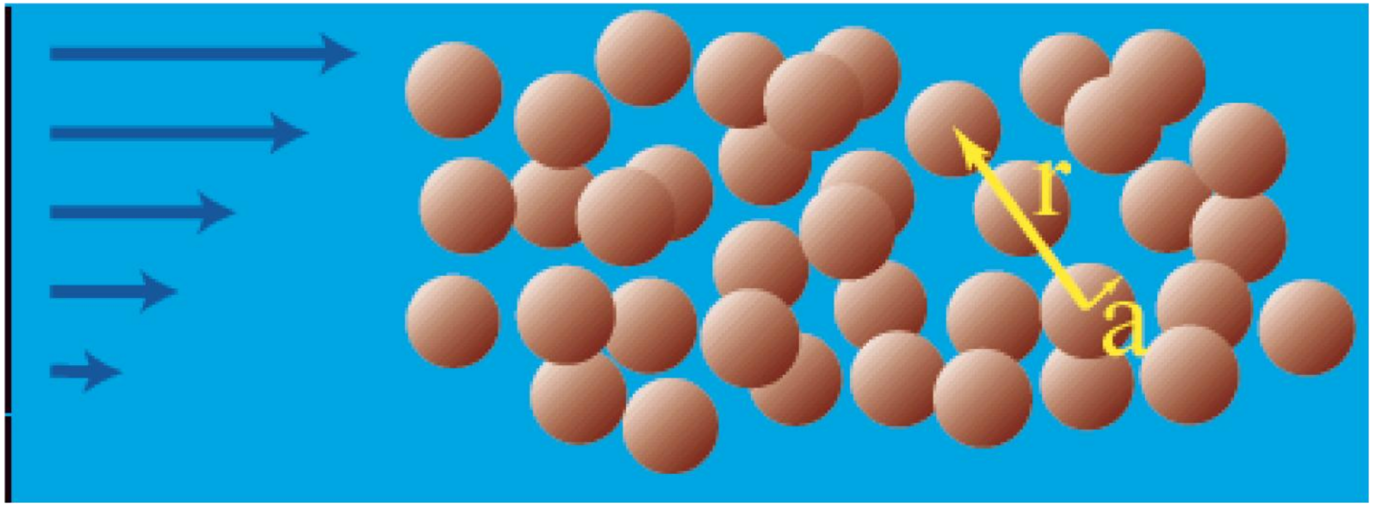
$$g(r) = \frac{P_2(r)}{n^2}$$, **normalized pair probability**



Equilibrium
Pair distribution function:
Agreement of experiment,
simulation and theory
(Percus-Yevick, HNC, …)

Supported by NSF DMR

Nonequilibrium dispersions



$$\mathrm{Re}_p \equiv \frac{\rho \dot{\gamma} a^2}{\eta} \approx \mathbf{0} \quad \textbf{(**)}$$

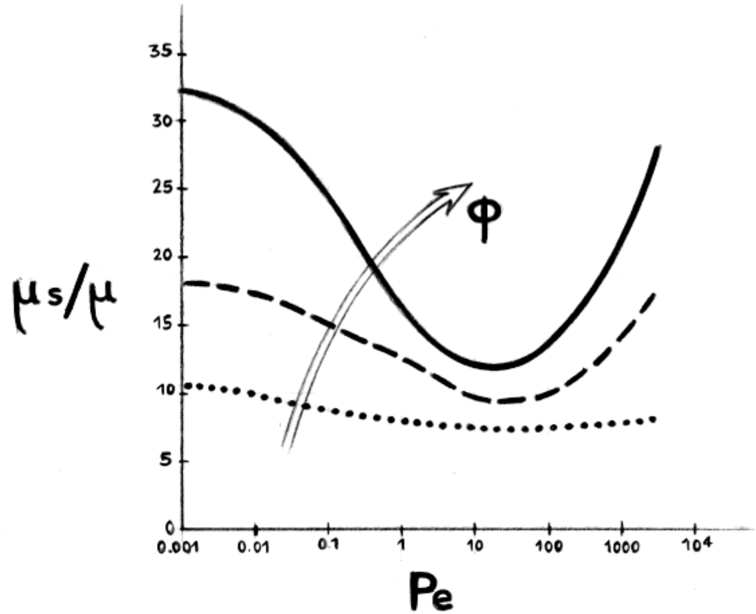
$$\phi = \frac{4\pi a^3}{3} n \;,\; n = \frac{\#}{\textbf{volume}}$$ **Concentration or "loading"**

$$\mathbf{Pe} \equiv \frac{\dot{\gamma} a^2}{D_0} = \frac{6\pi \eta \dot{\gamma} a^3}{kT}$$ **Distance from equilibrium**

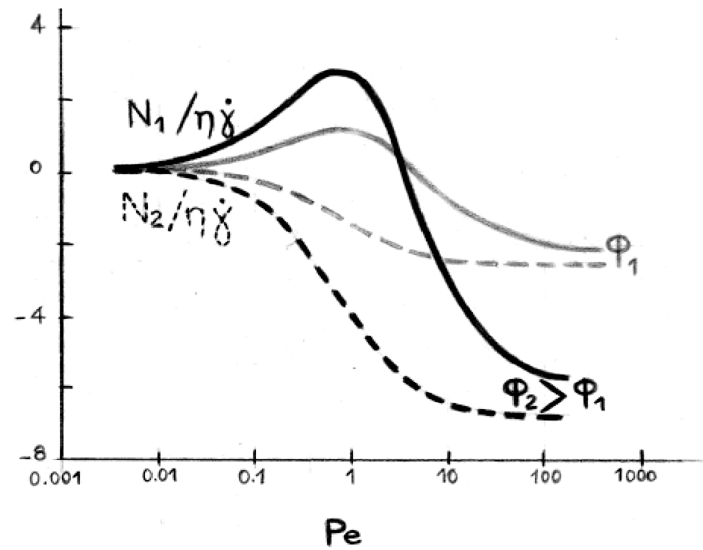
(**) Inertia…Kulkarni & Morris *JFM, PoF* 2008; Humphrey *et al PoF*
Haddadi & Morris submitted *JFM 2013*

Non-Newtonian Rheology

Shear Viscosity



Normal Stress Differences



$N_1 = \sigma_{xx} - \sigma_{yy}$ $N_2 = \sigma_{yy} - \sigma_{zz}$

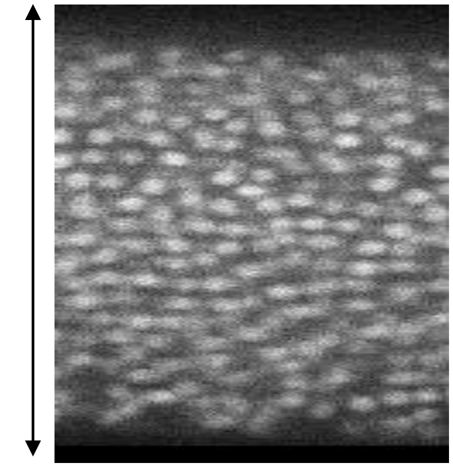
ONE GOAL: Microscopic basis for rheology

Flow Kinematics & Particle loading ~ Microstructure ~ Rheology

D. R. Foss & J. F. Brady 2000 J. Fluid Mech. 407, 167–200.
I. E. Zarraga, D. A. Hill, & D. T. Leighton 2000 J. Rheol. 44, 185.
Plots from E. Guazzelli & J. F. Morris 2012 *A Physical Introduction to Suspension Dynamics*, Cambridge.

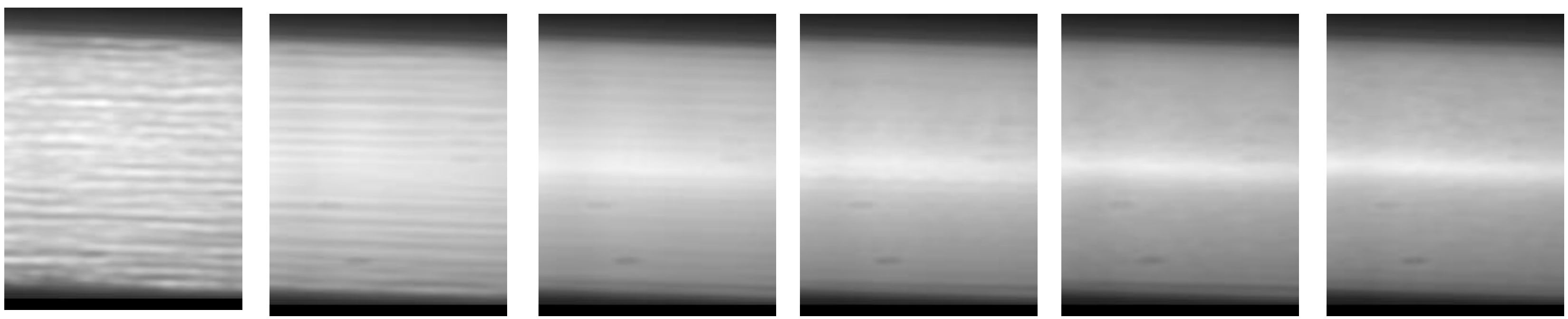
Macroscopic phenomena by microfluidics

(Confocal microscopy: Eric Weeks lab, Emory Univ.)



Volume fraction ϕ = 0.22

2 μm diam. PMMA, slight charge



Frank et al *J. Fluid Mech.* 2003

Semwogerere et al. *J. Fluid Mech.* 2007

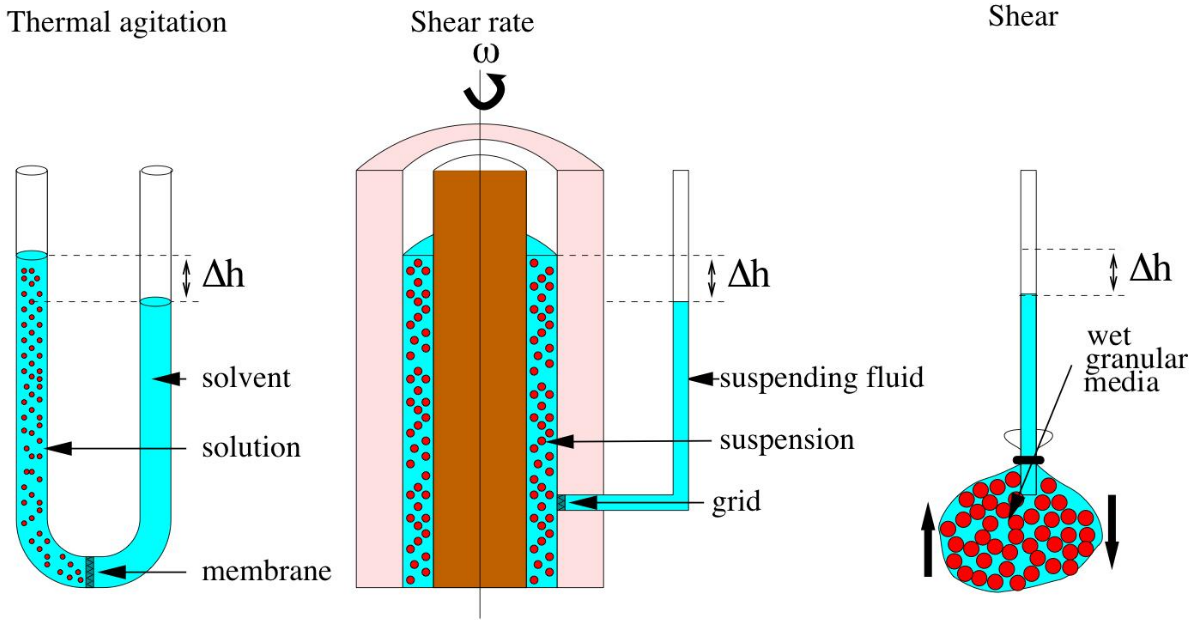
SECOND GOAL: Coupling migration to rheology

$\mathbf{j} \leftrightarrow \Sigma_P$, **particle stress**

Spreading in particulate mixtures

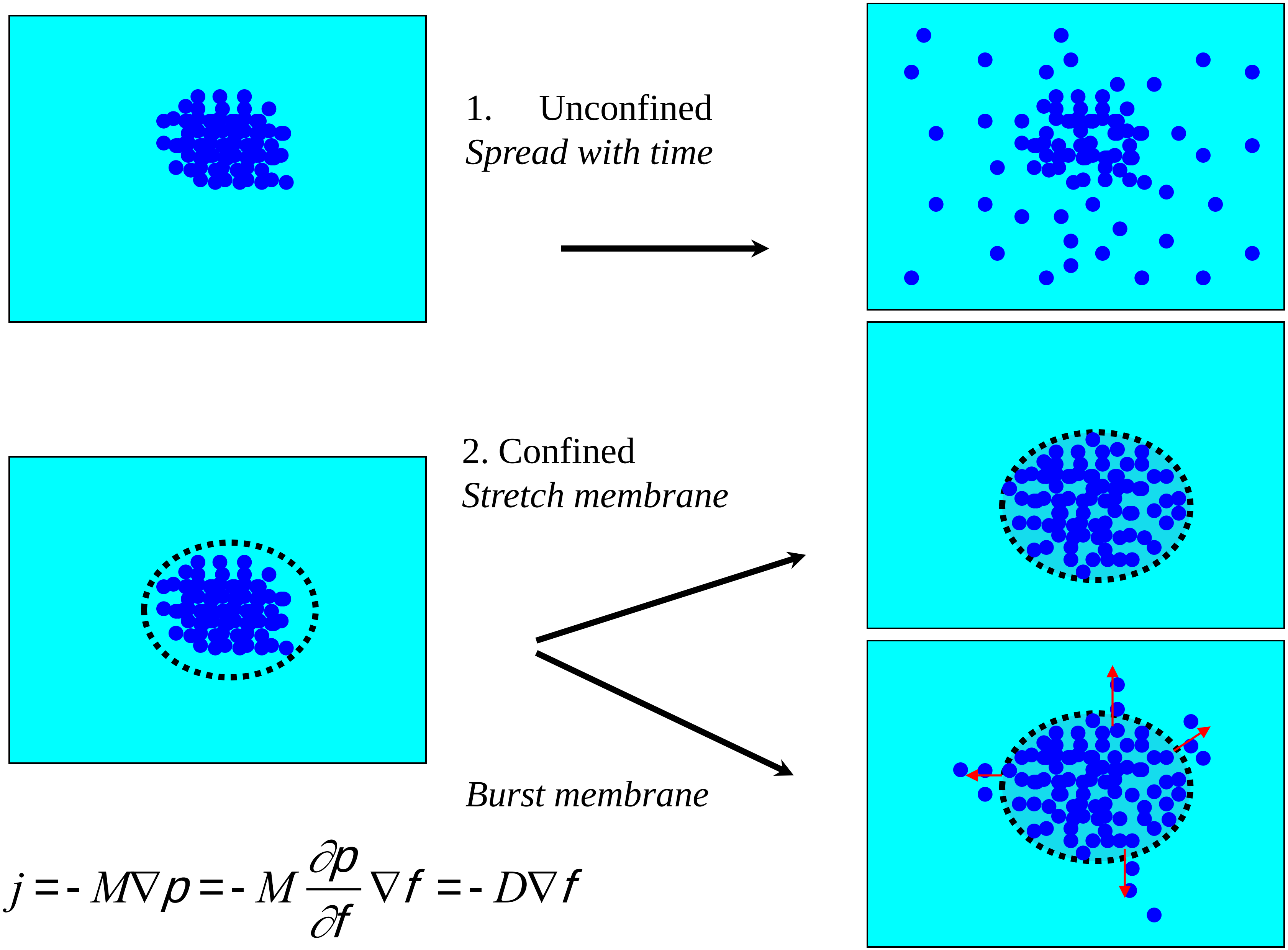
- Two extremes
  - Osmosis: driven by kT
  - Granular dilation: shear-driven contact stress

- Intermediate conditions…Particle pressure
  - Driven by both kT and shear
  - Contact and noncontact (hydrodynamic) stresses, in principle



Diffusion and stress

Constraining diffusion requires normal stress.



$$j = -M\nabla p = -M\frac{\partial p}{\partial f}\nabla f = -D\nabla f$$

Diffusion and stress in dispersions

Pe = 0: Brownian motion & classical osmotic pressure

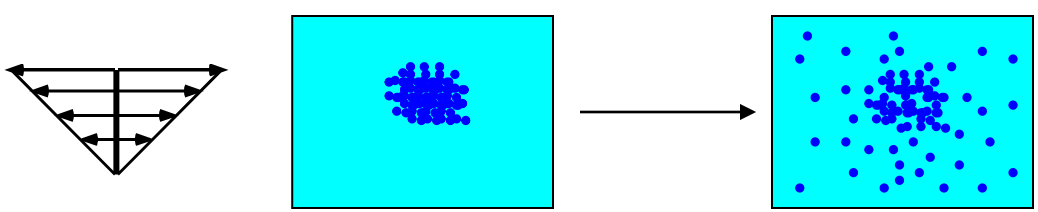
kT drives motion and sets stress scale

$$D \sim \frac{kT}{\eta a} \qquad \Sigma_{ij}^{P} = -\Pi \delta_{ij} \sim nkT$$

Pe >>1 : Shear-induced diffusion & particle pressure

Shear rate drives motion … plays *role* of temperature

$$D \sim \dot{\gamma} a^2 \qquad \Sigma_{ij}^{P} \sim (na^3)\eta\dot{\gamma} \sim f(\phi)\eta\dot{\gamma}$$



Pine *et al.* Nature 2005

Suspension stresses: Pe >> 1

Total **stress [Batchelor JFM 1970]**

$$\Sigma^{\mathbf{Total}} = \Sigma^{\mathbf{F}} + \Sigma^{\mathbf{P}}$$

Shear **stress**

$$\Sigma_{xy}^{\mathbf{F}} + \Sigma_{xy}^{P} = (\eta_{Fl} + \eta_P)\dot{\gamma} = \eta_s \dot{\gamma}$$

Normal **stresses [Morris & Boulay J. Rheol. 1999**

Differences

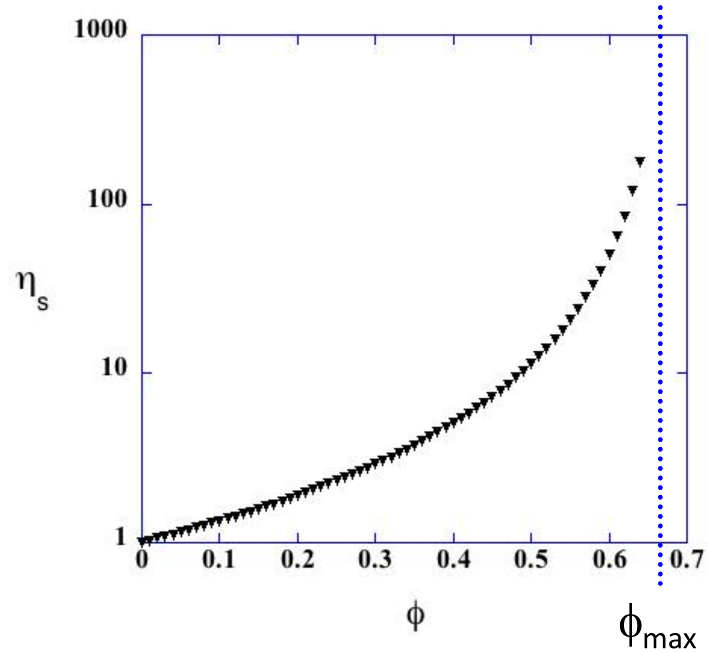
$$\mathbf{N_1} = \Sigma_{11}^P - \Sigma_{22}^P \qquad \mathbf{N_2} = \Sigma_{22}^P - \Sigma_{33}^P$$

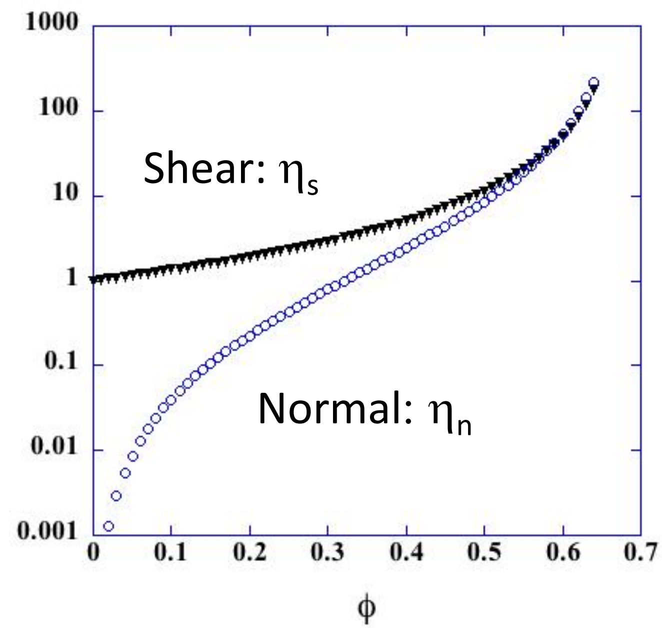
Particle pressure

$$\Pi = -\frac{1}{3}\,\boldsymbol{I} : \Sigma^P = -\frac{1}{3}[\Sigma_{11}^P + \Sigma_{22}^P + \Sigma_{33}^P]$$

$$\Pi, \mathbf{N_1}, \mathbf{N_2} \sim \eta_n \dot{\gamma}$$

$$\Rightarrow \nabla \Pi(\phi, \dot{\gamma}) = \frac{\partial \Pi}{\partial \phi} \nabla \phi + \frac{\partial \Pi}{\partial \dot{\gamma}} \nabla \dot{\gamma}$$





Two-fluid model and particle migration

Particle conservation: $$\frac{\partial \mathrm{f}}{\partial t} + \langle \boldsymbol{u} \rangle \cdot \nabla \mathrm{f} = - \nabla \cdot \boldsymbol{j}_{\wedge}$$

General momentum balance: $$\rho\left(\frac{\partial \boldsymbol{u}}{\partial t} + \boldsymbol{u} \cdot \nabla \boldsymbol{u}\right) = \nabla \cdot \Sigma$$

Average over particles (Re<<1): $$0 = \nabla \cdot \Sigma^{\mathbf{P}} + \boldsymbol{F}_{\mathrm{drag}}$$

$$\boldsymbol{F}_{\mathrm{drag}} \approx -\frac{9\eta_c}{2a^2} f(\phi)^{-1}\ \phi\left(\boldsymbol{U} - \langle \boldsymbol{u} \rangle\right)$$

$$\boldsymbol{j}_{\wedge}\ \mathrm{o}\ \mathrm{f}\ \left(\boldsymbol{U} - \langle \boldsymbol{u} \rangle\right)$$ migration flux

$$= \frac{2a^2}{9\eta_0} f(\phi) \nabla \cdot \Sigma^{\mathbf{P}}$$

Viscous suspensions:
Jenkins & McTigue 1990
Nott & Brady 1994
Morris & Boulay 1999

Similarly in polymeric fluids:
Onuki & Doi 1991
Mavrantzas & Beris 1994
MacDonald & Muller 1996

Two-fluid modeling

$$\boldsymbol{j}_{\perp} = \frac{2a^2}{9\eta_c} f(\phi) \nabla \cdot \Sigma^{\mathbf{P}} \sim -\nabla \Pi$$

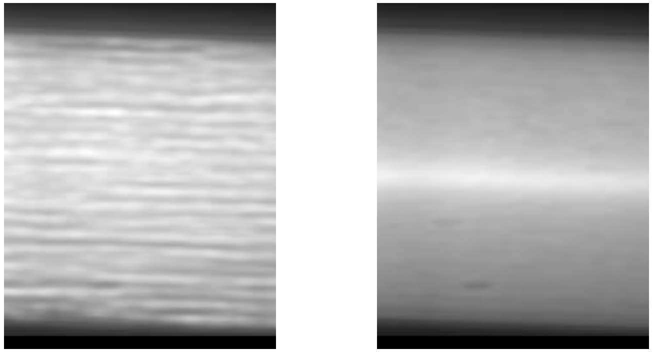
$$\frac{\partial \phi}{\partial t} + \langle \boldsymbol{u} \rangle \cdot \nabla \phi \approx \frac{2a^2}{9\eta_0} f(\phi) \nabla^2 \Pi$$

Bulk mixture motion

$$\nabla \cdot \langle \boldsymbol{u} \rangle = 0$$

$$\nabla \cdot \Sigma = \nabla \cdot \Sigma^{\mathbf{F}} + \nabla \cdot \Sigma^{\mathbf{P}} = 0$$

$$\Rightarrow \nabla \cdot \Sigma^{\mathbf{F}} = -\nabla \cdot \Sigma^{\mathbf{P}}$$



A **B**

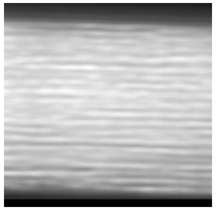
A. Low flowrate = small Pe:
Brownian stress – particles dispersed

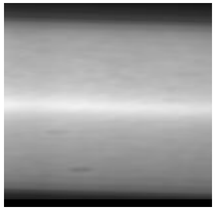
B. High flowrate = large Pe:
Hydrodynamic stress drives migration

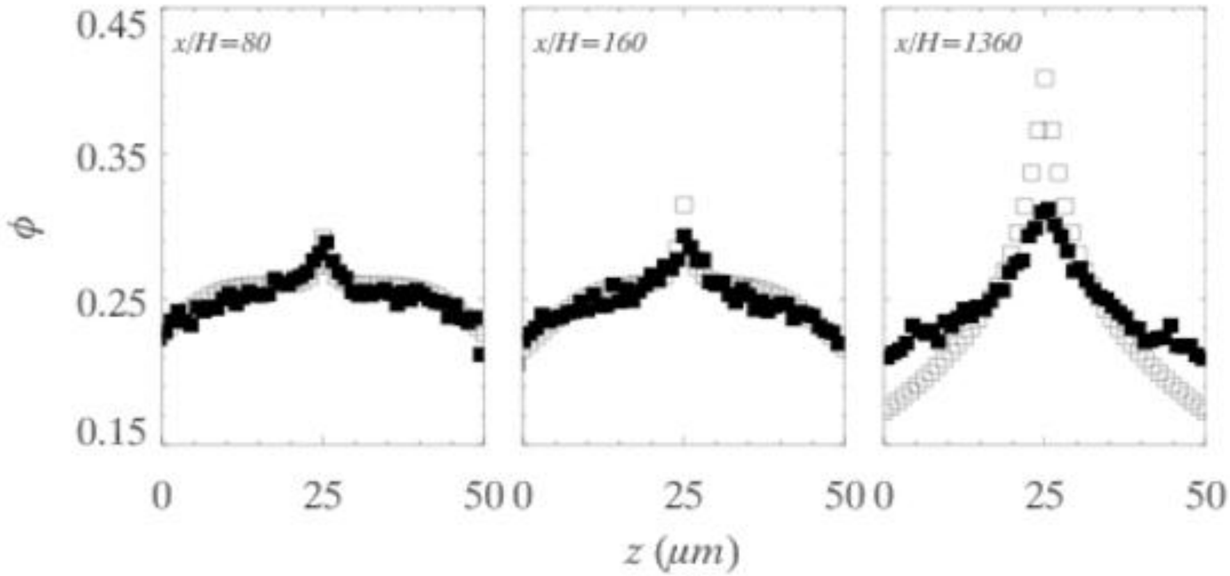
Σ^P (and Π) has hydrodynamic (H) and Brownian (B) terms: roughly speaking balance two osmotic contributions

Frank *et al JFM* 2003

Axial evolution







experiment (solid)
model (open)
$\phi = 0.26$
Pe = 130

Semwogerere, Morris & Weeks *JFM* 2007

So particle pressure is
useful for modeling …
but is it real (= measurable)?

Suspension stresses: Pe >> 1

Total stress [Batchelor JFM 1970]

$$S^{Total} = S^F + S^P$$

Shear stress

$$S_{xy}{}^F + S_{xy}{}^P = (h_{Fl} + h_P)\dot{g} = h_s \dot{g}$$

Normal stresses [Morris & Boulay J. Rheol. 1999]

Differences

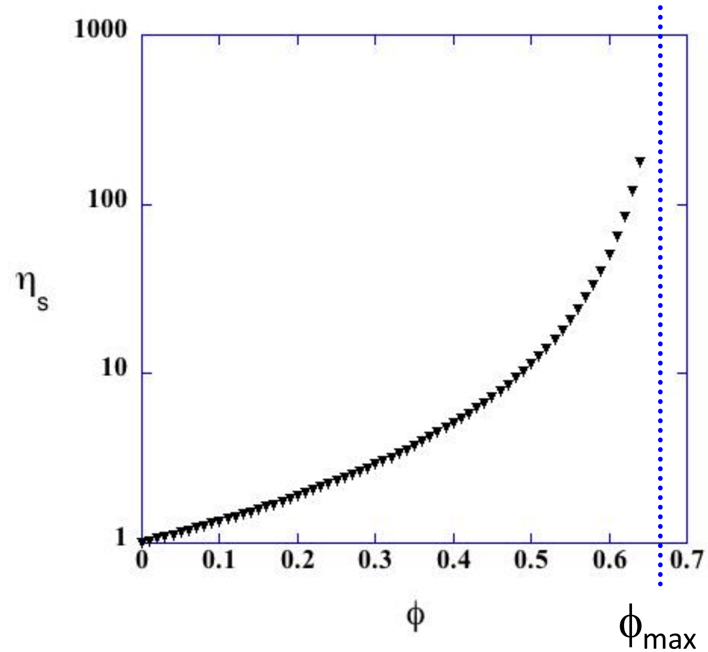
$$N_1 = S_{11}^P - S_{22}^P \qquad N_2 = S_{22}^P - S_{33}^P$$

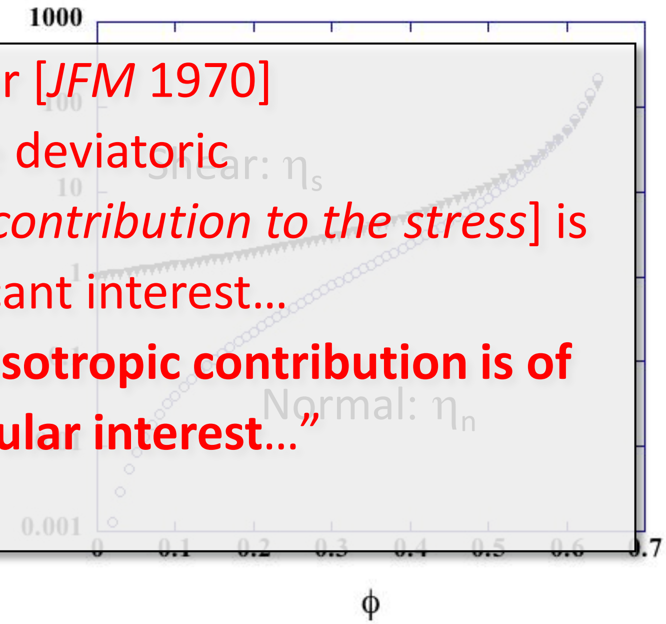
Suspension pressure

$$P = -\frac{1}{3}\mathbf{I} : S^P = -\frac{1}{3}[S_{11}^P + S_{22}^P + S_{33}^P]$$

$$P, N_1, N_2 \sim h_n \dot{g}$$

$$\Rightarrow \nabla P(f, \dot{g}) = \frac{\partial P}{\partial f}\nabla f + \frac{\partial P}{\partial \dot{g}}\nabla \dot{g}$$

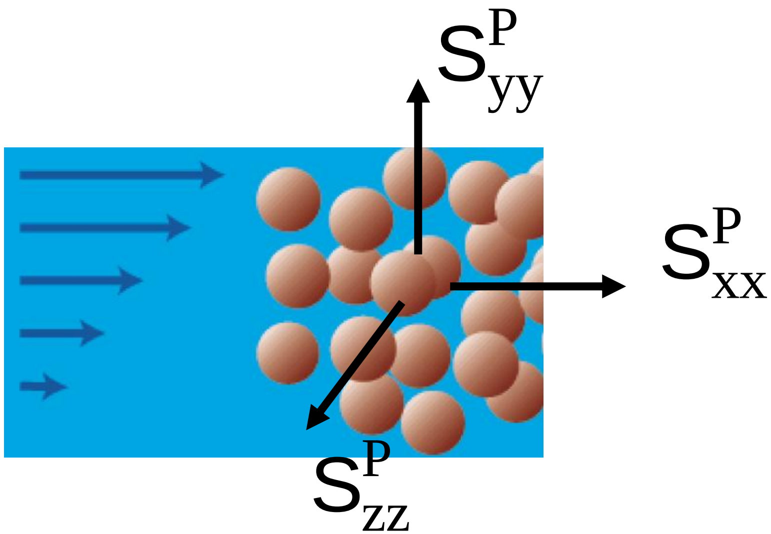




G. K. Batchelor [*JFM* 1970]

"Only the deviatoric [*particle contribution to the stress*] is of significant interest…
a purely isotropic contribution is of no particular interest…"

Rheometry:
Incompressibility constraint



$$S^{Total} = S^{F} + S^{P} \; Þ$$

$$P^{Total} = P^{Fluid} + \mathrm{P} = \text{confining pressure, } \mathrm{P}^{0} \text{ (reference level } \mathrm{P}^{0} = 0)$$

$$\mathrm{P} = - \frac{S^{P}_{xx} + S^{P}_{yy} + S^{P}_{zz}}{3}$$

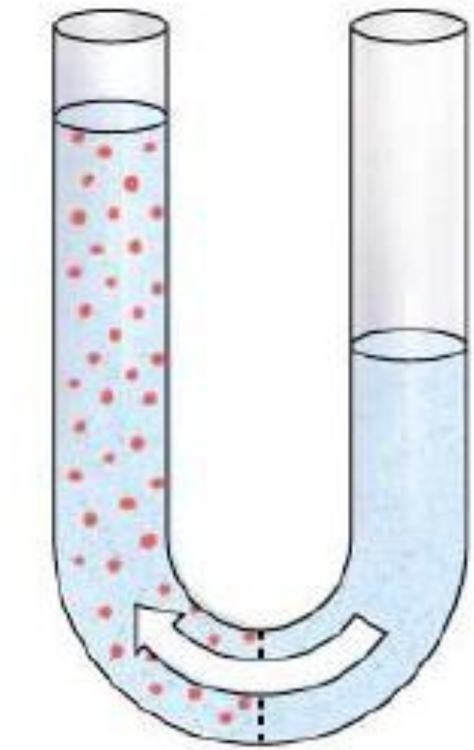
$$Þ \qquad P^{Fluid}(\dot{g}) = - \mathrm{P}(\dot{g})$$

$\backslash$ Summation obscures : need to discriminate particles & fluid.

Yurkovetsky & Morris *J. Rheol.* 2008
See also : Prasad & Kytomaa *Int. J. Multiphase Flow* 1995

Suction into a mixture…osmosis

Osmotic pressure, Π



Thermodynamics: $\Pi = -\left.\frac{\partial A}{\partial V}\right|_{T,N}$

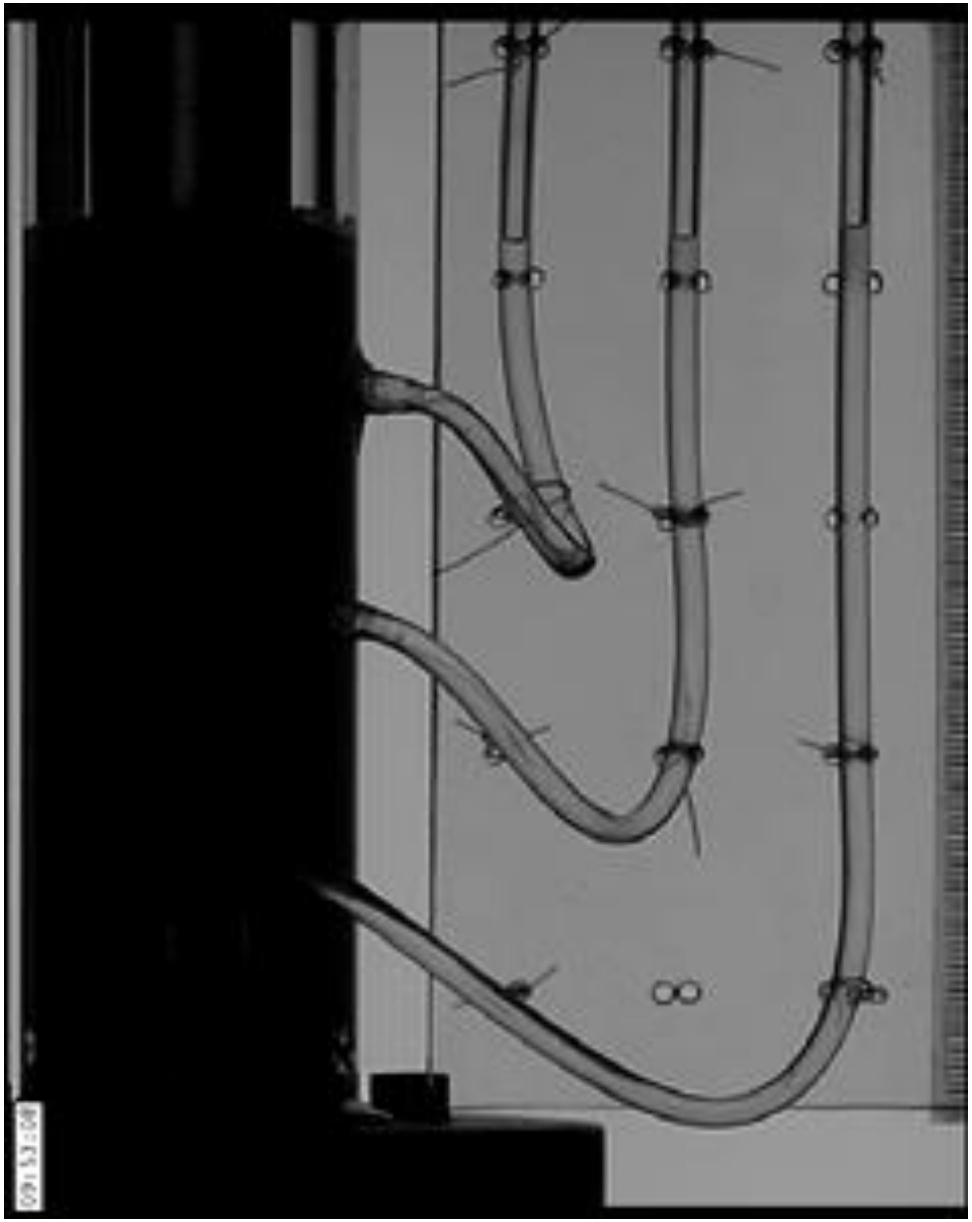
A = Helmholtz energy

Colloidal dispersions [Russel *et al*. 1989] :

$\phi = N v_1 / V = n v_1$ solid fraction

$$\Pi = -\left.\frac{\partial A}{\partial V}\right|_{T,N} = \frac{\phi}{V} \left.\frac{\partial A}{\partial \phi}\right|_{T,N}$$

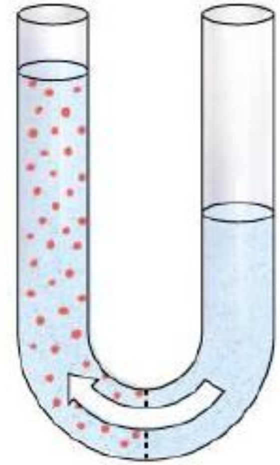
Hard or repulsive particles--
$\Pi > 0$:
Free energy minimized at $\phi = 0$



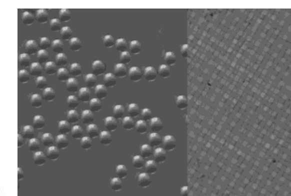
Concentrated suspension / 3 mm gap

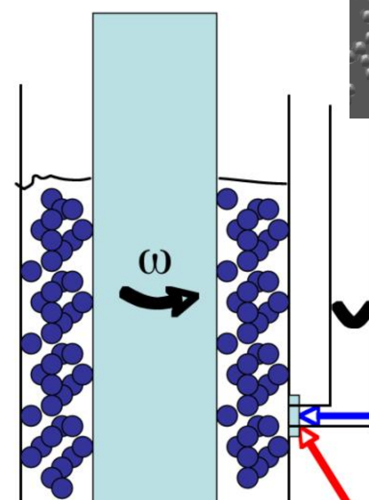
Re << 1, Pe >>1, $\phi = 0.45$

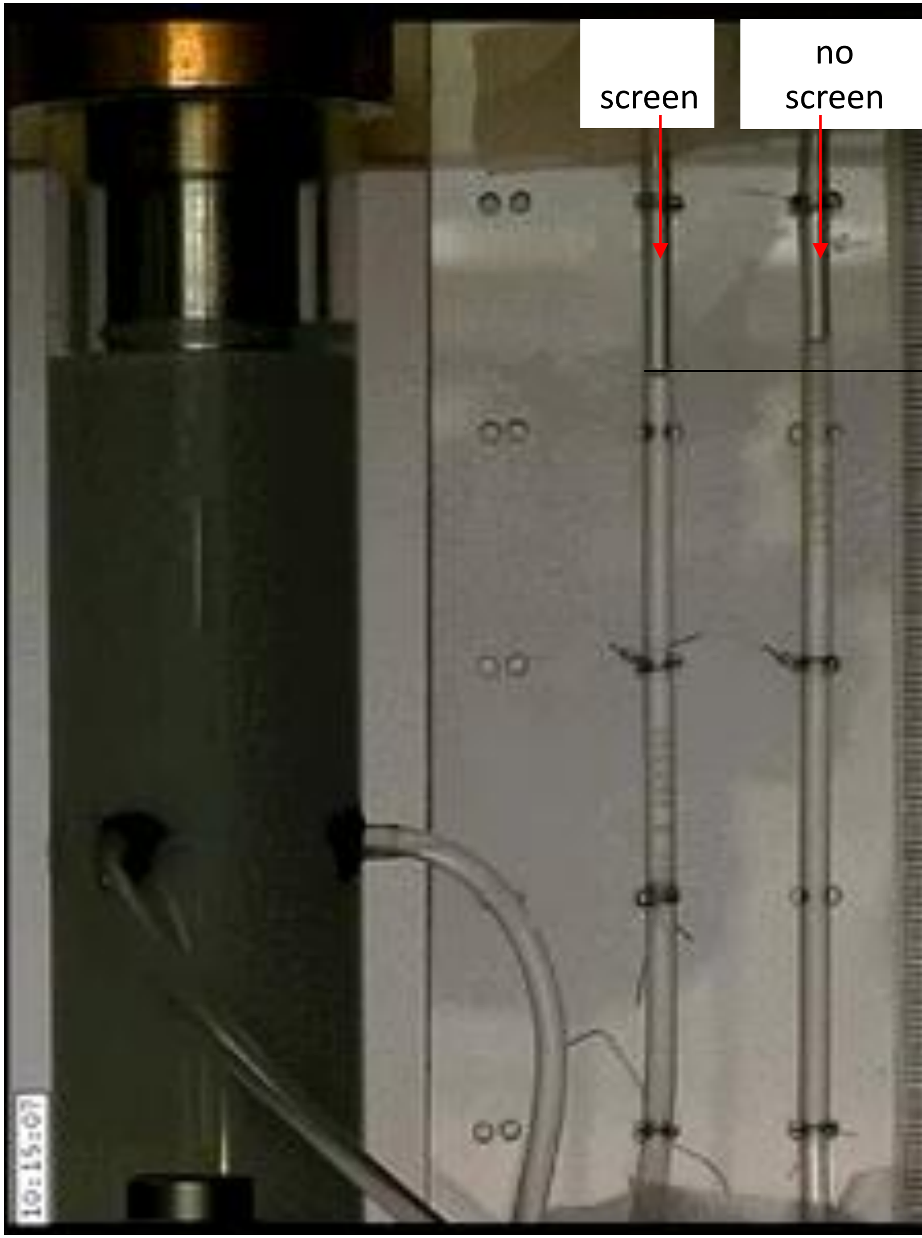
Osmosis - classical



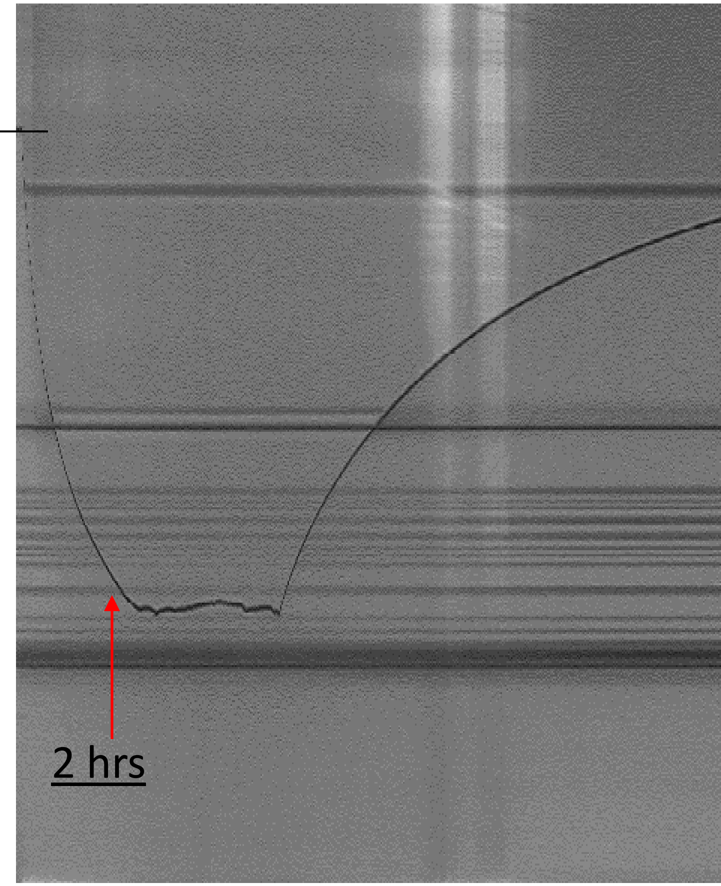
Osmosis - shear-induced?







Deboeuf *et al. Phys. Rev. Lett.* 2009



$\phi = 0.45$ $\dot{\gamma} = 20\ s^{-1}$

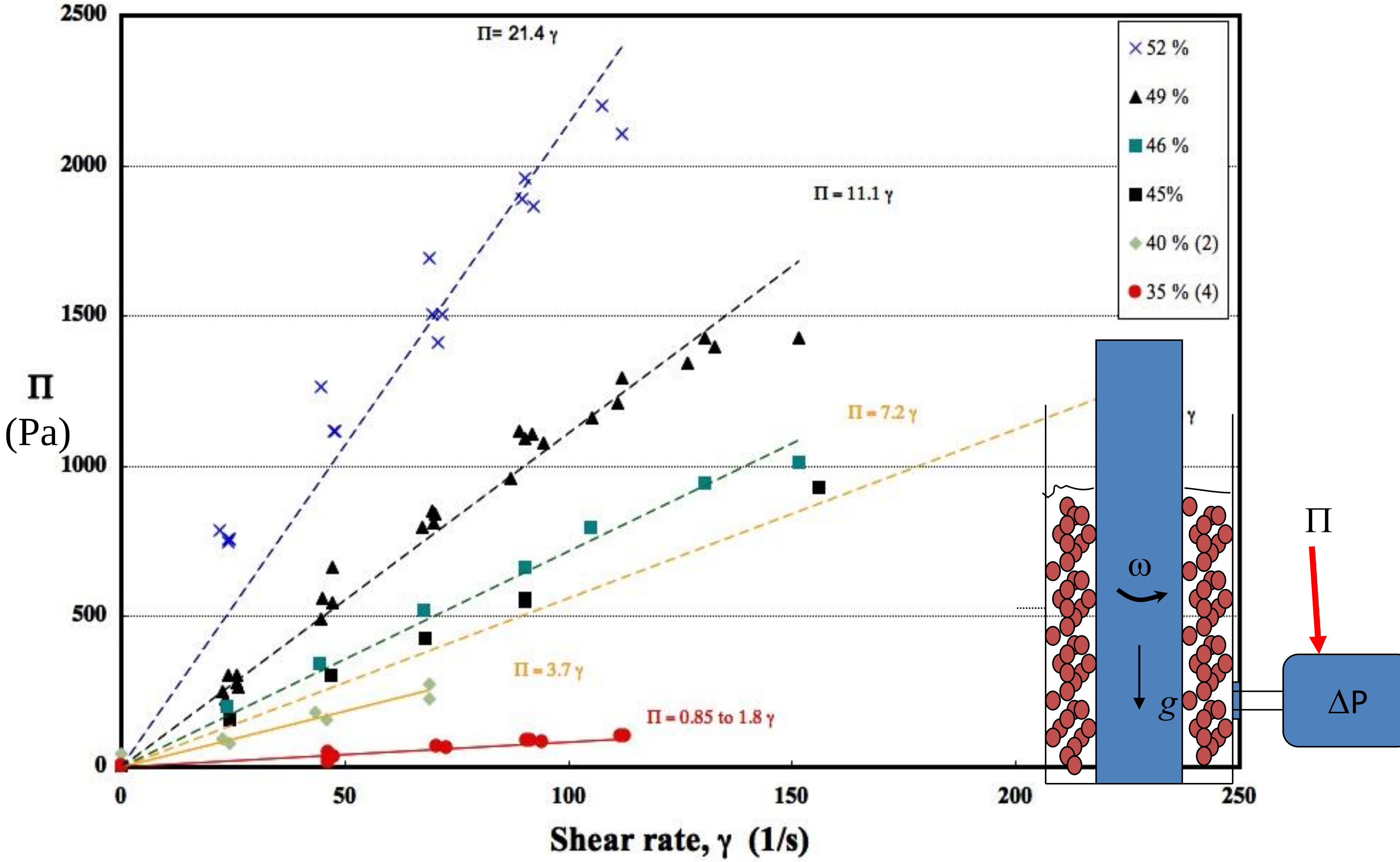
Neutrally - buoyant, $d = 80\ \mu m$

fluid viscosity : $\eta_0 = 2000$ cP

Quantitative rheology

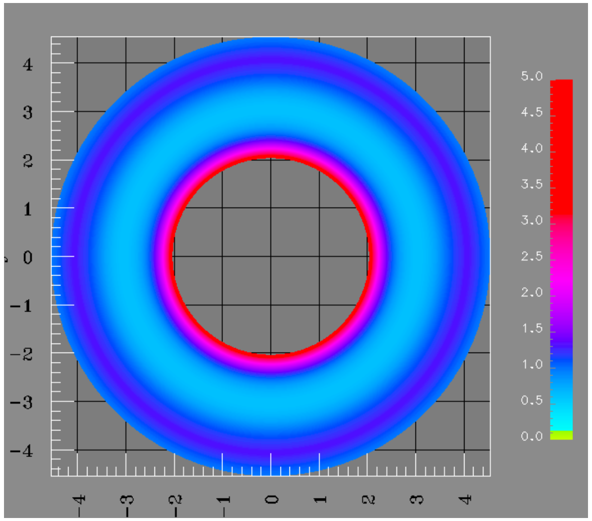
Deboeuf *et al. PRL* 2009

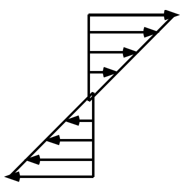
Details: Garland *et al. J Rheol.* 2013 (extension to $\phi = 0.2$)

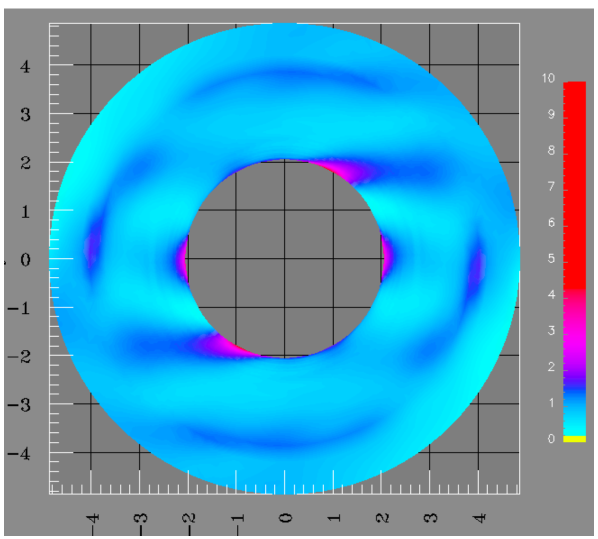


Π: the role of microstructure

Pe = 0
(eqm)

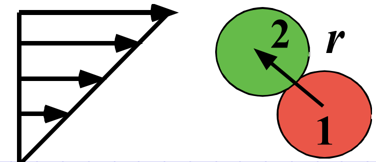


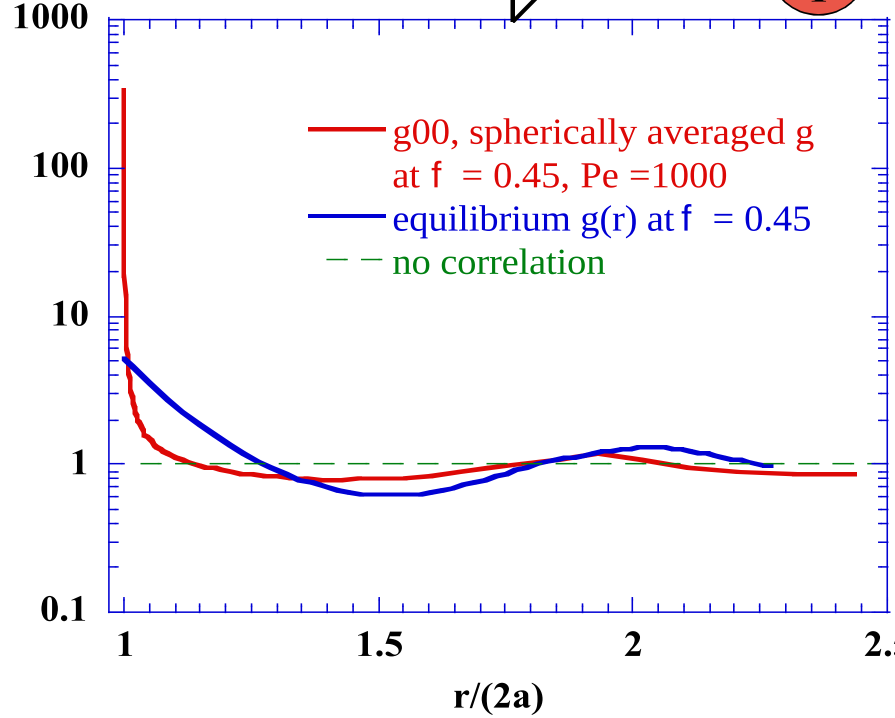




Pe = 10^3
(strong shear)

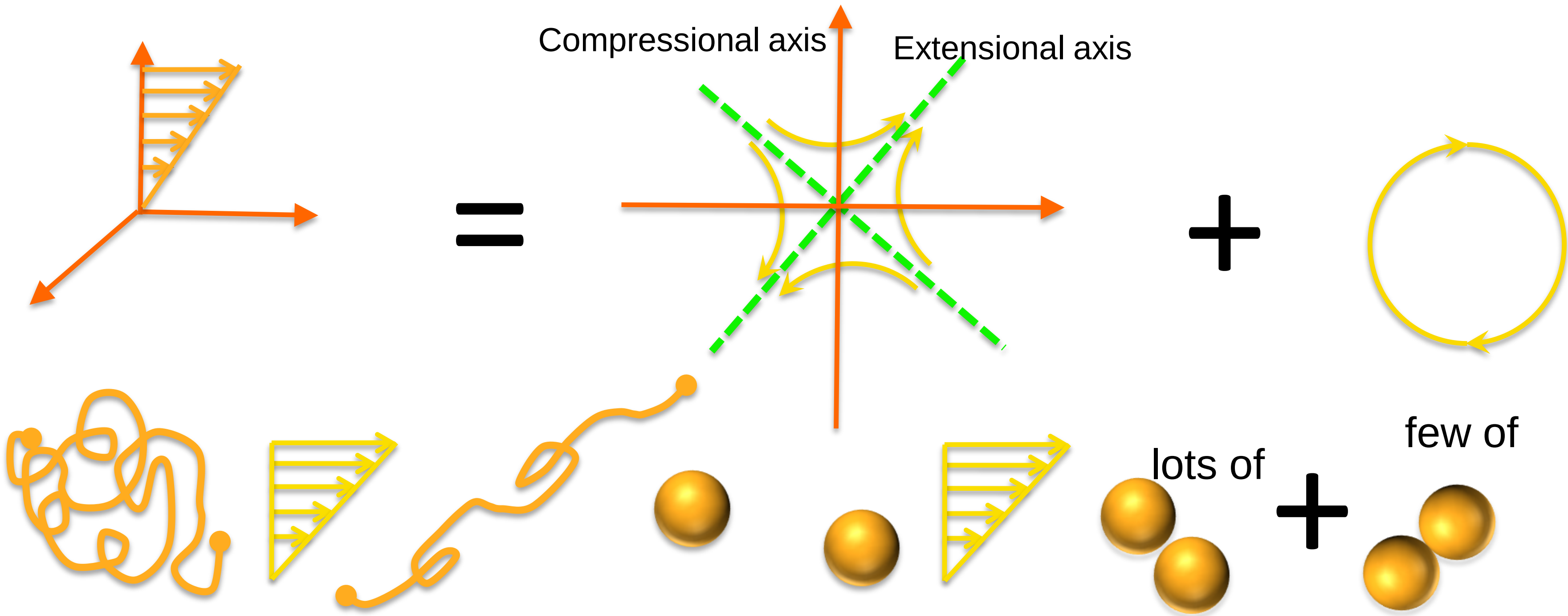
$g(\mathbf{r}) = P_{1/1}/n$



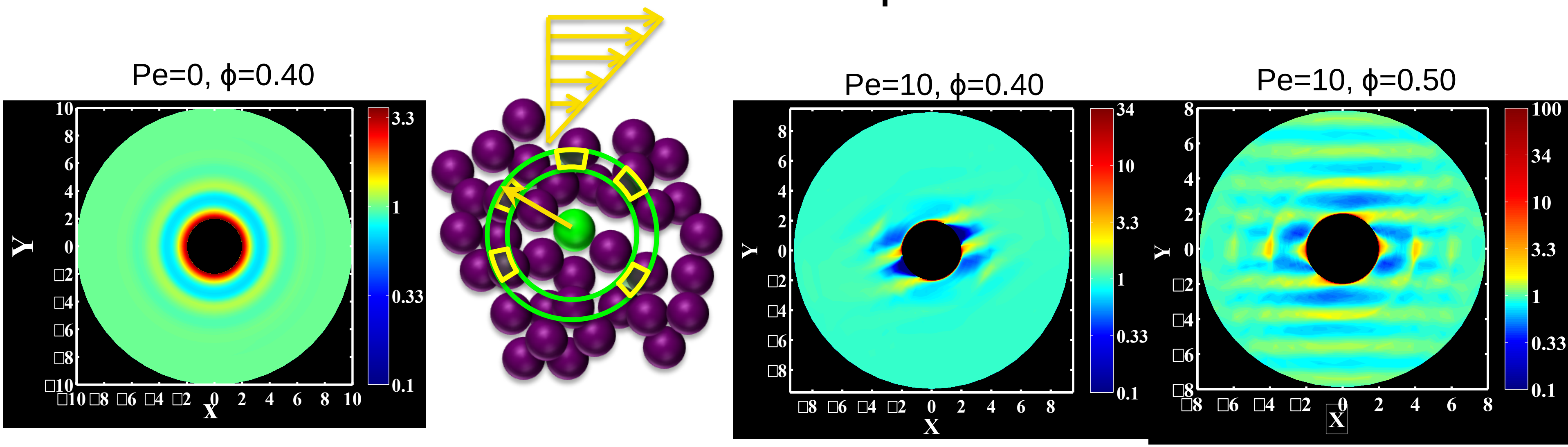


Configurational sampling from Stokesian Dynamics simulations.
[Morris & Katyal *Phys. Fluids* 2002
Kulkarni & Morris *J. Rheol.* 2009]

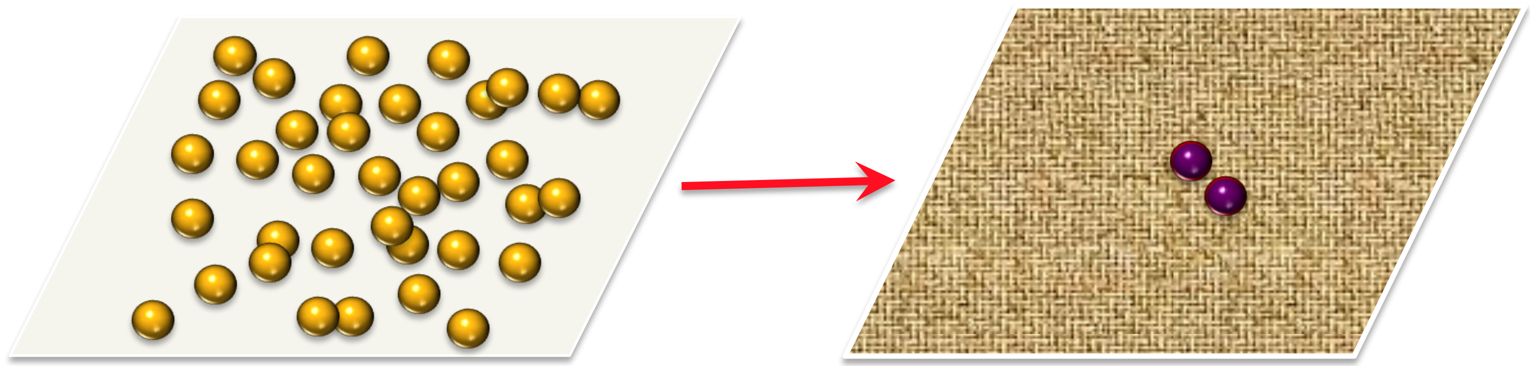
Flow-induced microstructure



Sheared Anisotropic Structure



N - Body → 2 - Body



$$\nabla \cdot \left[U g(r) - D \cdot \nabla g(r) \right] = 0$$

U(r) : Relative pair velocity

D(r) : Relative pair diffusivity

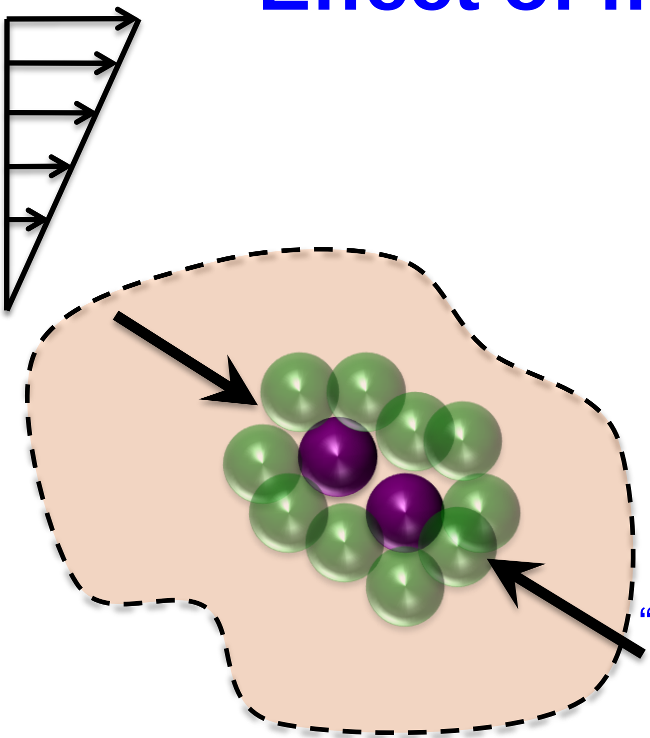
Boundary Conditions:

$j_r = 0$ at $r=2a$	Zero radial flux at contact
$g(r) = 1$ at $r/a >> 1$	Two particles become de-correlated

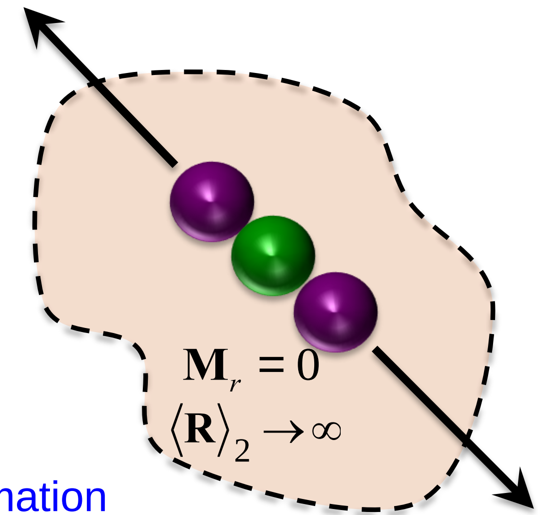
E. Nazockdast & J. F. Morris *JFM* 2012

E. Nazockdast & J. F. Morris *Soft Matter* 2012

Effect of many-body interactions

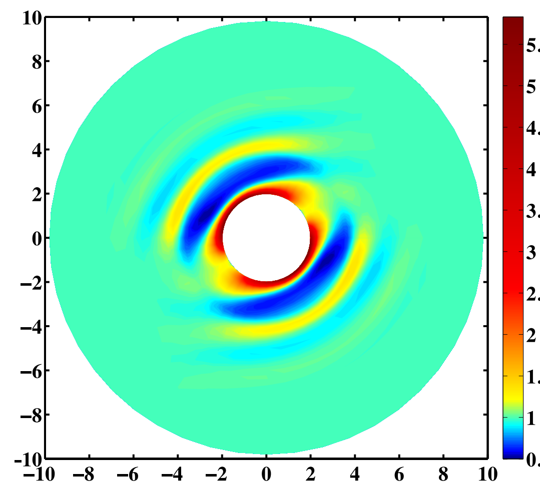


“Bath” and discrete particle information



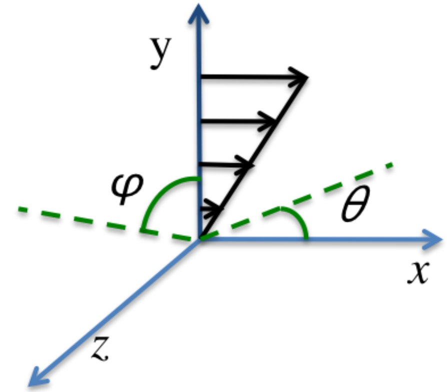
Generates correlation and
shear-induced diffusion

Propagation of correlation

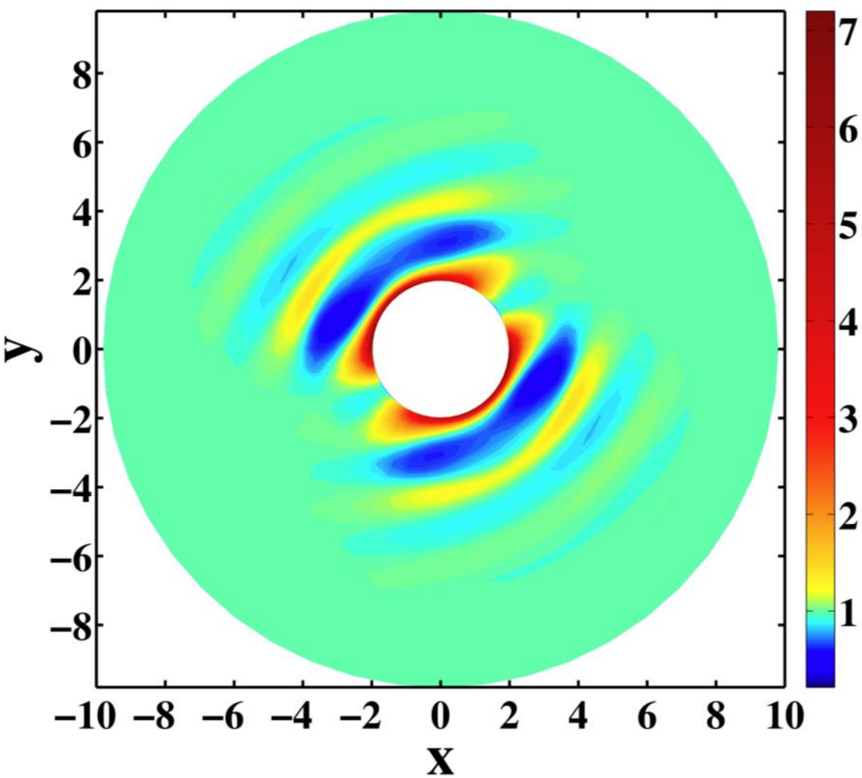


Details:
E. Nazockdast & J. F. Morris *JFM* 2012

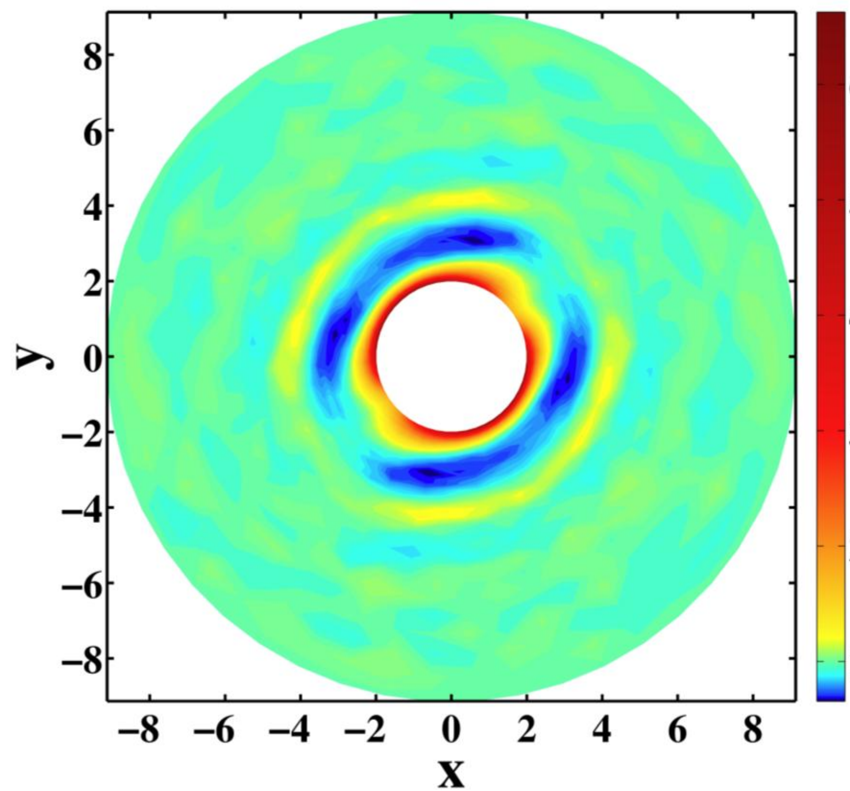
Microstructure



Theory, ϕ=0.40, Pe=1

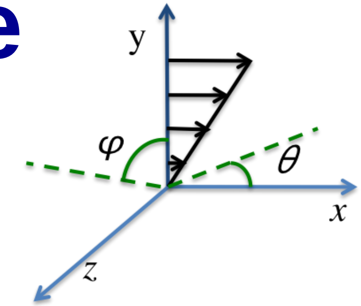


Simulation, ϕ=0.40, Pe=1

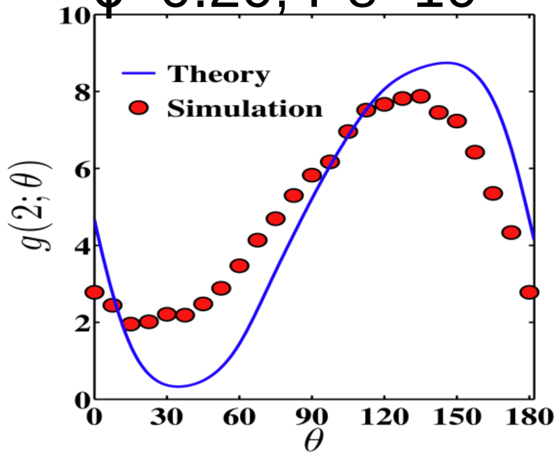


Simulation: Accelerated Stokesian Dynamics
Banchio & Brady *J Chem Phys* 2003

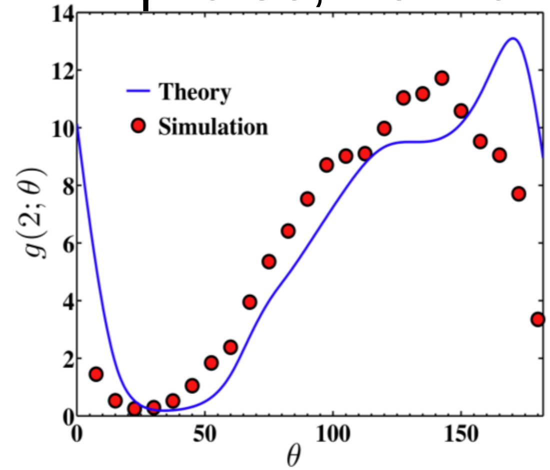
Microstructure – contact surface



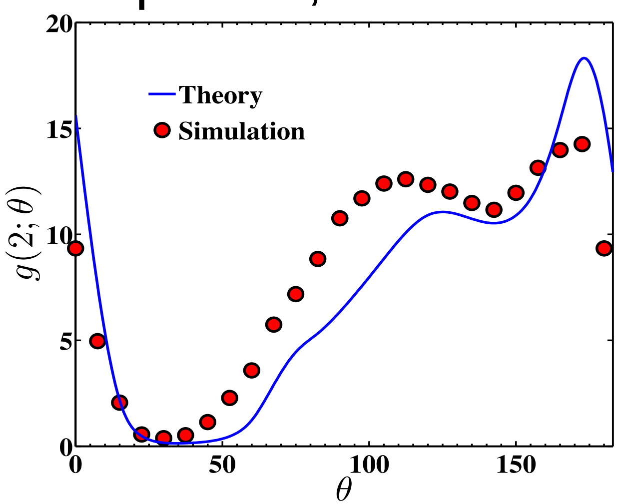
ϕ=0.20, Pe=10



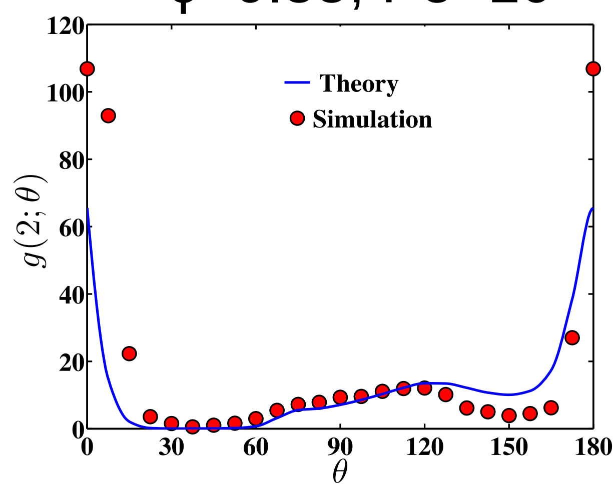
ϕ=0.30, Pe=10



ϕ=0.40, Pe=10

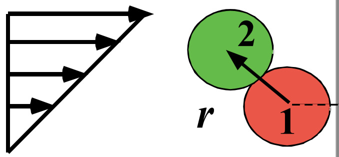


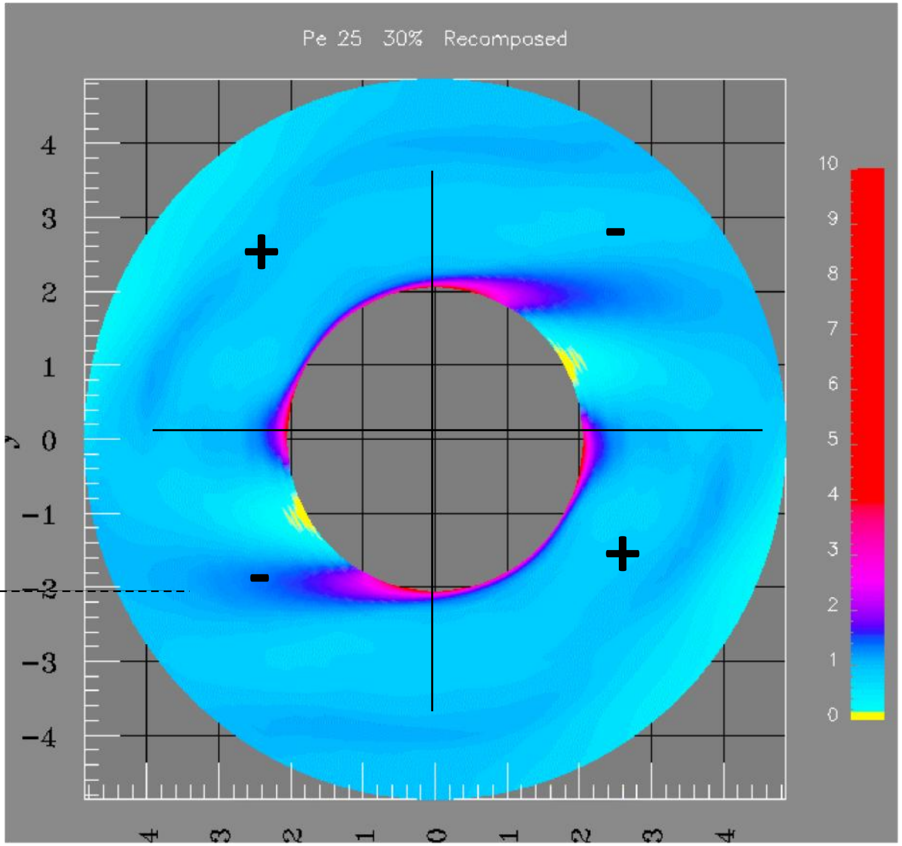
ϕ=0.55, Pe=10



Hydrodynamic theory (contact is not essential) of particle pressure, Π

Π sign map





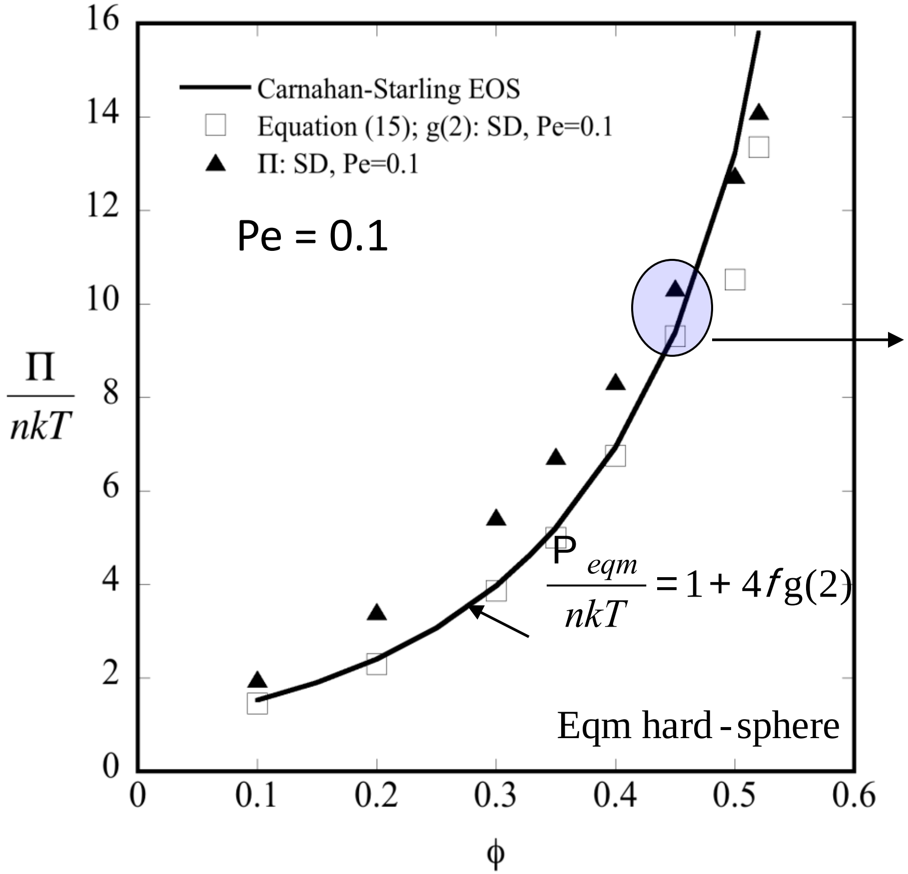
Jeffrey, Morris & Brady *Phys Fluids* 1993

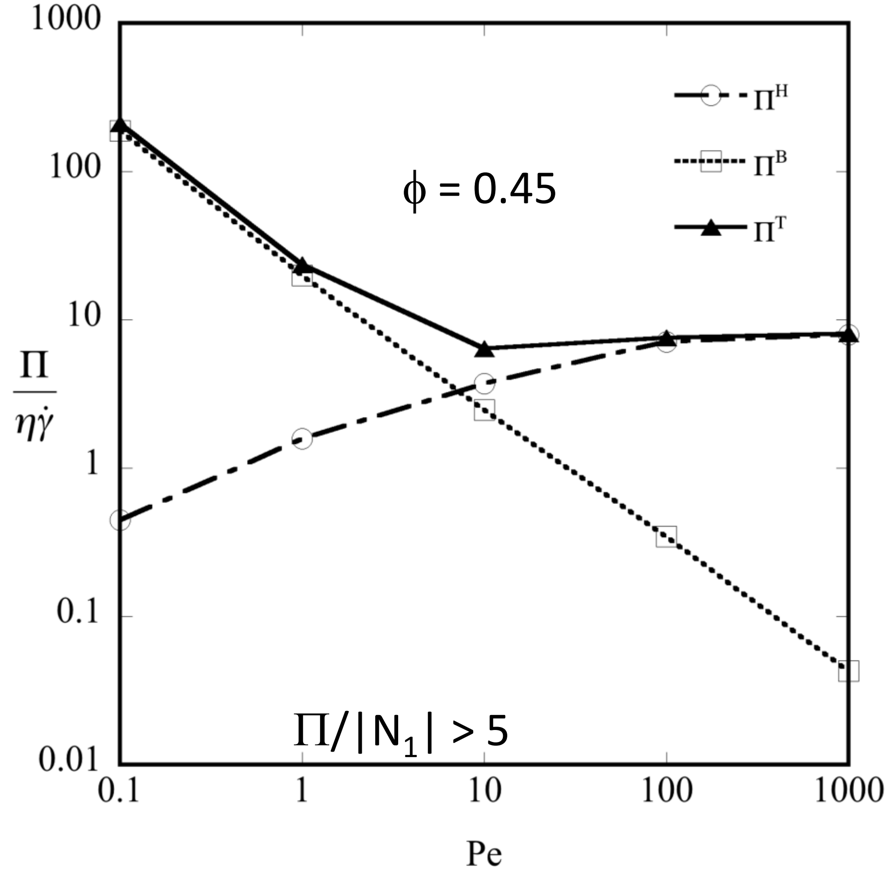
Morris & Katyal *Phys Fluids* 2002

Melrose & Ball *J. Rheol* 2004

Simulation (Stokesian Dynamics) for varying Pe: *osmotic pressure* to "*viscous dilation*"

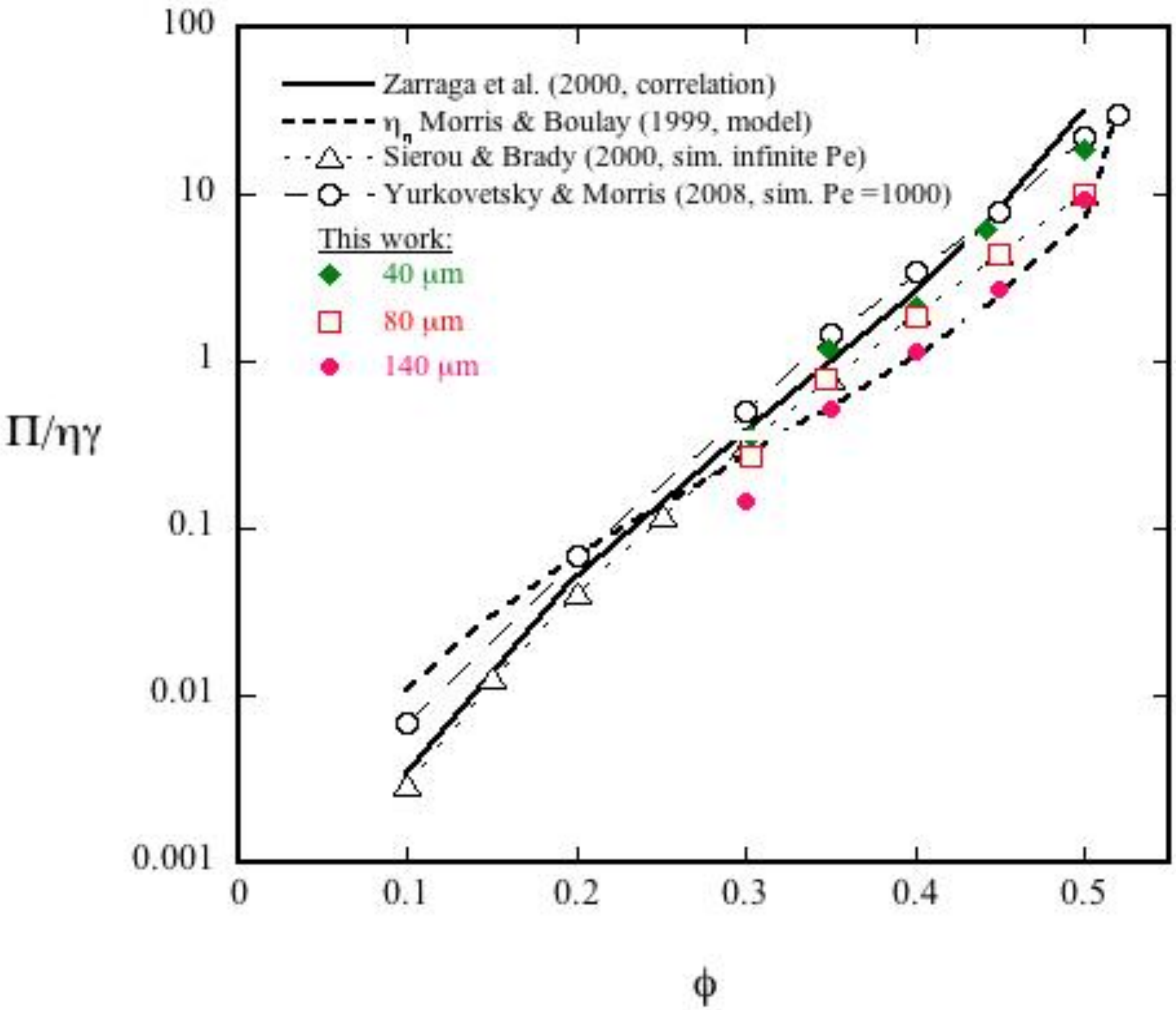
Bagnold *Proc. Roy. Soc.* 1954





Yurkovetsky & Morris *J Rheol.* 2008

Simulated and experimental Π



Size dependence:
due to capillary force limitation:
Garland *et al. J. Rheol* 2013

$$\Pi_{max} \approx \frac{\sigma}{a}, \quad \sigma \textbf{ : surface tension}$$

Yurkovetsky & Morris *J. Rheol.* 2008

Deboeuf *et al. Phys. Rev. Lett.* 2009

Contact is not essential for particle pressure –
but **it happens

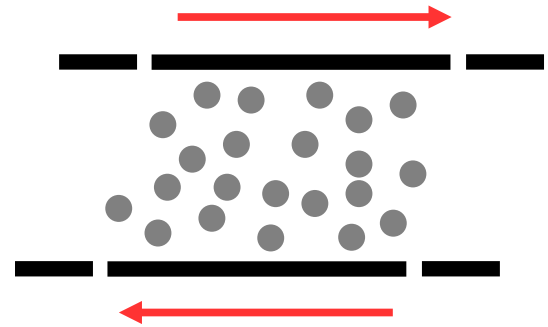
Discontinuous Shear Thickening in frictional particle suspensions

with Ryohei Seto, Romain Mari, Mort Denn

Levich Institute, City College of New York

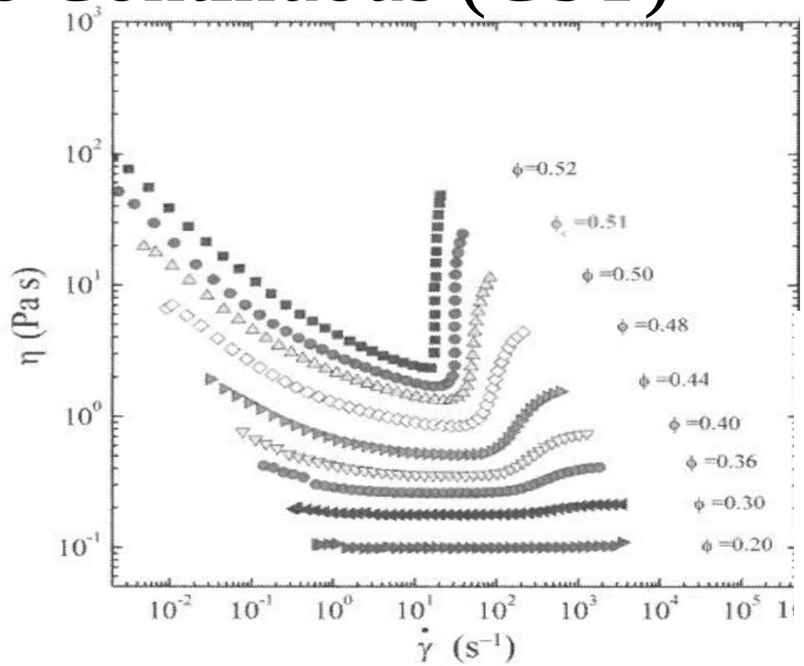
R. Seto, R. Mari, J. F. Morris & M.M. Denn *PRL* Nov. 2013 (available at ArXiv now)

Shear Thickening: Discontinuous (DST) vs Continuous (CST)

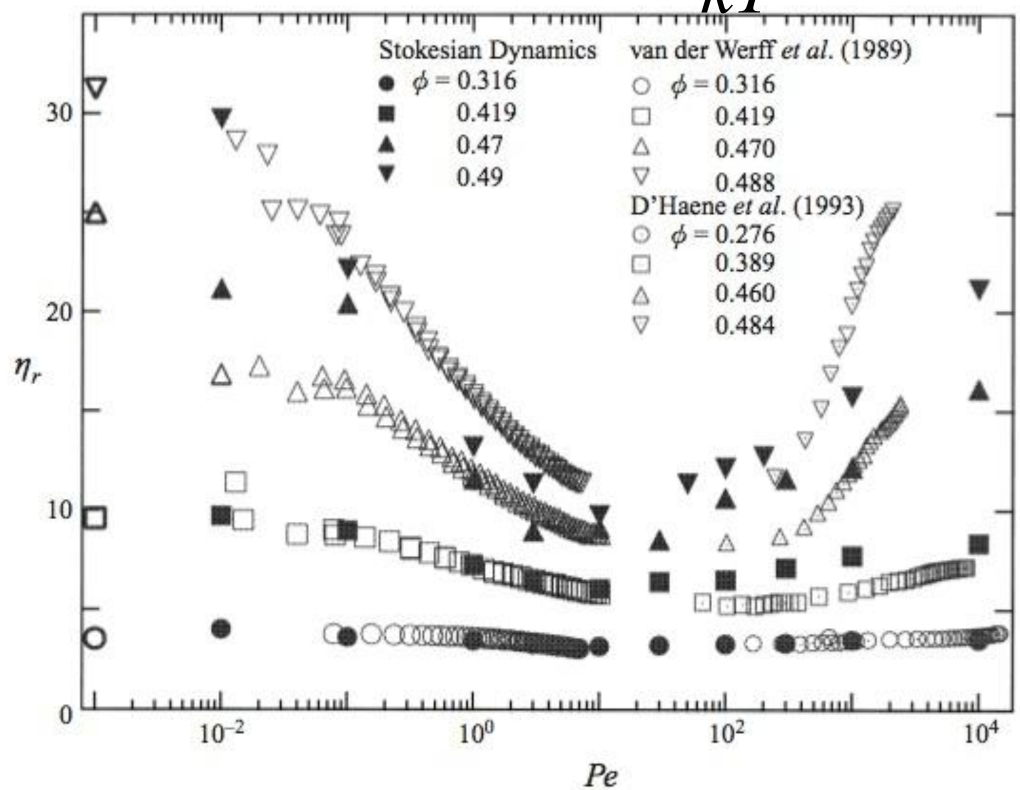


$$\eta(\dot{\gamma}, \phi)$$

$$\eta\left(Pe \sim \frac{\eta_0 \dot{\gamma} a^3}{kT}, \phi\right)$$



R. Egres, U Delaware



Foss & Brady *JFM* 2000

Simulation of friction + hydrodynamics

Stokes hydrodynamics

Bidisperse (radius 1 and 1.4)

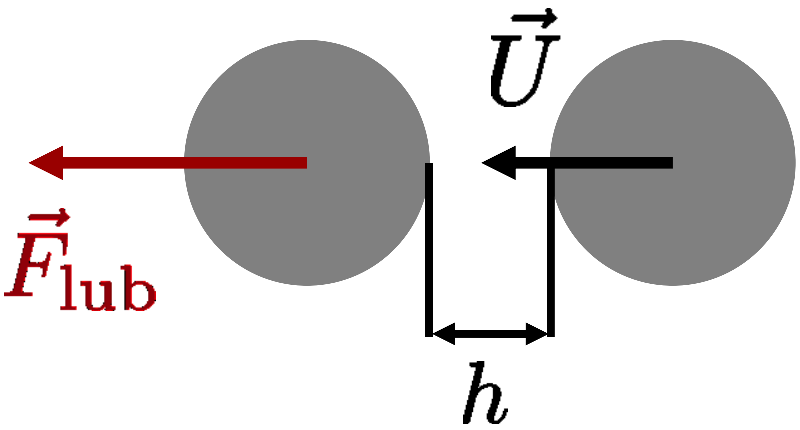
Short-range HI: lubrication

Electrostatic forces

Frictional hard sphere contacts

Roughly speaking--
our model = Stokesian Dyn. - long-range HI + contacts

Contacts?

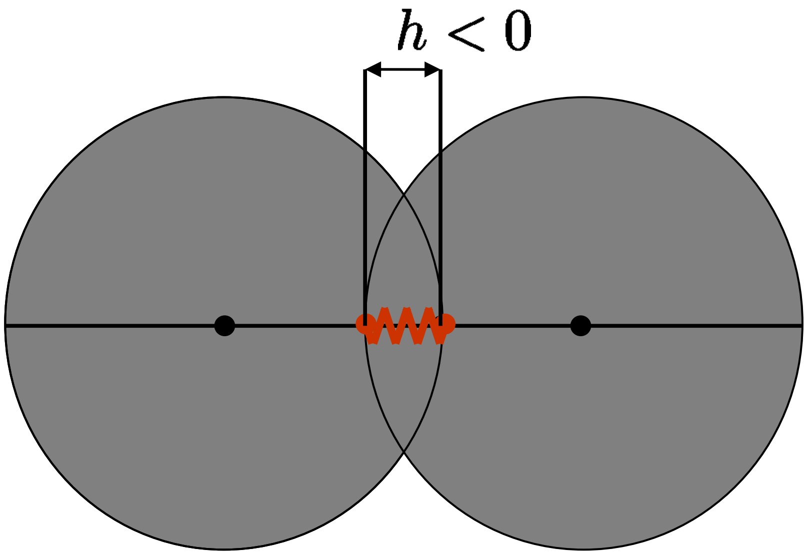


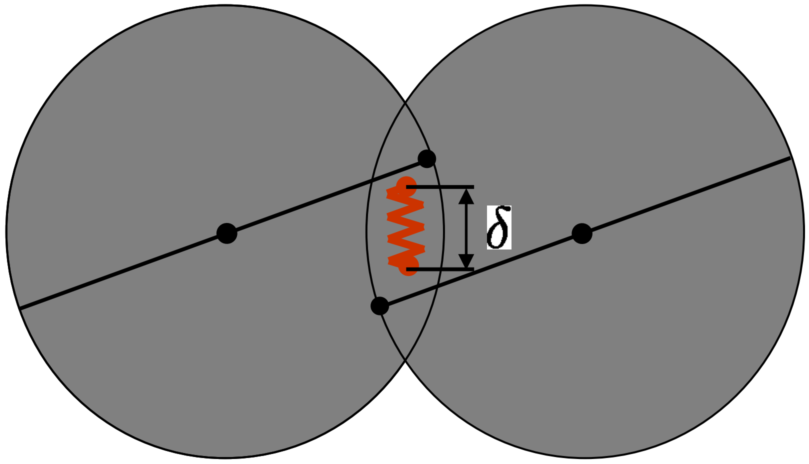
$$\vec{F}_{\mathrm{lub}} = \frac{C}{h+\delta}(\vec{U}.\vec{n})\vec{n}$$

$$\delta = 10^{-3} \times \mathrm{radius}$$

Contacts expected at this scale:
nm physics for micron-scale particles

Contact model





normal:

$$\vec{F}_{\mathrm{C}}^{\mathrm{norm}} = k_{\mathrm{n}} h \vec{n}$$

tangential:

$$\vec{F}_{\mathrm{C}}^{\mathrm{tan}} = k_{\mathrm{t}} \delta \vec{t}$$

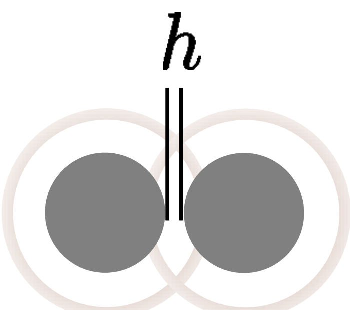
$$|\vec{F}_{\mathrm{C}}^{\mathrm{tan}}| \leq \mu |\vec{F}_{\mathrm{C}}^{\mathrm{norm}}|$$

Electrostatic interaction: stabilization

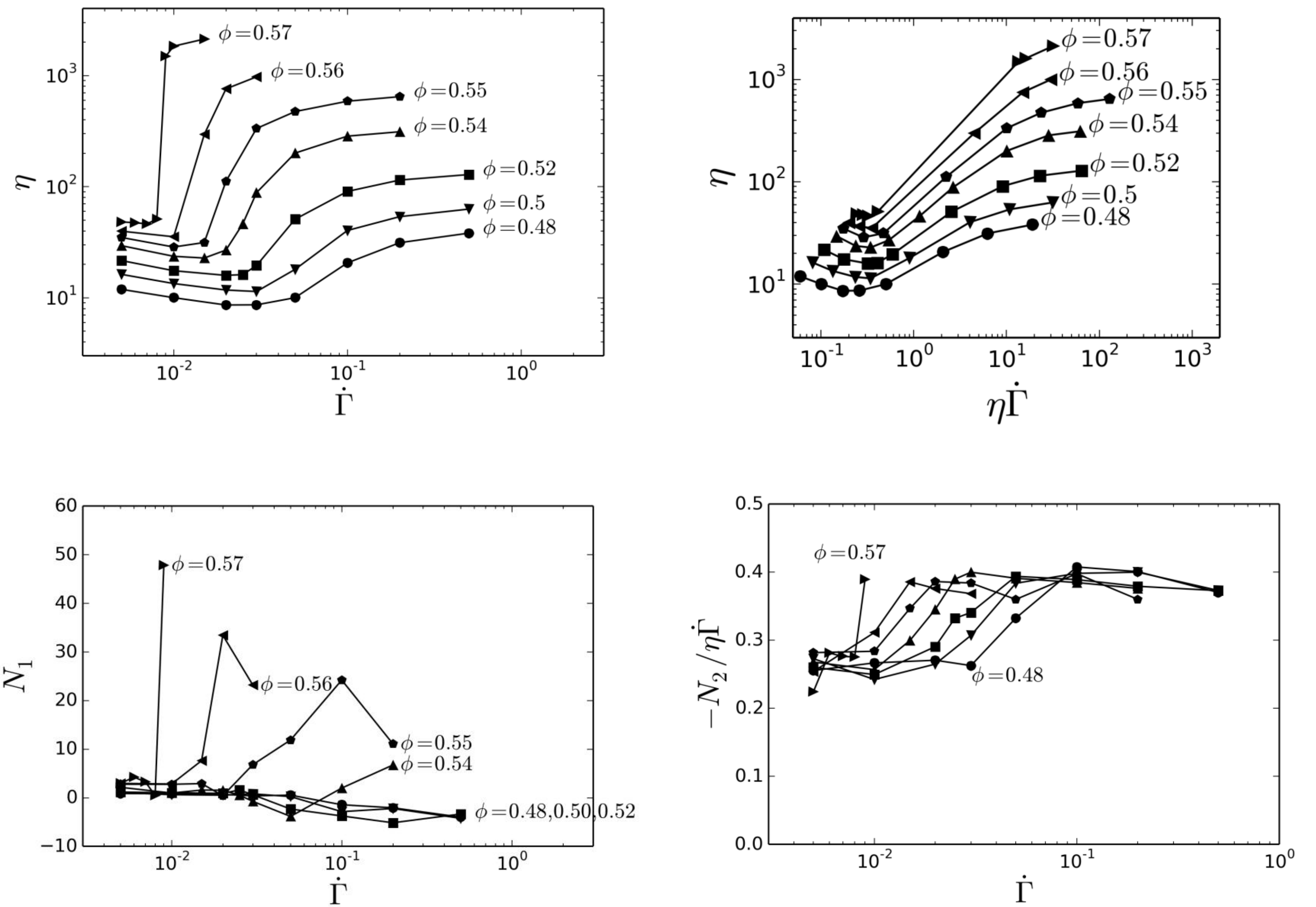
- Stokes hydrodynamics + hard spheres:
- no shear rate dependence

- electrostatic double layer repulsion (colloidal particle model):

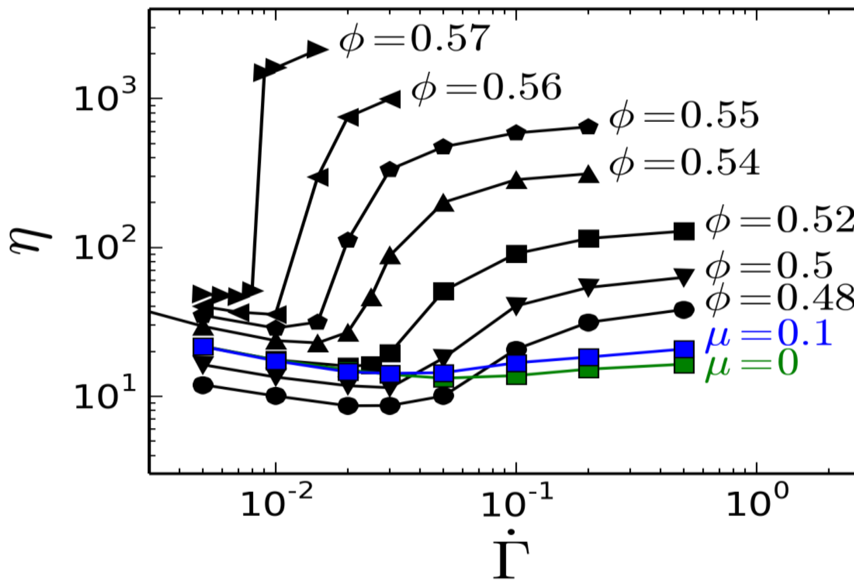
$$F_{\mathrm{el}} = A_{\mathrm{D}} e^{-h/\kappa}$$

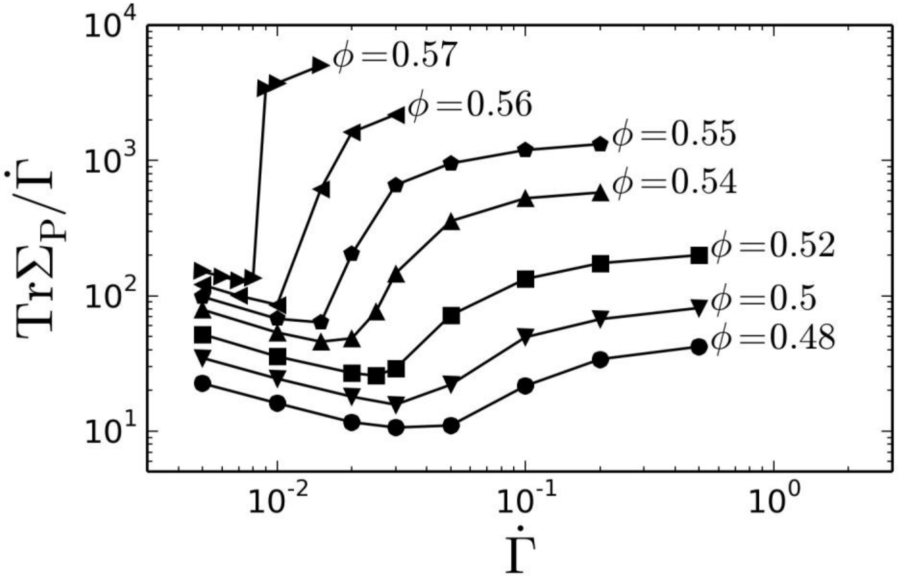


$$\dot{\Gamma} = \frac{6\pi\eta_0 a^2 \dot{\gamma}}{A_{\mathrm{D}}}$$

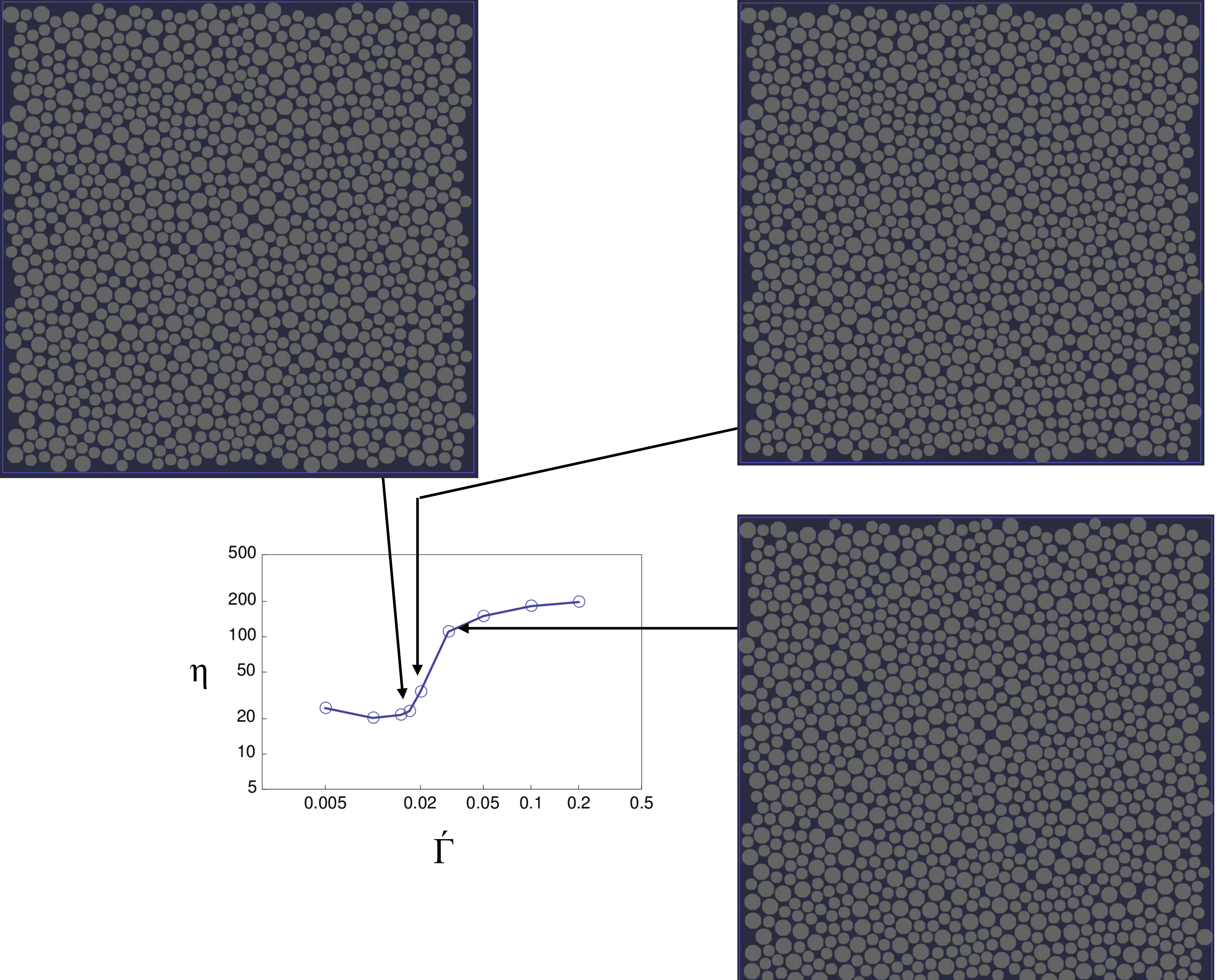


φ=0.57
φ=0.56
φ=0.55
φ=0.54
φ=0.52
φ=0.5
φ=0.48
η
Γ̇
ηΓ̇
N1
φ=0.48,0.50,0.52
−N2/ηΓ̇





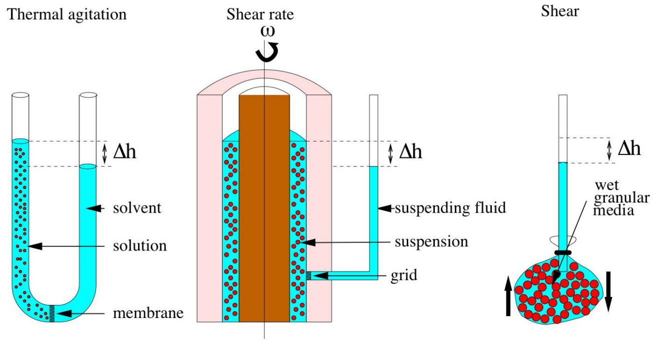
$$\Pi/\dot{\Gamma} = -Tr\Sigma_p/3$$



500
200
100
50
20
10
5
η
0.005
0.02
0.05
0.1
0.2
0.5
Γ́

SUMMARY

- Two phase mixtures
  - stress active objects (e.g. particles, polymers, …) migrate
  - driving force can be related to normal stresses
  - two phases are in very different (normal) stress states



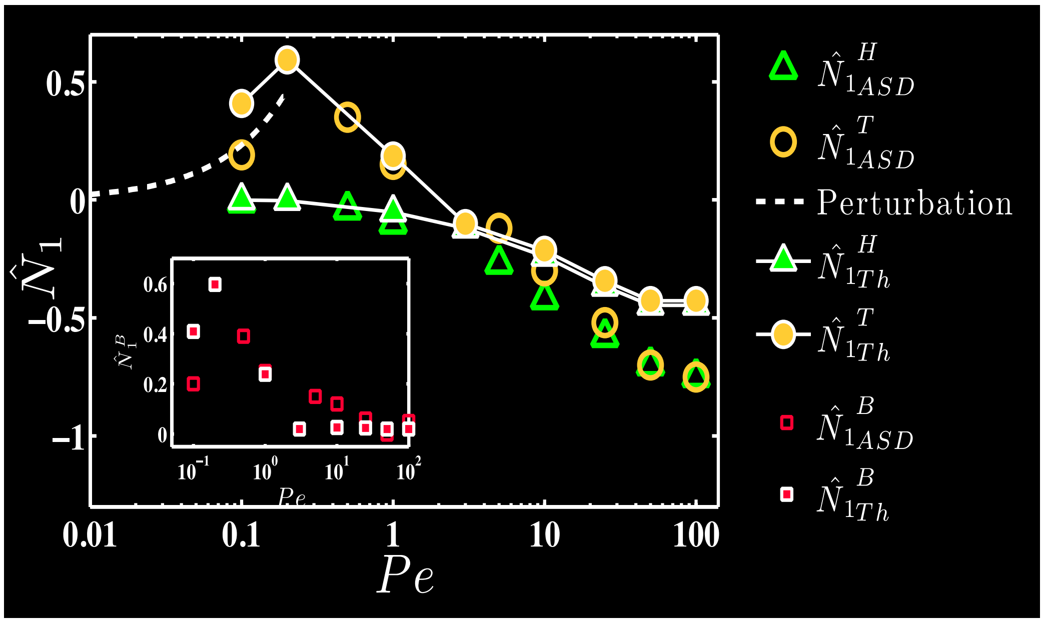
- Normal stress plays a key role
  - ***Particle pressure***
    - Not an analog of osmotic pressure, but a generalization
    - Connection to granular pore pressure established
    - Feedback to fluid mechanics (through ϕ)
  - ***Normal stress differences***
    - velocity effects (secondary flows)
    - Zrehen & Ramachandran *PRL* 2013

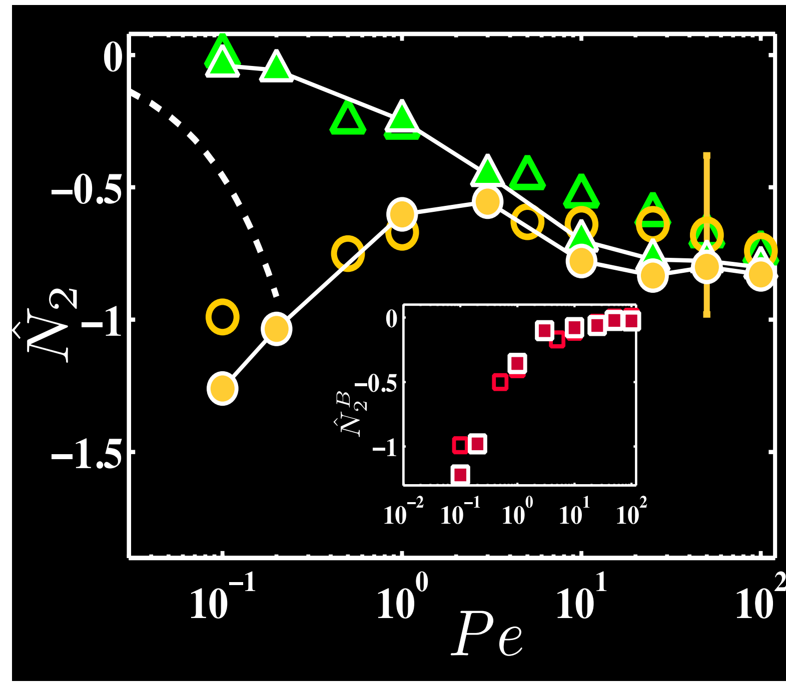
- ***Role of contact forces with hydrodynamics***
  - Simulations show phenomena seen experimentally
  - Next question: what about large-scale flows, with gradients in Π?

CHALLENGES

- ***Complex geometries***: rheology in general flows
  - Proposed frame-invariant rheology (Miller, Singh & Morris *CES* 2009)
  - More experiments !!
  - Need to explore algorithms
    - Micro-macro coupling (with S. Marenne)

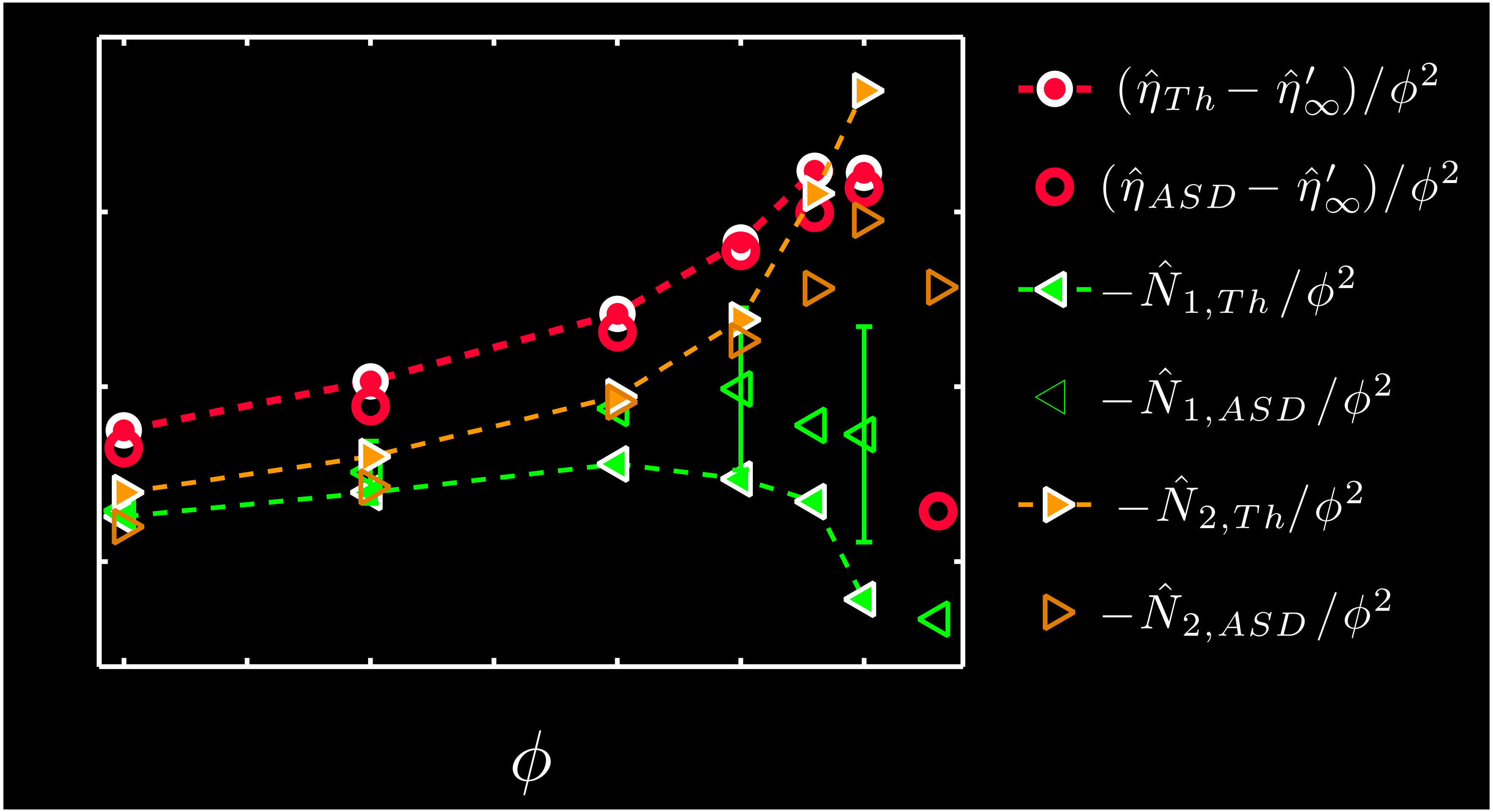
Normal stress differences, ϕ=0.40





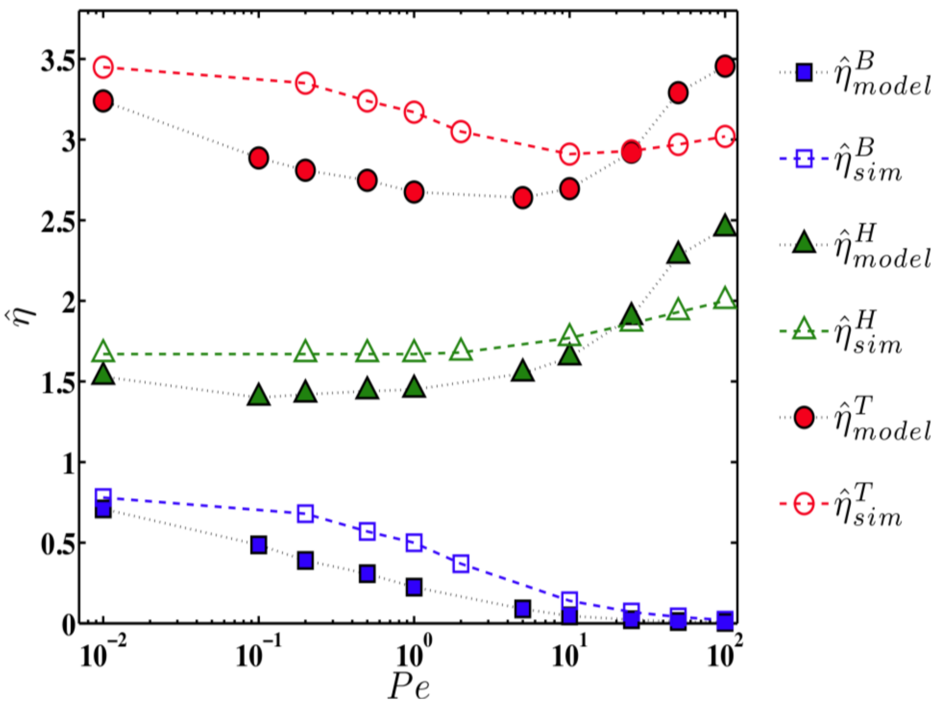
Normalized by η γ

Non-Newtonian Rheology at Pe = 270

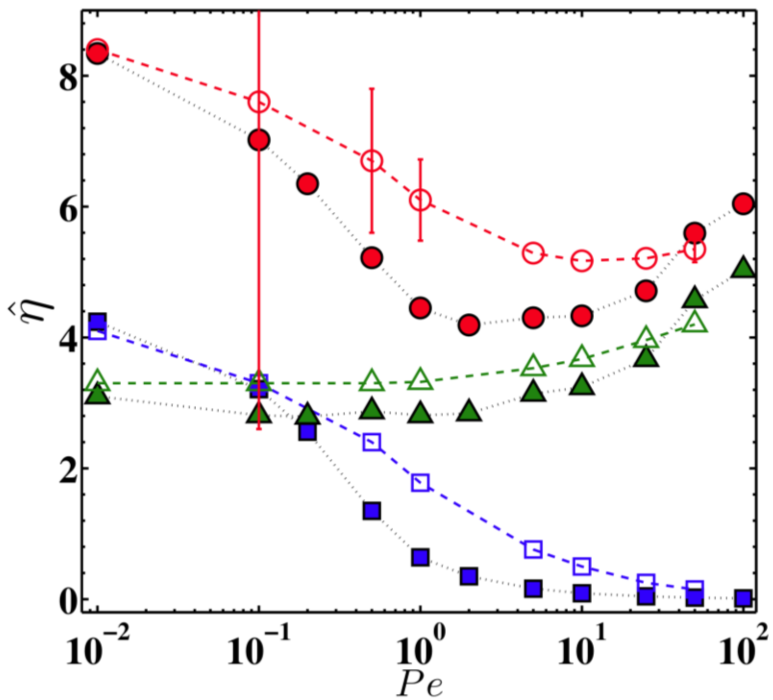


Shear Viscosity

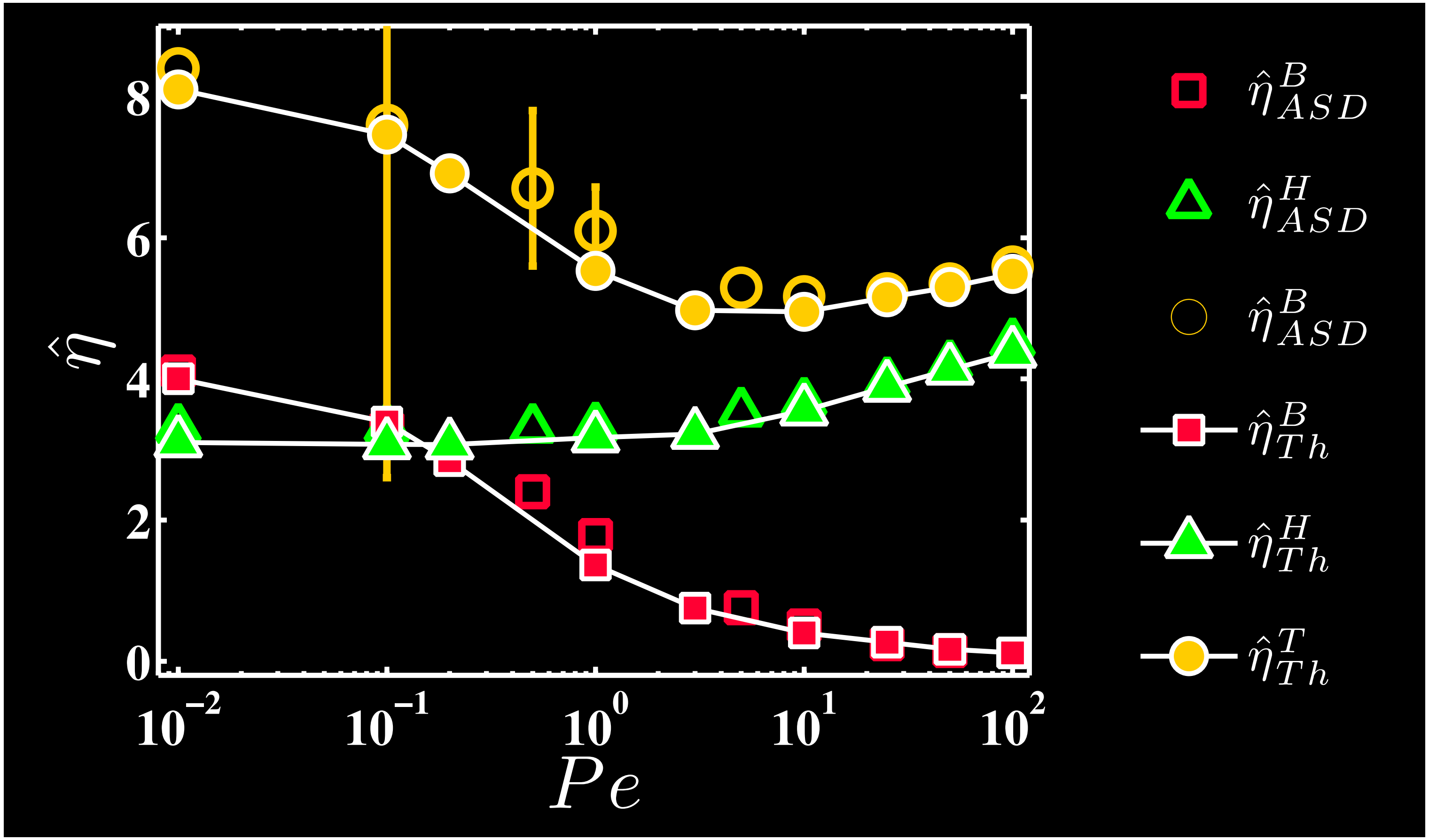
ϕ=0.30



ϕ=0.40

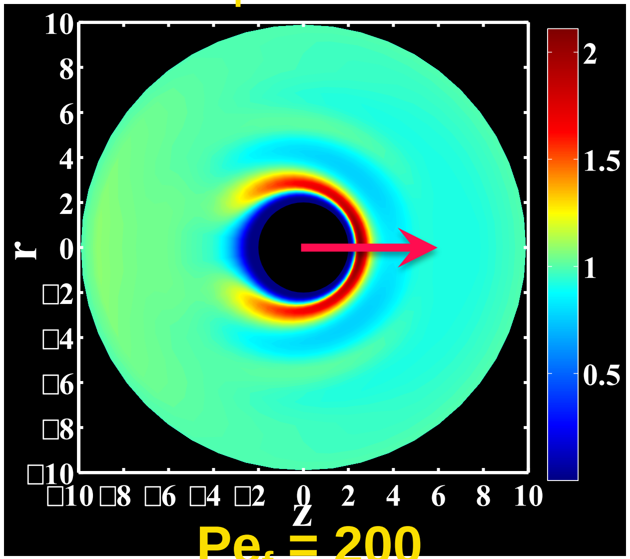


Shear Viscosity, ϕ=0.40

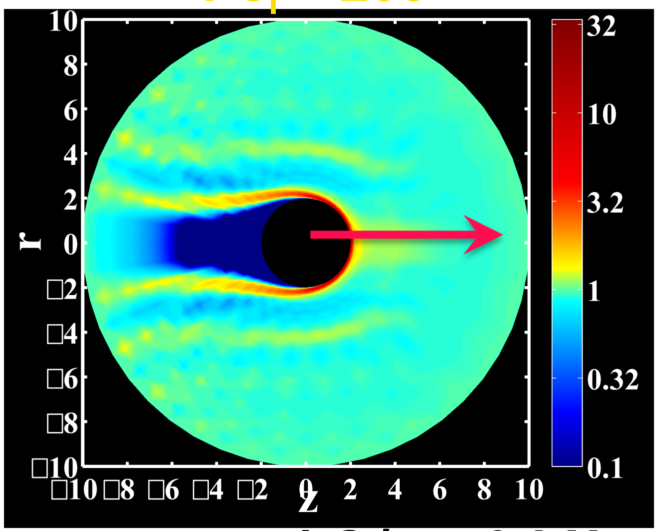


Soft Colloids, *Comparison with experiments*

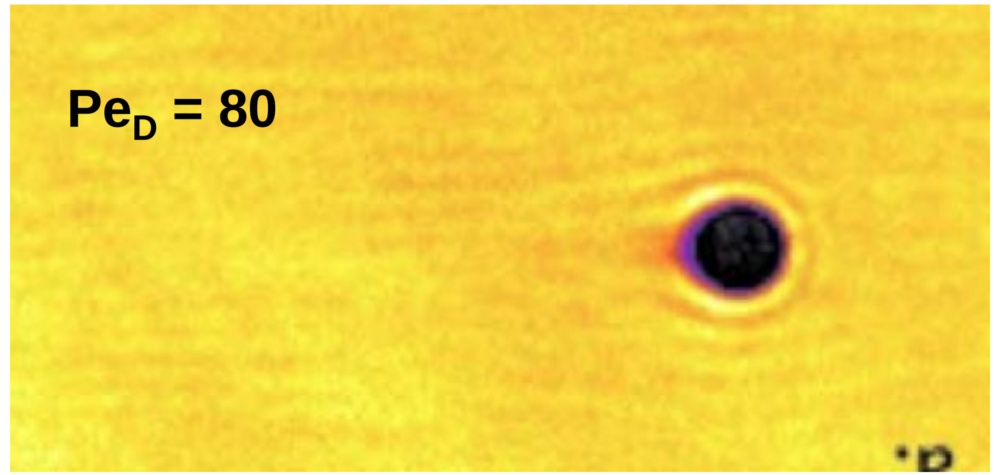
$Pe_f = 25$

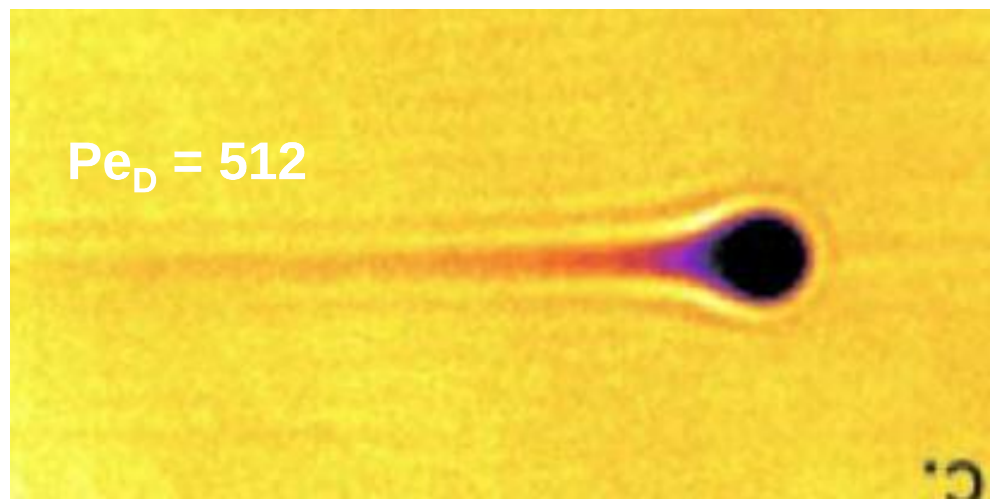


$Pe_f = 200$



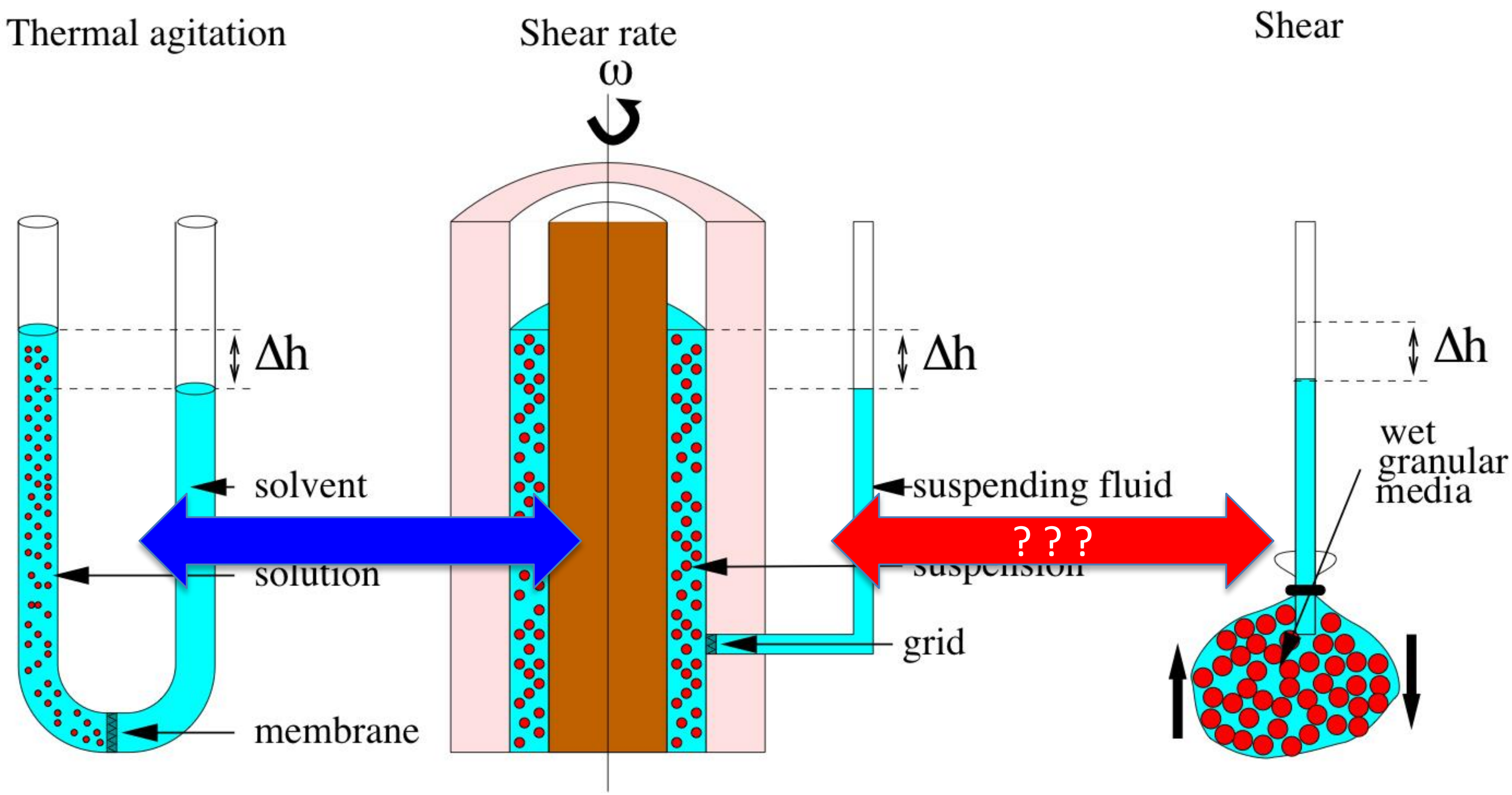
$2.67Pe_f \approx Pe_D$





I. Sriram & A Meyer & E. M. Furst (2010) *Phys. of Fluids* **22**, 062003

Osmotic pressure to athermal shear-induced particle pressure



Dense suspension flow through a contraction

Noncolloidal suspension :

380-500 μm PS spheres UCON 50-HB-660

Density matched $\qquad \eta_f = 300\, cP$ at $23^{o}C$

➔ **<u>Very low Reynolds number</u>**

Contraction ratio : $\dfrac{w}{W} = 1/6$ (also 1/3)

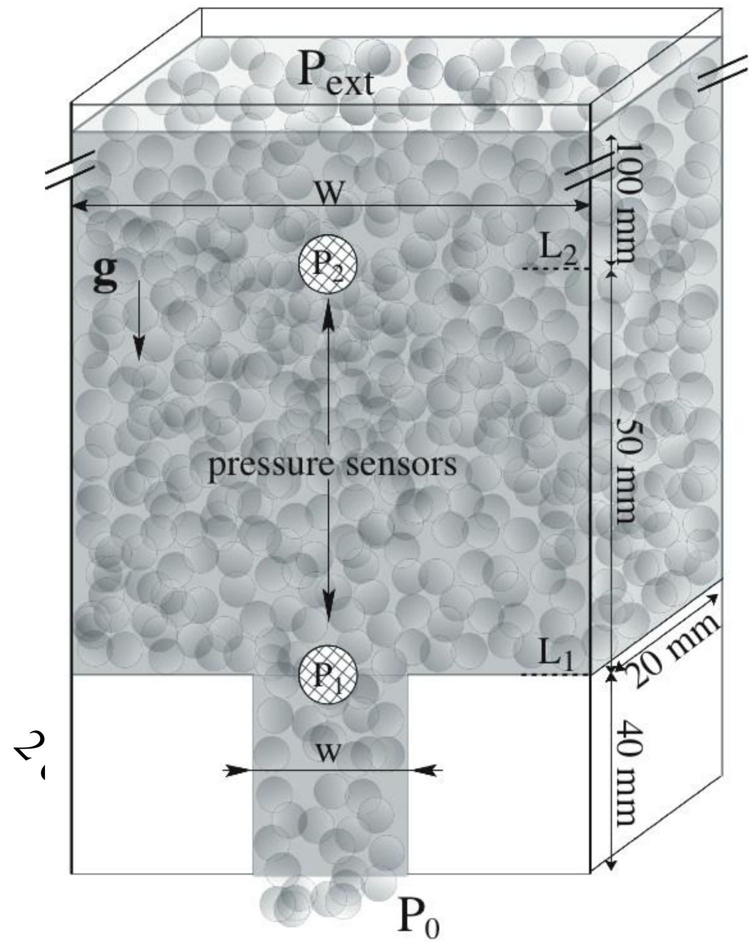
$w/d \sim 10$ (also 20)

Experiments:

Flow visualization at the wall

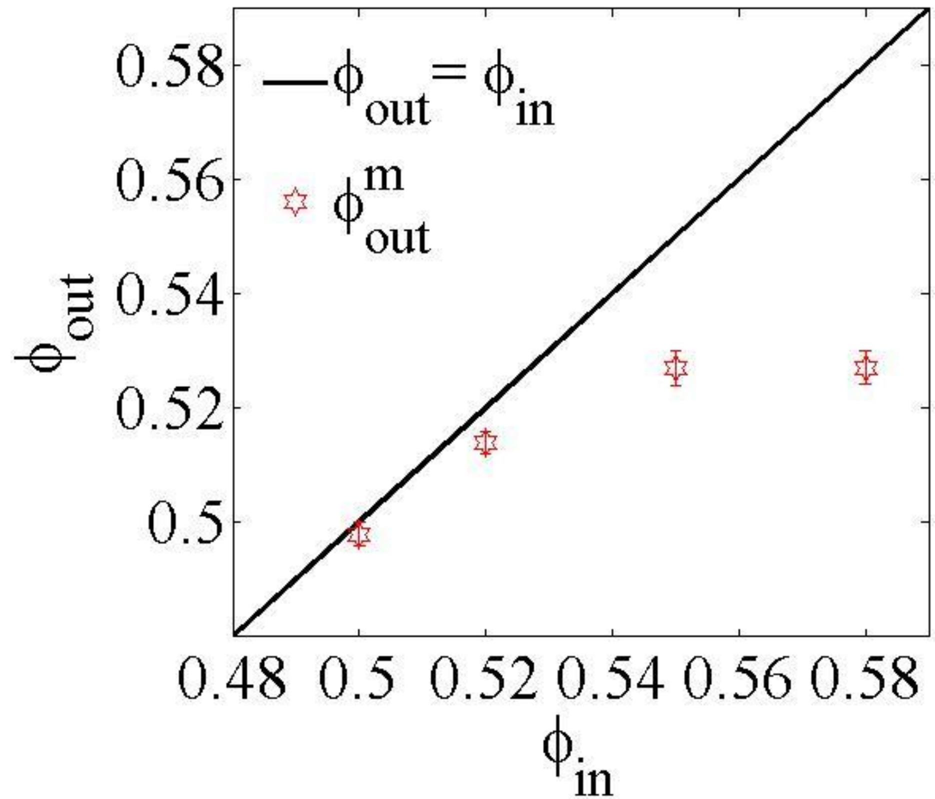
Liquid pressure measured

Impose ϕ_{in}; measure effluent ϕ_{out}



Self-filtration*

$$f_{out}^{m} < f_{in}$$



$(f_{in}$ - $f_{out}^{m})$- as f_{in} -

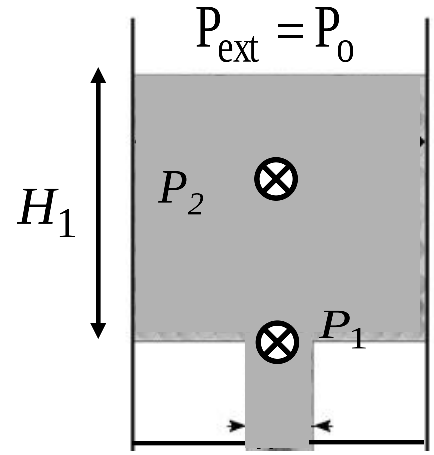
Saturation :

f_{in} ³ 0.55, f_{out}^{m} » 0.527 ± 0.003

*Haw *Phys. Rev. Lett*. (2004)

Viscous liquid flow (*sans* particles)

liquid X ($\eta_s = 36.5\ Pa.s$), liquid Y ($\eta_s = 7\ Pa.s$)



- Stokes flow

$$P_1 = \rho\, g\, H_1 - \Delta P_1$$

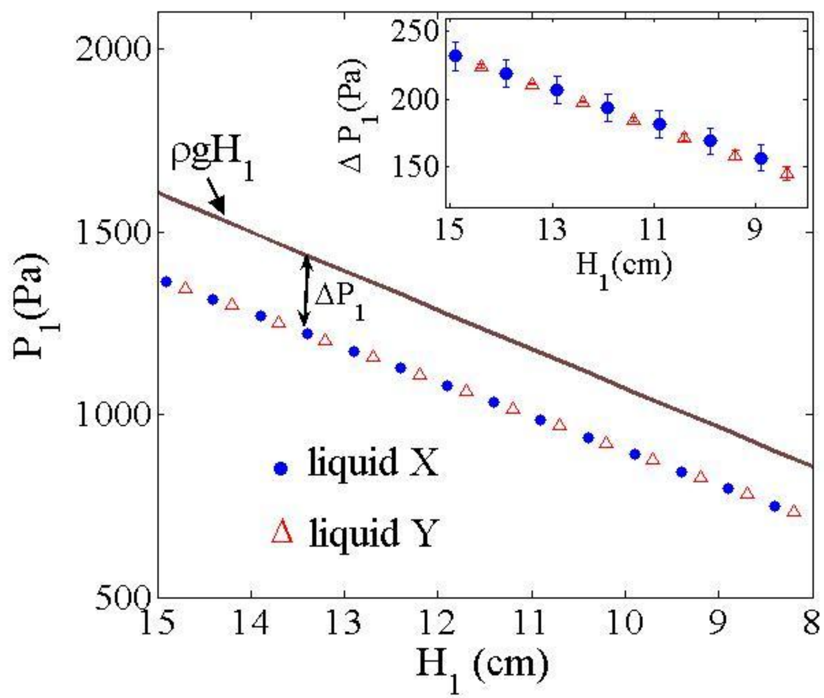
ΔP_1 is independent of the material viscosity

$$\Delta P_1 \propto \eta_s \dot{\gamma} \propto \rho\, g\, H_1$$

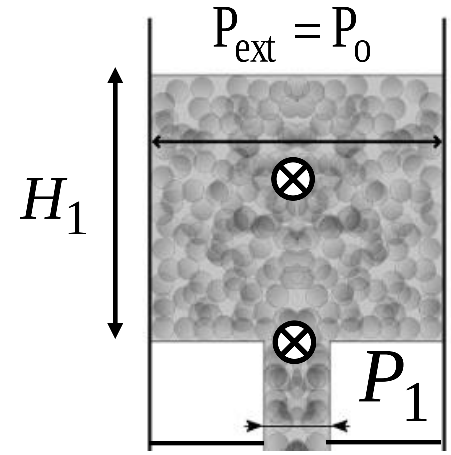
$$\mathrm{D}P_1 = 0.16\, r\, g H_1$$

Likewise:

$$\mathrm{D}P_2 = 0.030\, r\, g H_1$$



Suspension flow

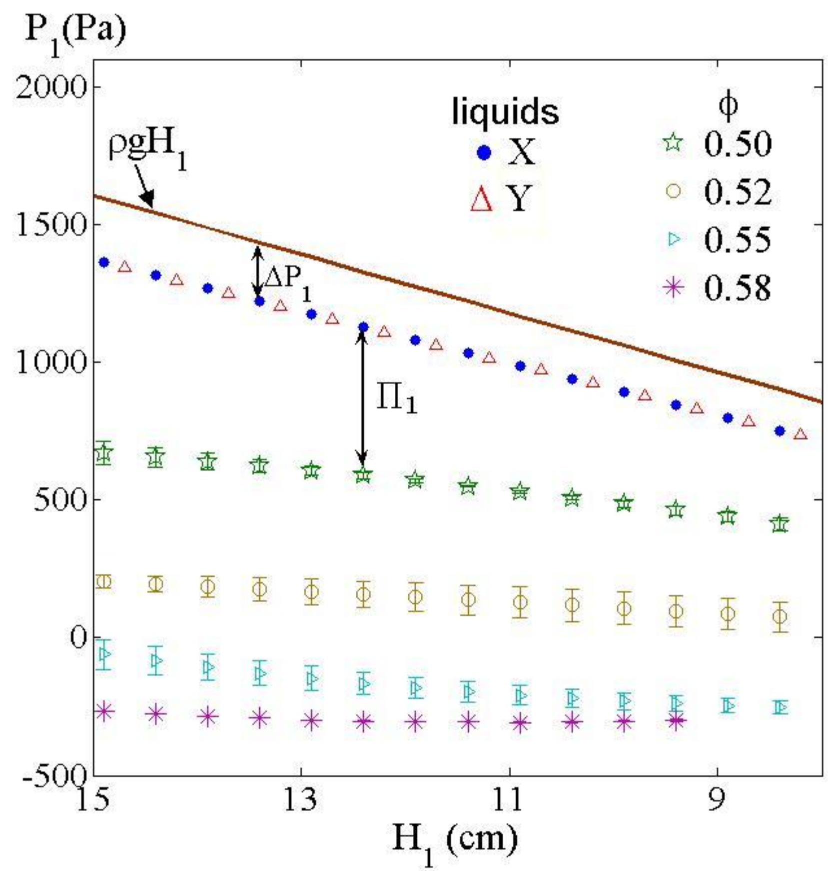


Experiment:

Liquid pressure *alone* is measured across a screen

$$\text{For } \phi = 0.50 - 0.58,\ P_1 \downarrow \text{ as } \phi \uparrow$$

ΔP_1 is independent of material viscosity → ***decrease in P_1 is a two-phase flow phenomenon***.



- Shearing of suspensions generates suction pressure in the suspending liquid

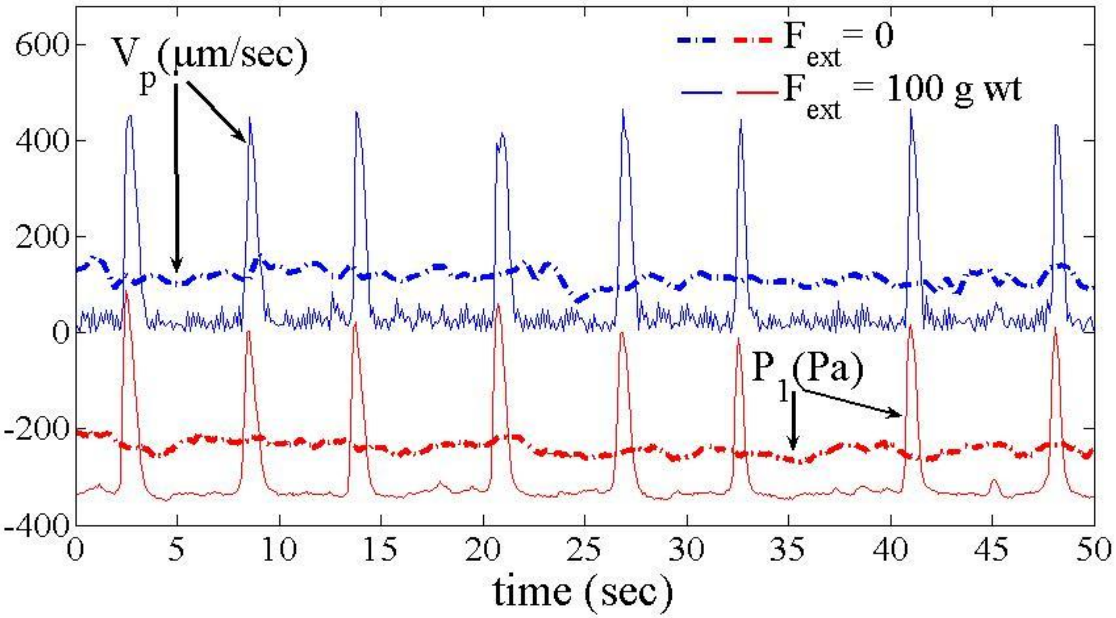
$$\Pi_{liq} = -\Pi(\dot{\gamma}, \phi)$$

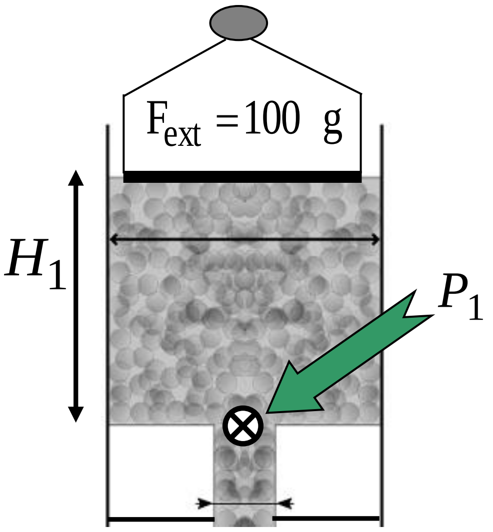
[Yurkovetsky and Morris (2008), Deboeuf *et al*. (2009)]

- The expression for P_1 (similarly P_2) is modified:

$$P_1 = \rho g H_1 - \Delta P_1 - \Pi_1$$

Suspension flow under external load





$$f_{in} = 0.58 \qquad f_{out}^{m} = 0.527 \pm 0.003$$

<u>Periodic</u> flow with alternating ''fast" and "slow" motions.

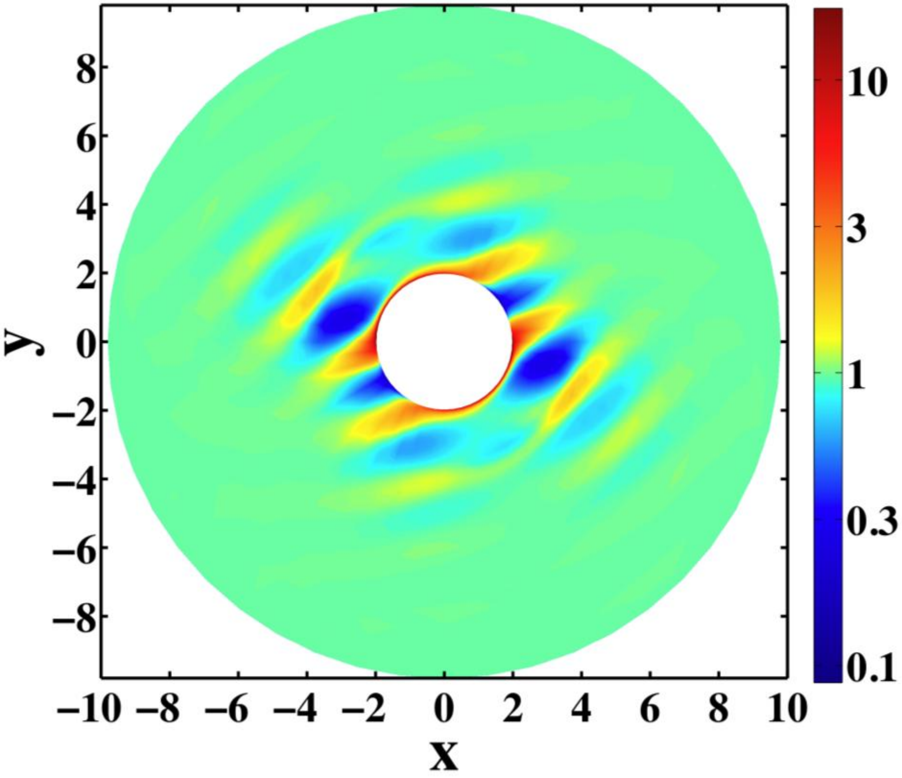
V^p in "slow" motion under *<u>100 g</u>* load < V^p under *<u>no</u>* external load.

"Slow" motion ←→ ***deforming granular network*** (decrease in P_1)

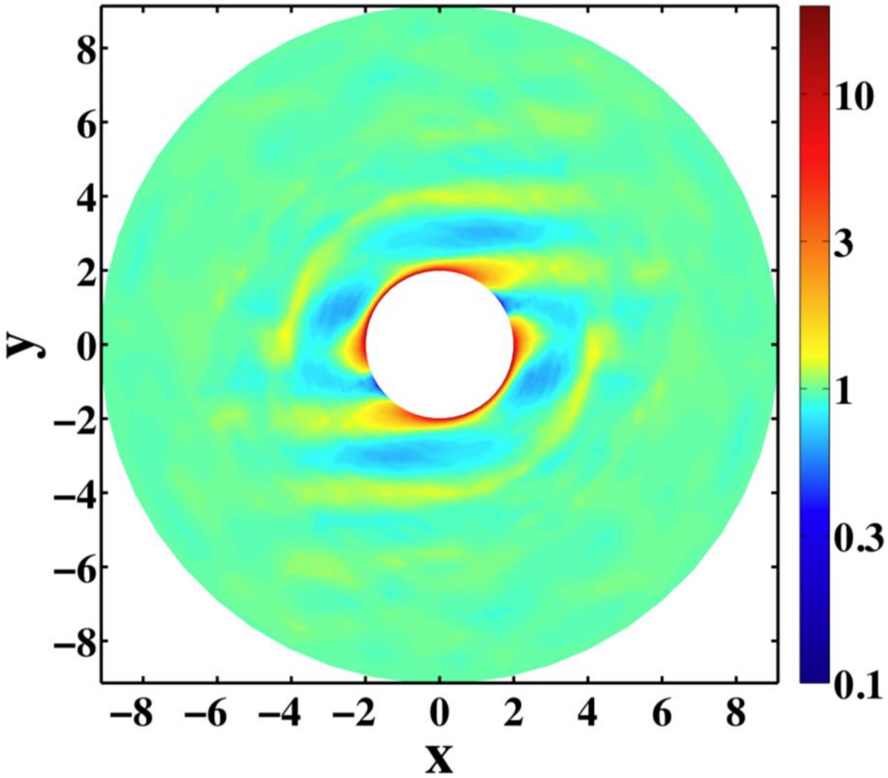
"Fast" motion ←→ ***suspension flow*** (pressure peaks)

Microstructure

Theory, ϕ=0.40, Pe=10



Simulation, ϕ=0.40, Pe=10

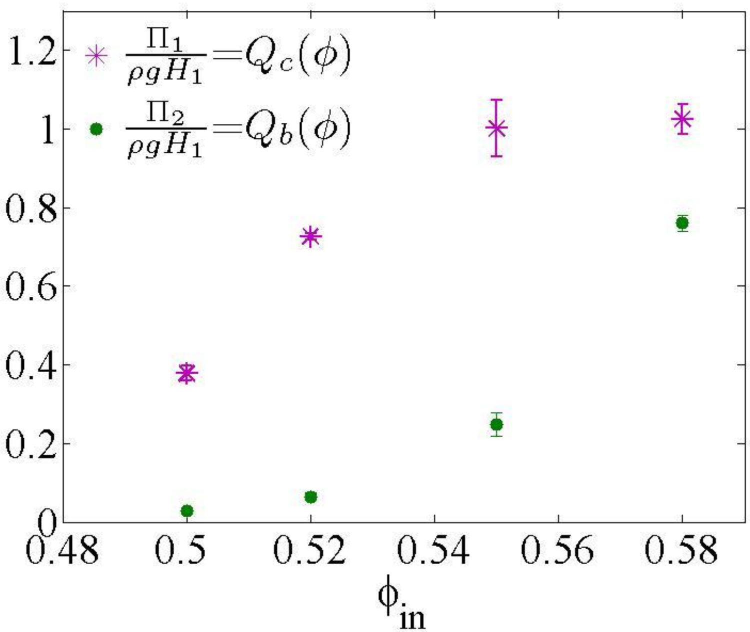


Relating liquid pressure to self-filtration

Combining local rheology $\Pi \propto \eta_n \dot{\gamma}$ with head dependence $\Pi \propto \rho g H_1$

$$\frac{\Pi}{\rho g H_1} = Q(\phi, x) = K(x)\,\frac{\eta_n(\phi)}{\eta_s(\phi)}$$

Specific to geometry



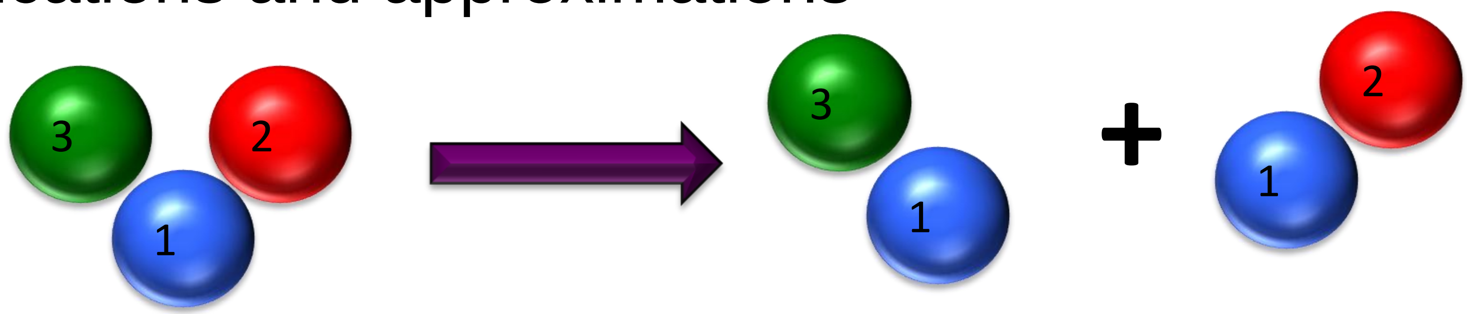
Q_c flattens at high $\phi_{in} \Rightarrow \phi_c \neq \phi_{in}$

Liquid suction ahead of the particles into contraction.

$\phi_c (< \phi_{in})$ remains constant for $\phi_{in} \geq 0.55$

Simplifications and approximations

(I)



Hydrodynamic interactions are summation of pairs near contact

(II) $F^{H} = F^{EXT} + F^{HD} = 0$

F^{EXT} External force driving particles with mean flow

F^{HD} Hydrodynamic/lubrication force imposing the excluded volume