Properties of Complex Particle-Laden Polymeric Solutions

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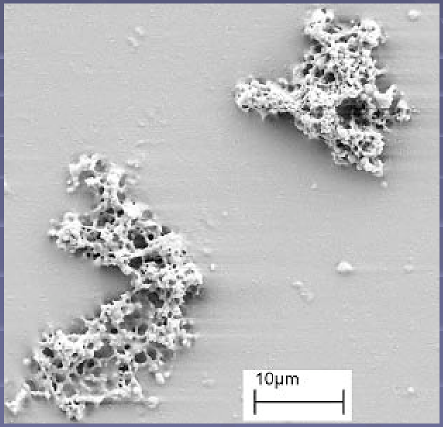
What's in the World Around You?

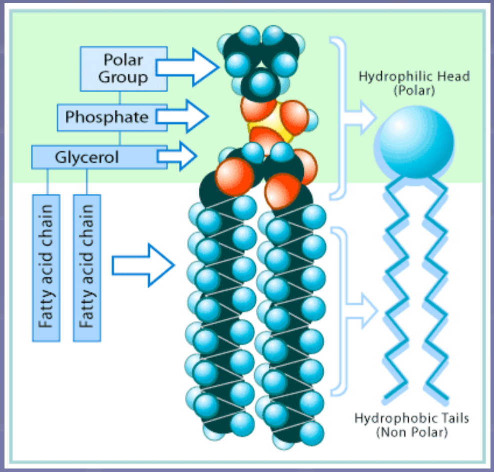
- Suspensions are ubiquitous in Nature!

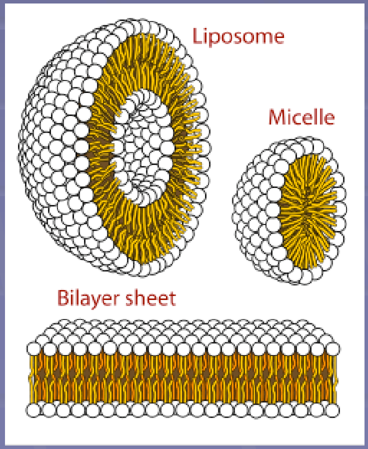
Aggregation of nanoparticle suspensions,
similar to those proposed for
medical dispersion.



(Savara Pharmaceuticals)

- Polymers are equally ubiquitous!





How Can One Hope to Understand Such Complexities?

- A good starting point is to look at relevant time, length, and energy scales.
- In many cases one can prepare system in “limiting” cases.
- In many cases the system behavior is non-linear.

We must think geometrically: Factors of 10 - logarithmically

Power Law → Scaling!

Characteristic Response Times

- Inertial: →

$$\tau = \frac{2\pi a^3 \eta}{k_B T f_v}$$

- Turbulent: →

$$\tau_\eta = \sqrt{\left(\frac{\mu}{\rho}\right)^\alpha / \epsilon}$$

- Elastic: →

$$\tau_e \approx \frac{\eta_s}{T^2}$$

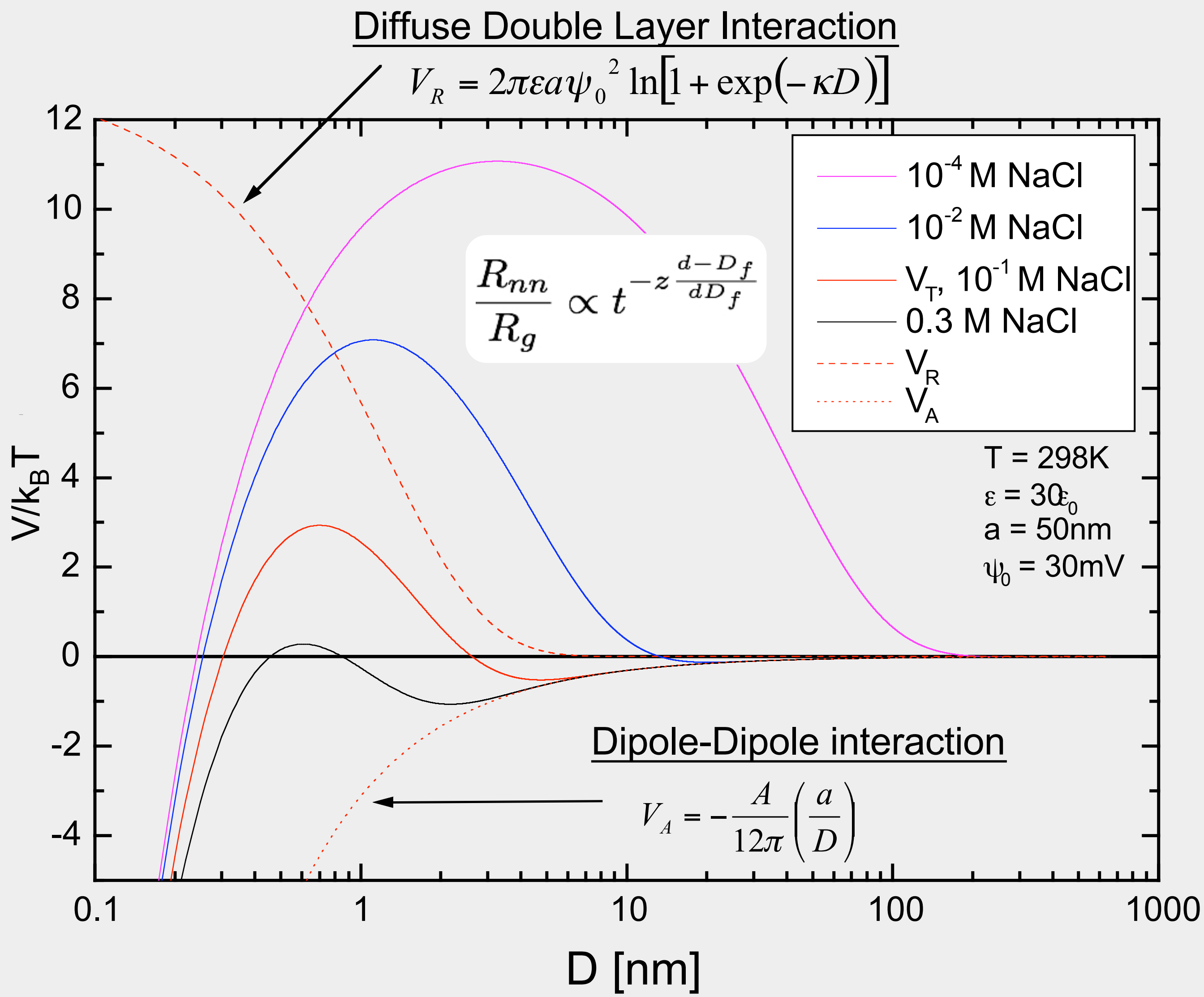
- Flow: →

$$\tau_f \approx \dot{\gamma}^{-1}$$

- Diffusive: →

$$\begin{aligned} \tau_r &\propto D_r^{-1} \\ D_r &= \frac{3k_B T[ln(L/d) - 0.8]}{\pi \eta L^3} \end{aligned}$$

Particulate Interactions



Diffuse Double Layer Interaction

$$V_R = 2\pi\varepsilon a\psi_0^{\ 2}\ln\left[1+\exp(-\kappa D)\right]$$

$$\frac{R_{nn}}{R_g} \propto t^{-z\frac{d-D_f}{dD_f}}$$

T = 298K
$\varepsilon = 30\varepsilon_0$
a = 50nm
ψ_0 = 30mV

Dipole-Dipole interaction

$$V_A = -\frac{A}{12\pi}\left(\frac{a}{D}\right)$$

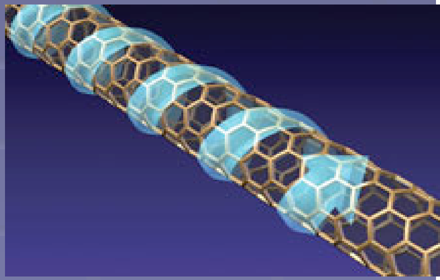
Polymeric-Nanotube Suspensions

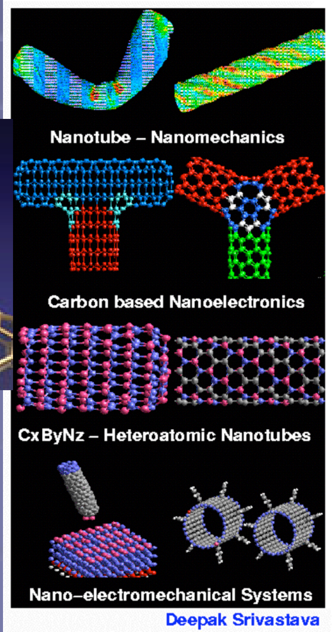
- Brownian nature controlled by both tube concentration, flow velocity/shear rate (Reynolds number), and elastic contribution from suspending medium.

- High-molecular weight polymer suspensions can be made “visco-elastic”, in some cases non-Newtonian:

$$\tau_{x,y} \neq \eta\dot{\gamma}$$

Response not proportional to how hard you “push”!





Deepak Srivastava

Polymeric-Nanotube Suspensions

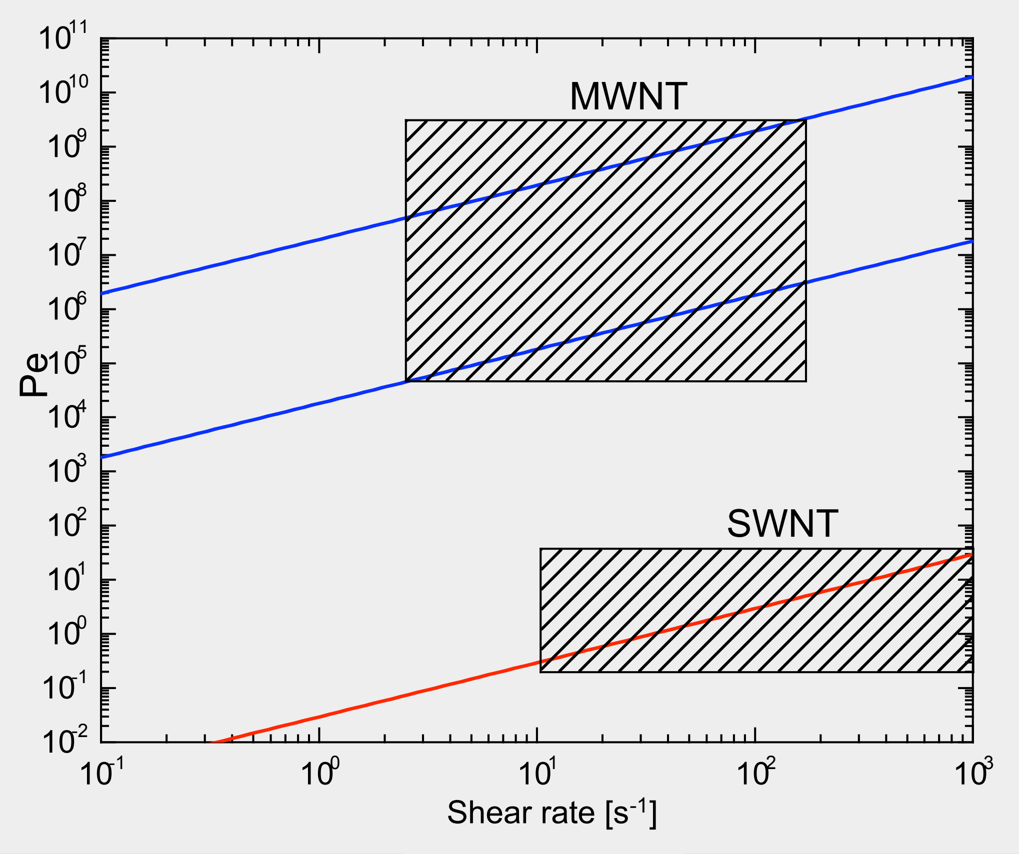
SWNT

Solvent: 0.6% NaDDBS in D_2O.
η ~$0.9*10^{-3}$ Pa s
Screens van der Waals attraction between tubes.
Forms micelles.

MWNT

Solvent: PIB/Boger
η~0.6 – 10 Pa s
ρ = 0.91gm/cm^3
Newtonian to 100 s^{-1}

PIB - polysiobutylene, M_W = 500
Boger Fluid - constant-viscosity / elastic, M_W = 800 PIB mixed with 0.1% M_W = $4.7X10^6$ PIB.



	SWNT	MWNT
L [mm]	**0.5-1**	**10-12**
d [nm]	**12-15**	**50**
(L/d)	**~60**	**200**
f	**$4.3*10^{-4}$ – $8.7*10^{-4}$**	**$1.1*10^{-4}$ – $3.6*10^{-3}$**
nL^3	**2 – 4**	**6 – 183**
nL^2d	**0.03 – 0.06**	**0.3 – 0.9**
Pe	**0.2 - 100**	**10^4 – $4*10^{10}$**
Re	**$5*10^{-2}$ – 15**	**10^{-5} – 10^{-3}**

Defining "Limiting" Behavior

- Convenient to define dimensionless scale factors as ratios of time, length, and energy:

In general these can be controlled experimentally!

  - Stokes Number (ratio of particle response to turbulent response): $$St = \frac{\tau_p}{\tau_\eta}$$
  - Reynolds Number (ratio of inertial to viscous forces): $$Re = \frac{\rho_s \dot{\gamma} \ell^2}{\eta_s}$$
  - Weisenberg Number (ratio of flow rate to elastic relaxation time): $$We = \dot{\gamma}\lambda_c$$
  - Rotational Peclet Number (ratio of flow time to rotation time): $$Pe = \frac{\dot{\gamma}}{D_r}$$

Observation: Light Scattering is Our Eyes into System Behavior

- Remember geometric optics?
  - What matters is the ratio of characteristic size to the wavelength of incident light.

<u>Small Angle Light Scat. (SALS)</u>
q(~1/λ) range: 0.58 – 4.9 μm^{-1}
Length scale probed: 0.2 -1.7 μm

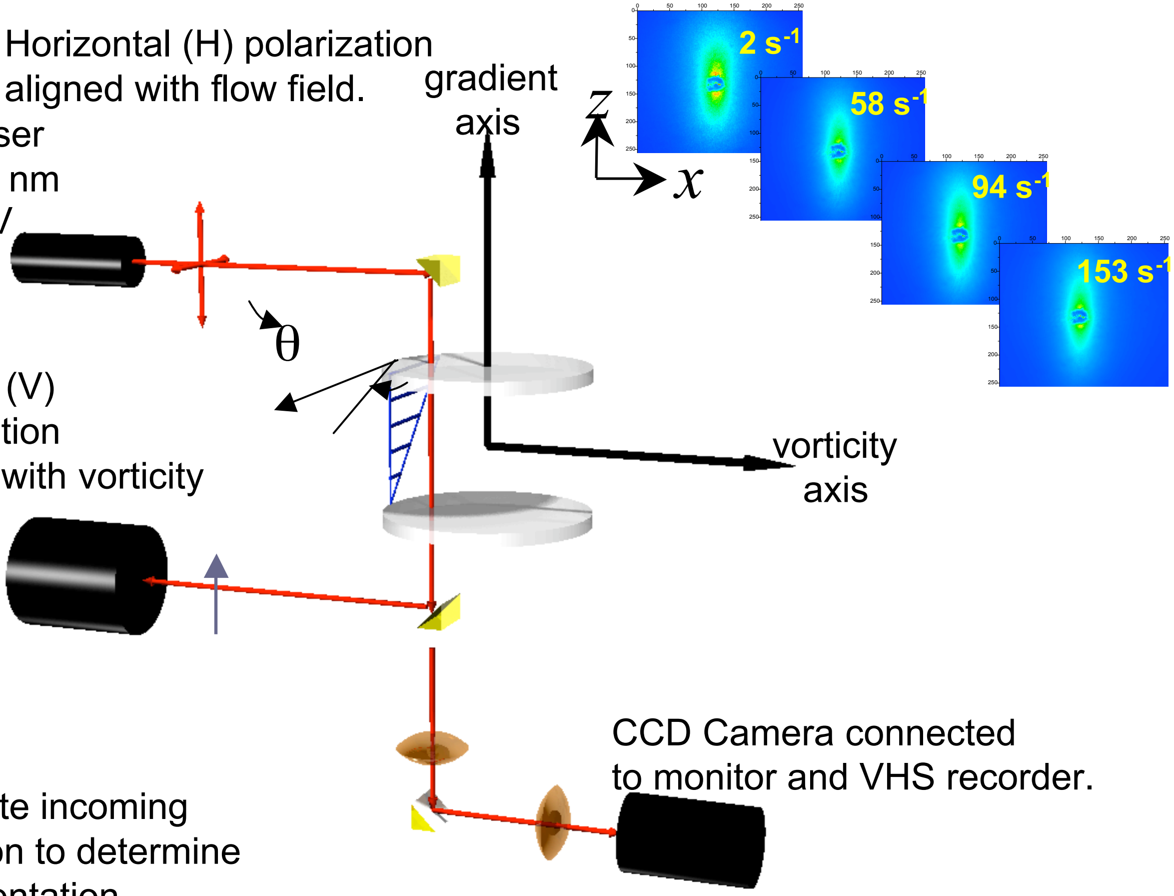
Q gives insight
into structure size!

$$q = \frac{4\pi}{\lambda} sin(\theta)$$

<u>Birefringence - </u>Orientation dependent electric field decomposition.

<u>Dichroism - </u>Orientation dependent absorption

Observational Setup



Horizontal (H) polarization aligned with flow field.

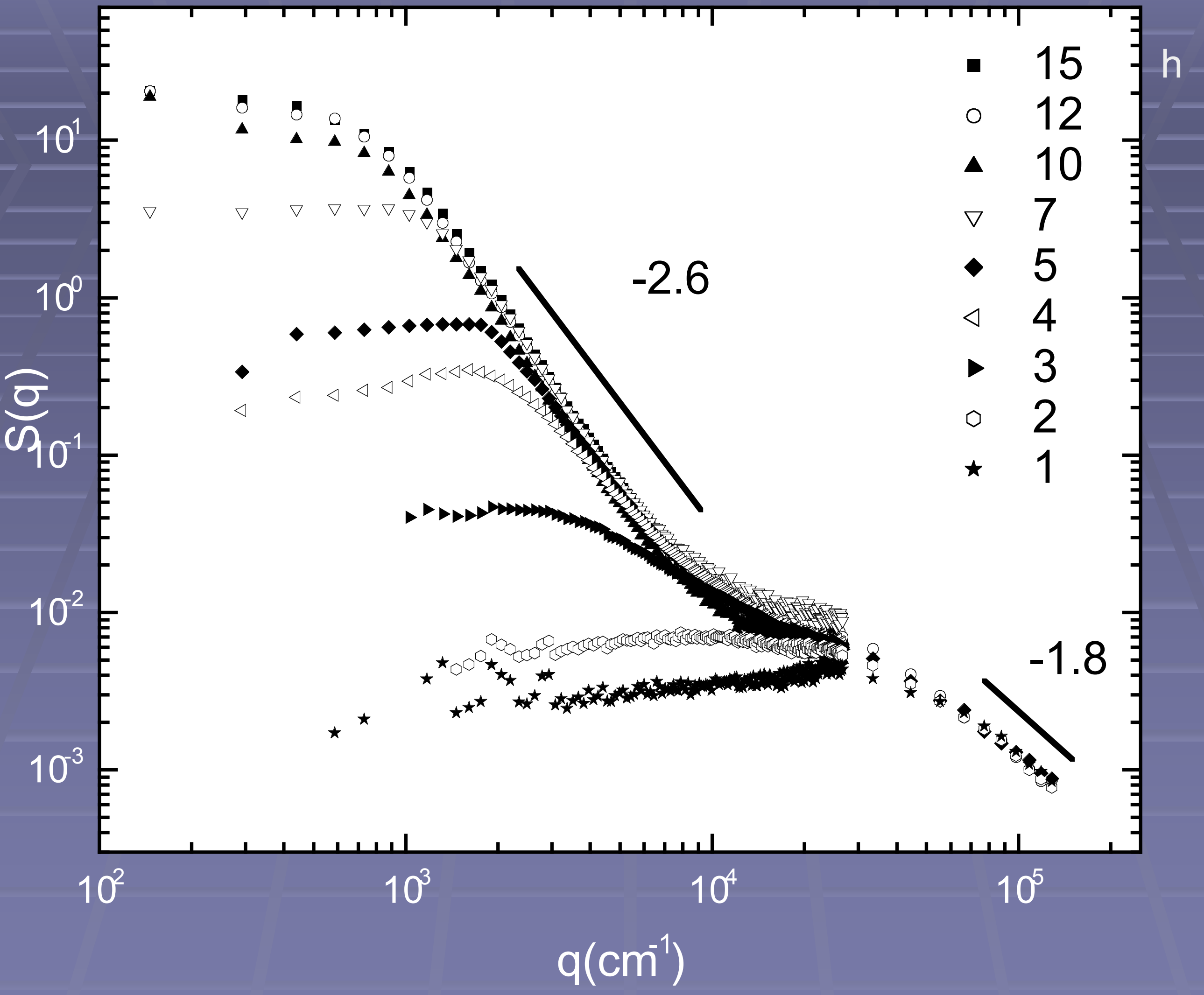
He-Ne Laser
632.8/670 nm
hν ~ 1.9eV

Vertical (V) polarization aligned with vorticity axis.

Modulate incoming polarization to determine orientation.

CCD Camera connected to monitor and VHS recorder.

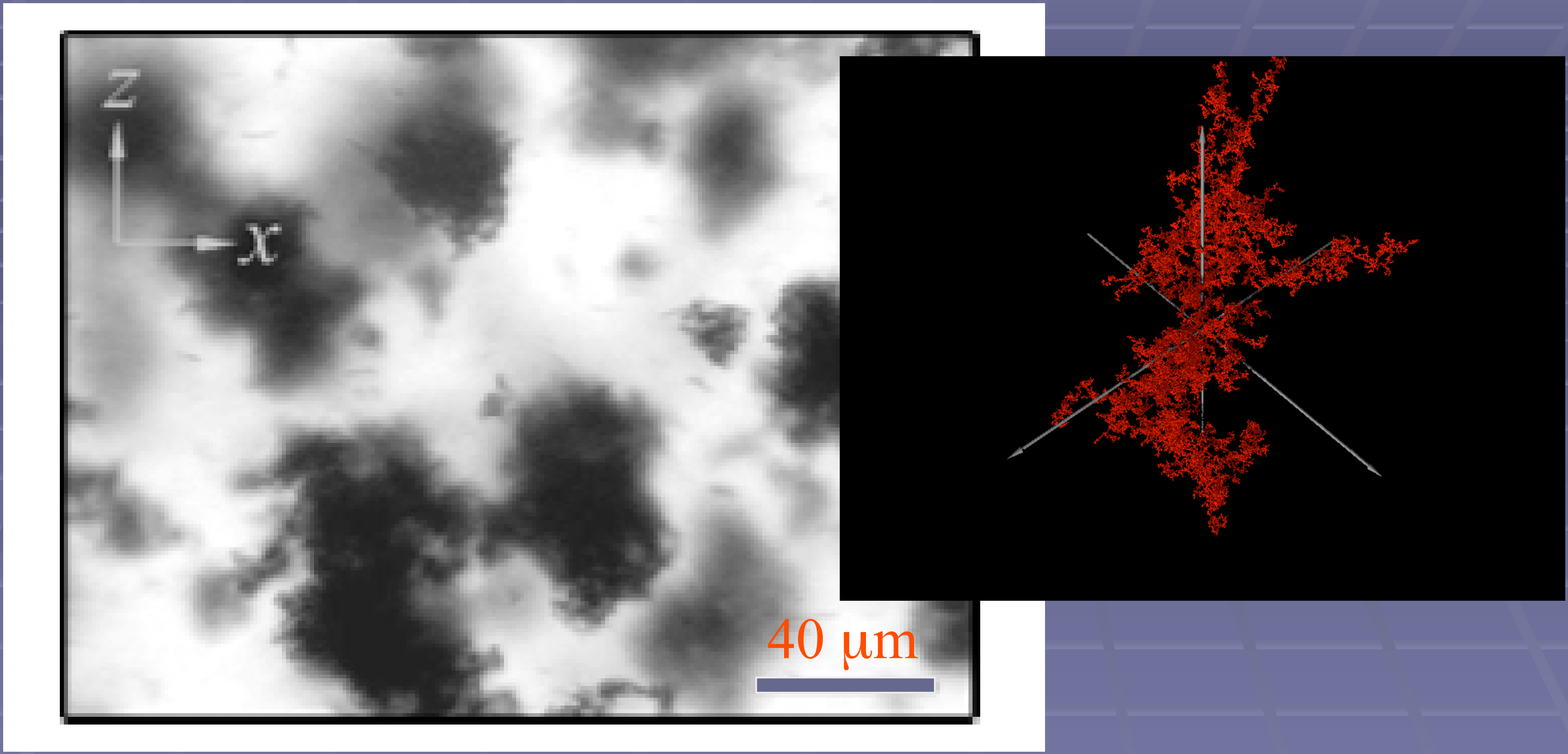
100 % C_2H_2



Intensity of scattered light, I(q) = NS(q)

(Kim et al.)

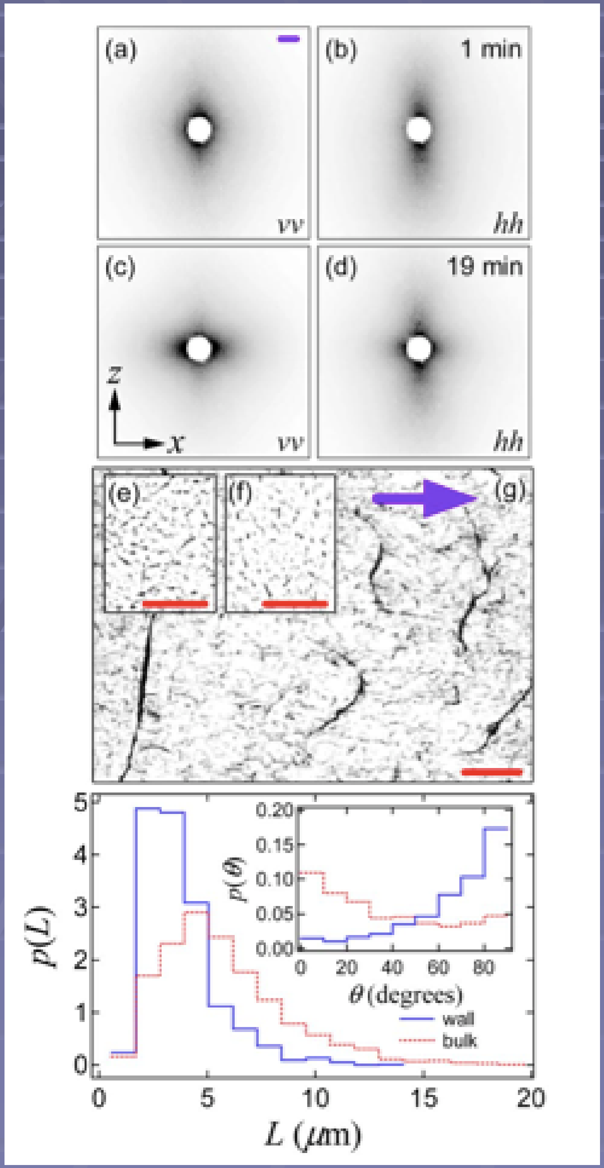
Clustering in the Presence of Shear



- Nanotubes have an attractive interparticle potential and floc (aggregate) in quiescence.

- Because of the packing nature of high aspect ratio tubes, and the viscoelastic nature of the background fluid, aggregate structure tends to be more compact than diffusion-limited aggregation.

Size Segregation



•Light scattering patterns don’t show a strong flow alignment.

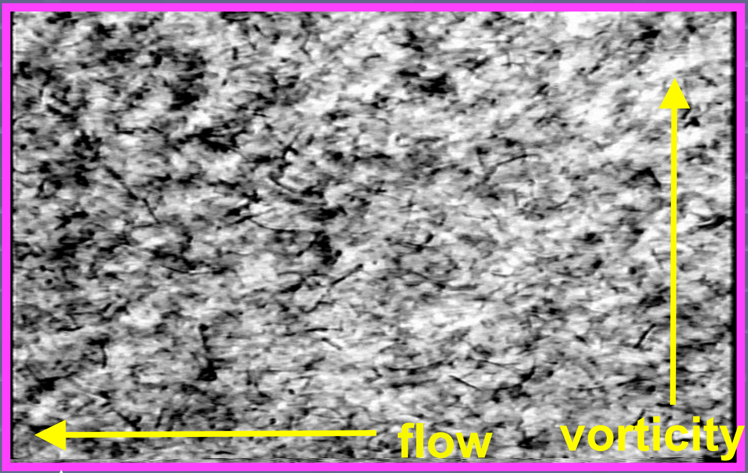
•“Bulge” in vv and hh light scattering patterns at long times implies some degree of separation into two characteristic length scales.

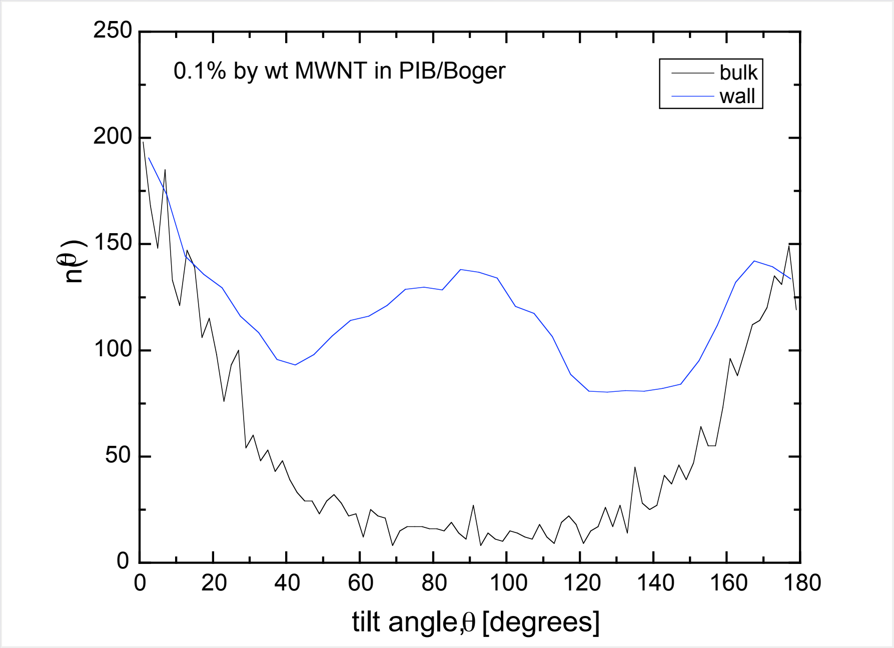
•Through microscopy we see small tubes close to shear cell walls, larger tubes towards center of cell.

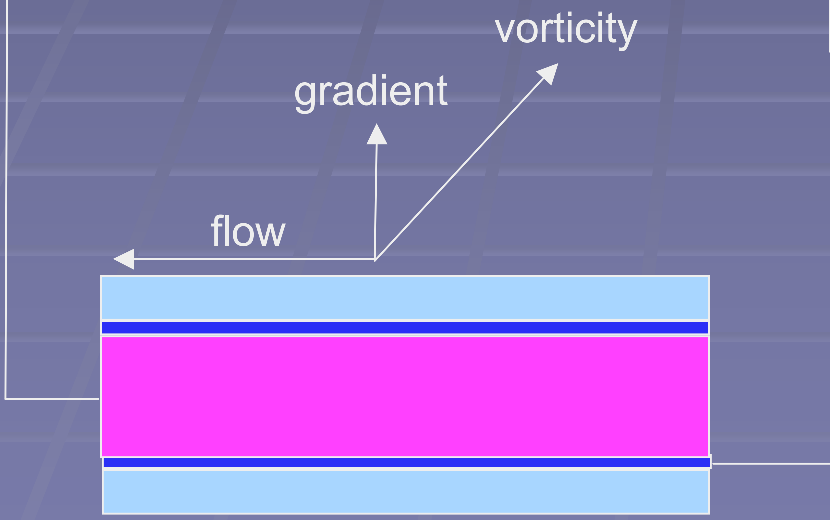
•Jefferey orbits of longer MWNTs drives flow aligned tubes into bulk.

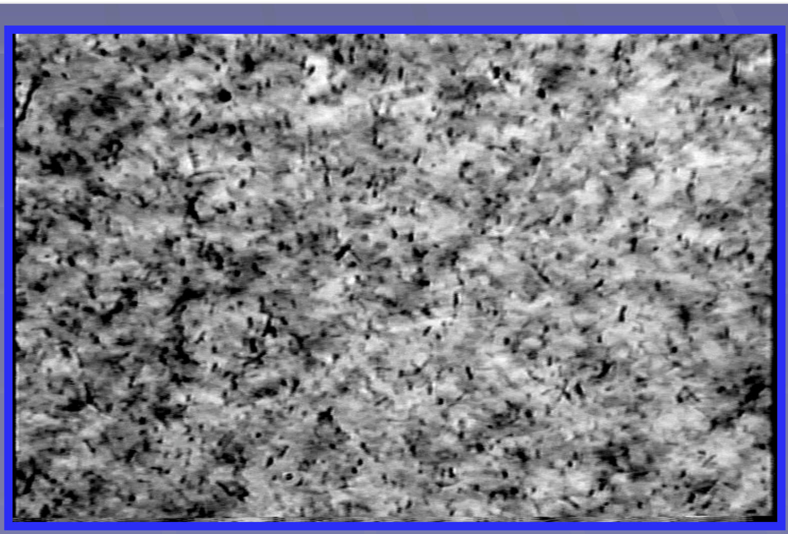
•Tube-Tube interactions drive shorter tubes to wall where they align with the vorticity direction.

Orientation Segregation







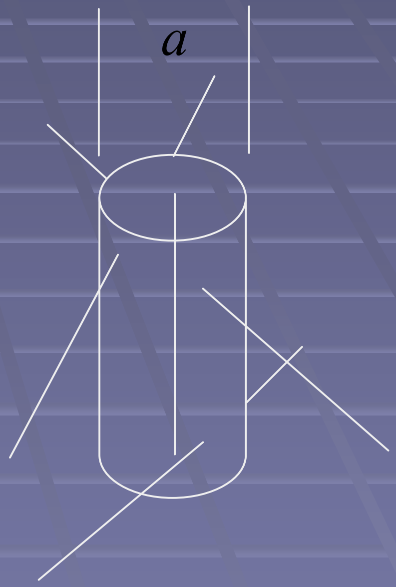


“Classical” Rigid-Rod Approximation

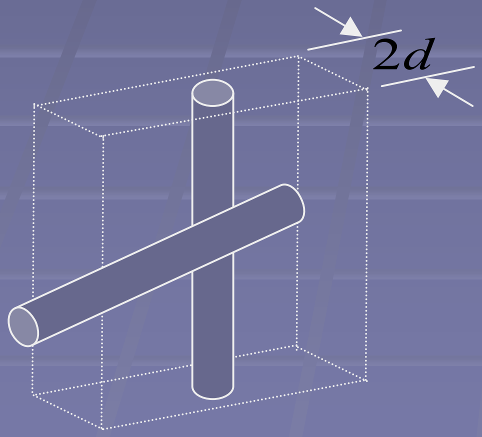
Dilute limit for rigid rods :

$$D_R = D_{Ro} = \frac{3k_B T[\ln(L/d) - 0.8]}{\pi\eta L^3}$$

Semi-dilute limit: tube-tube interaction begins to play a role and excluded volume restricts rotary diffusion coefficient.



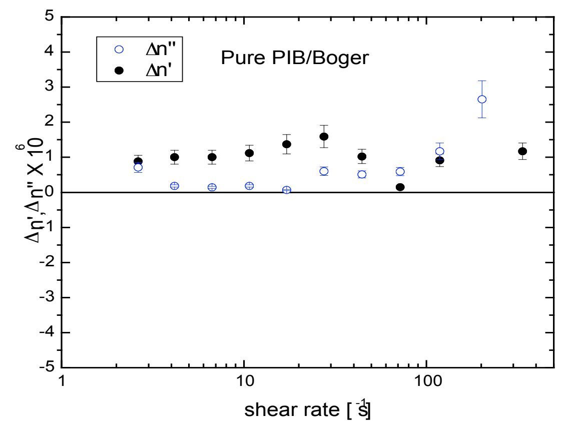
Excluded volume via Doi-Edwards:

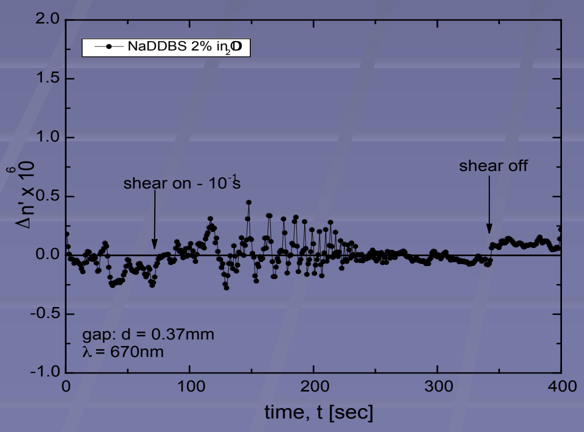


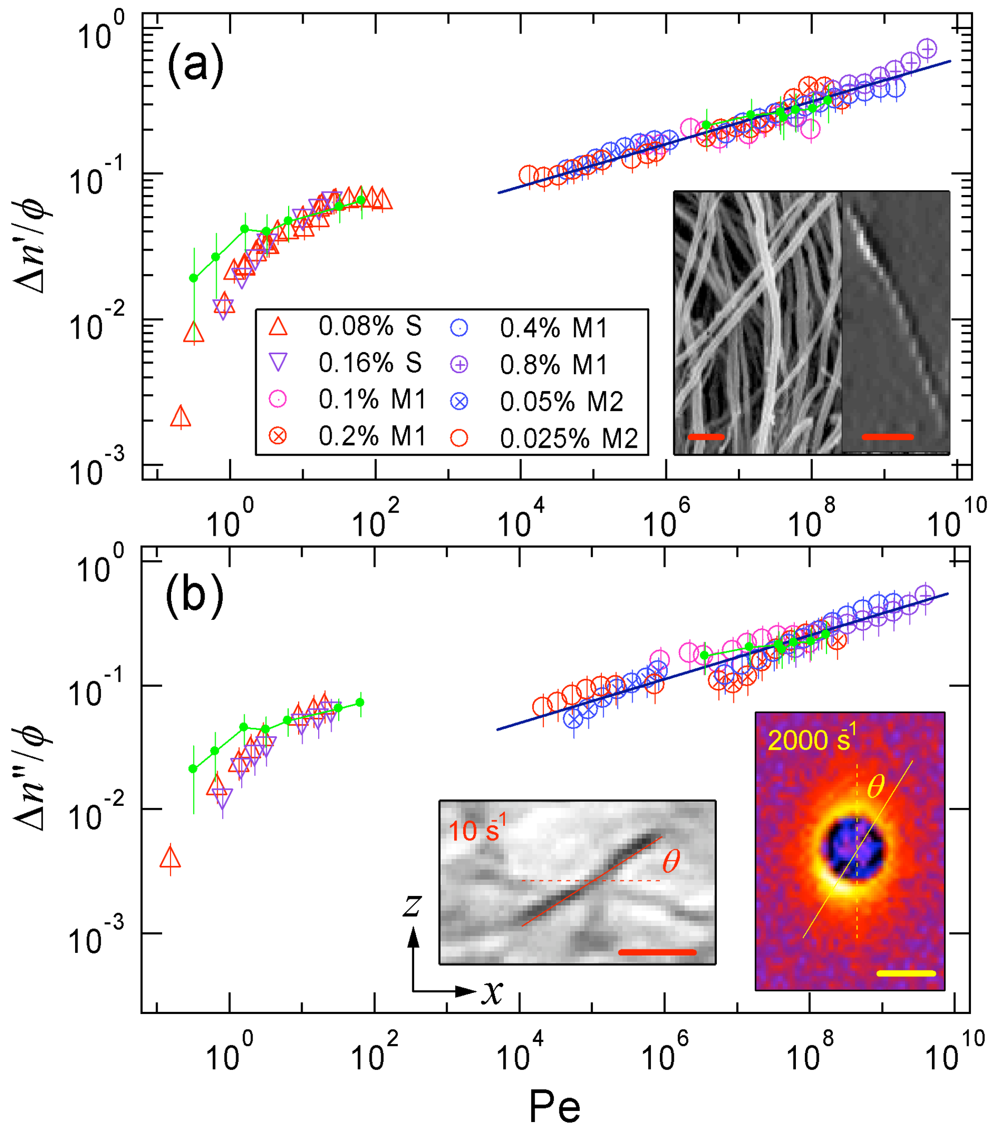
$$D_R \propto D_{Ro}\phi^{-2}$$

$$Pe = \frac{\dot{\gamma}}{D_R} \propto \dot{\gamma}\phi^2$$

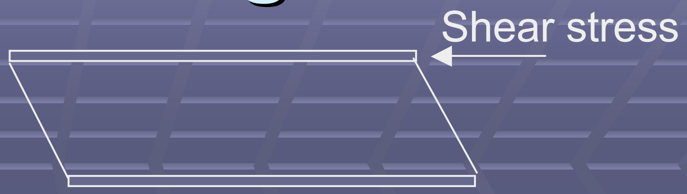
Universal Scaling

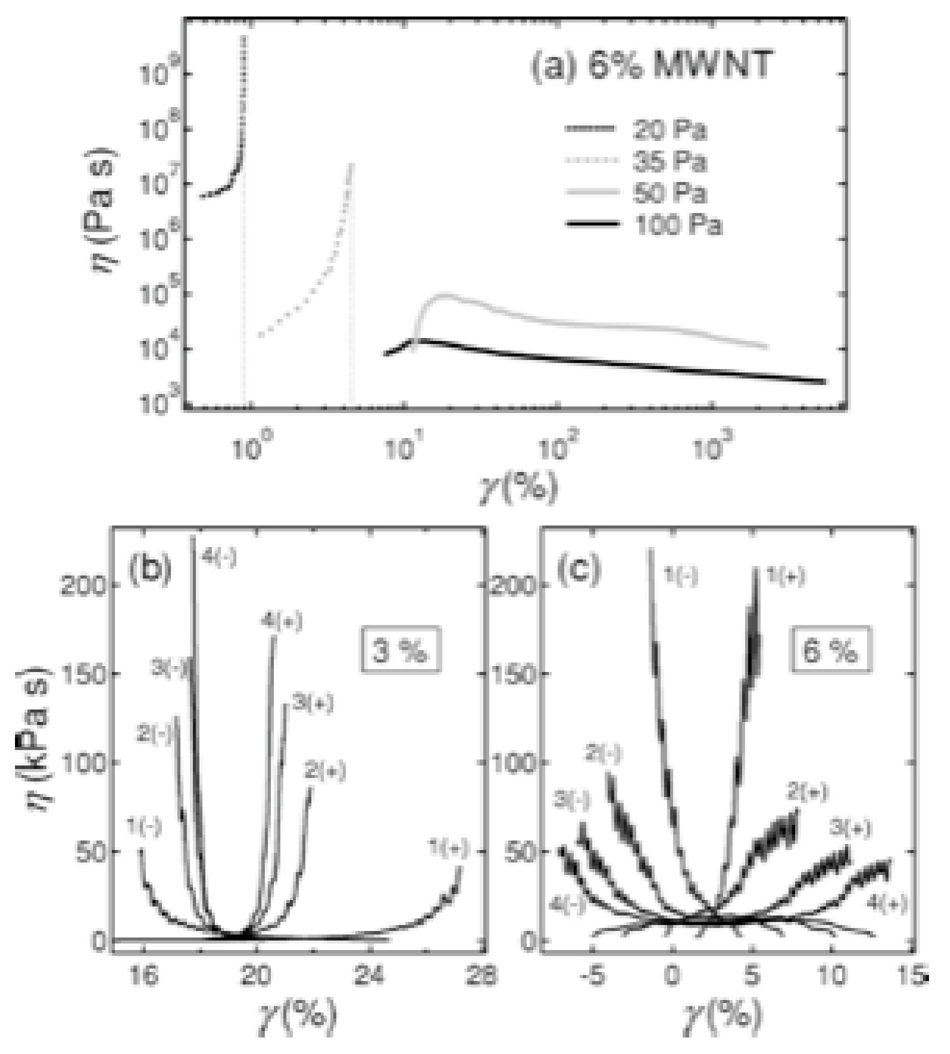






Yield Stress: Jamming



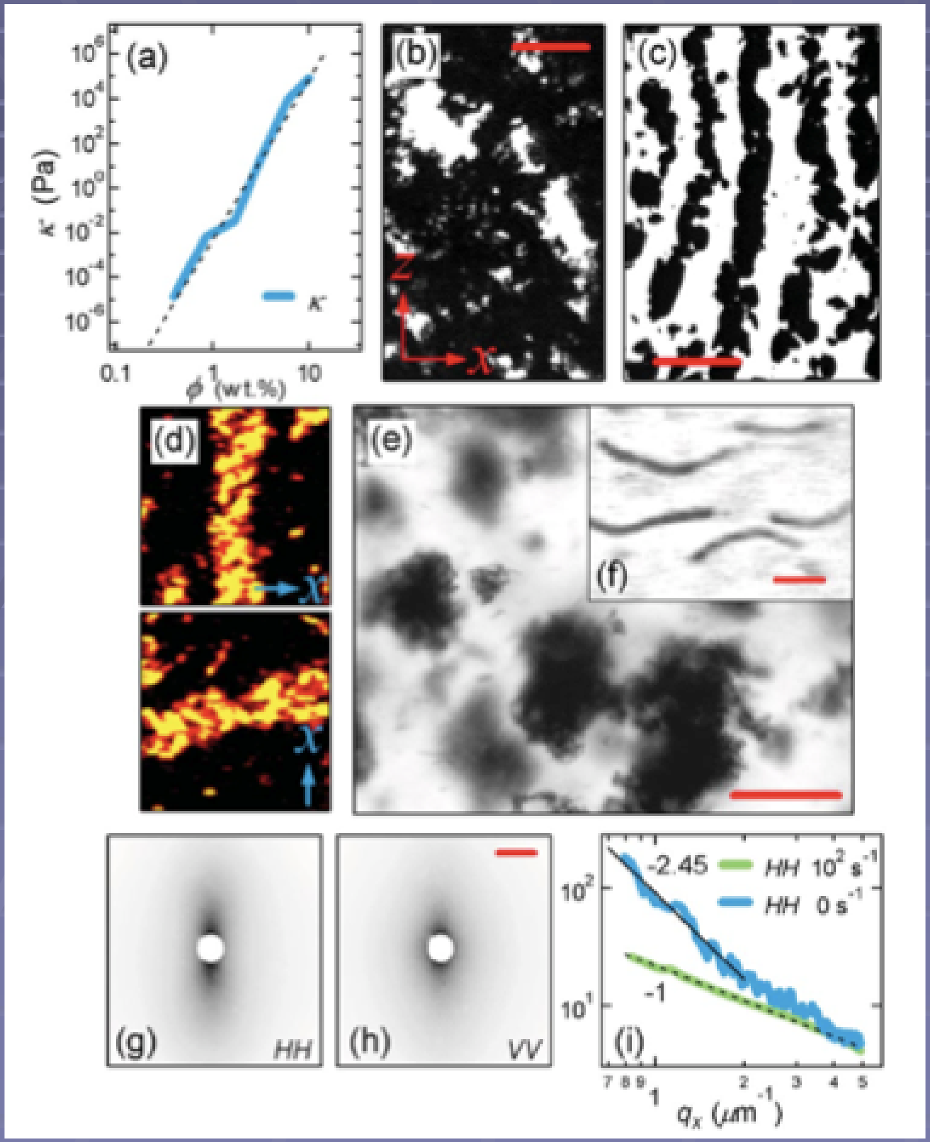


- •By definition, a liquid cannot sustain a non-zero shear stress.

- •Some particulate suspensions are unique in that they exhibit a transition from liquid to solid behavior - they jam, or develop a yield stress.

- •The degree to which they jam is dependent on particulate concentration and how hard you push on them.

Shear-Induced Phase Transition



- (c-d)Below a critical shear stress (rate) there is not sufficient energy to break the contact bonds between tubes formed by overlapping orbits.

- (c-d)When the system size (shear cell gap) becomes comparable to tube orbits they are confined and floc end-to-end in x-z plane along z.

- (c-d)Stripped pattern results from band growth at expense of smaller clusters.

- (b) Increasing concentration φ results in a cavitated network.

Future Applications

- Magnetic Viruses: biologically functionalized magnetic nanoparticles:
  - DNA removed from virus interior. Casing is then used as a template for Fe_3O_4 particle.
- Biohazard Detoxification: poly(lactic-glycolic acid) nanospheres carrying surface receptors to remove invaders from blood.
- PEG Shell / Drug Emulsion: delivery of time-sensitive contents to circulatory system of stroke victim.

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