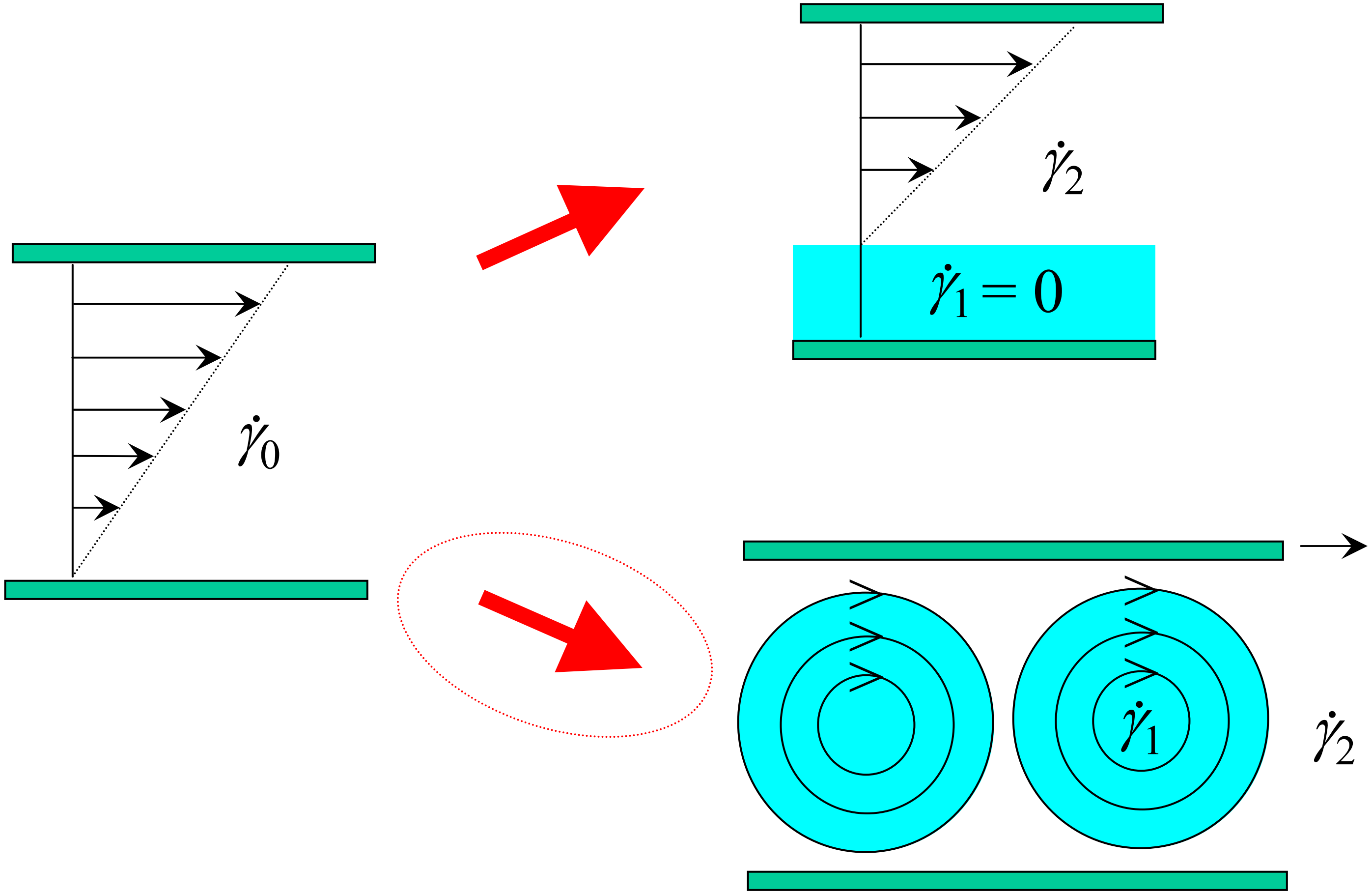
Shear Banding in Entangled Carbon Nanotube Networks

Erik K. Hobbie
NIST Polymers Division

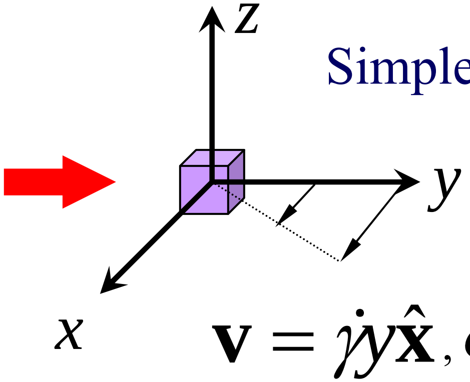
Euromech 2007 – Shear Banding in Entangled Systems

Generalized Definition of Shear Banding

Shear-induced separation into two or more macroscopic regions of different strain rate



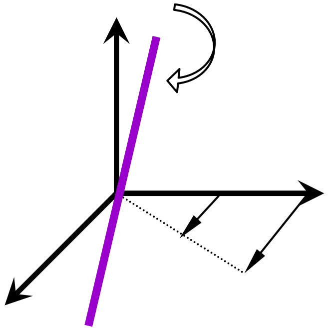
Sheared Carbon Nanotube Suspensions



Simple Shear Flow

$$\mathbf{v} = \dot{\gamma} y \hat{\mathbf{x}}, \sigma_{xy} = \eta \dot{\gamma}$$

Nanotubes are in closed periodic Jeffery orbits



$cL^3 \leq 1,\ cL^2 d < 1$ (dilute)

$cL^3 >> 1,\ cL^2 d < 1$ (semi-dilute)

$cL^3 >> 1,\ cL^2 d > 1$ (concentrated)

Orbit period scales inversely with shear rate

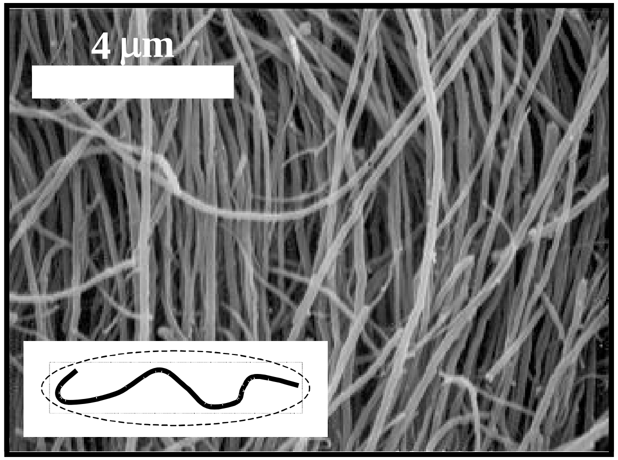
Sheared Carbon Nanotube Suspensions

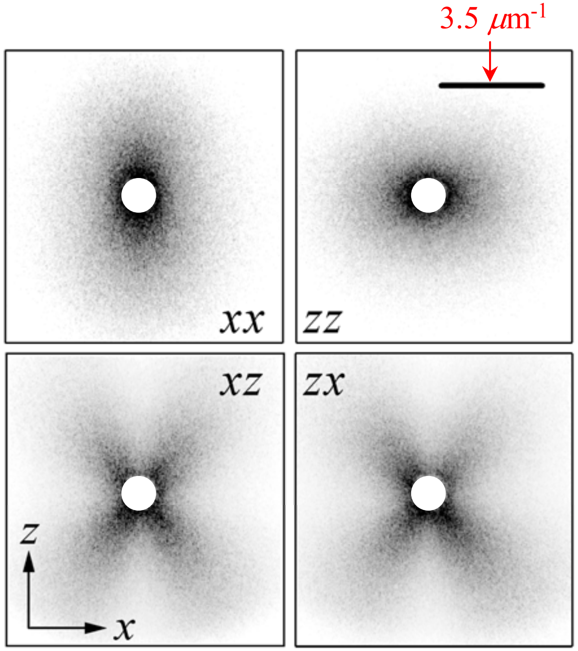
Nanotubes Movie

(nanotubes.avi)

Width of image = 200 micrometers

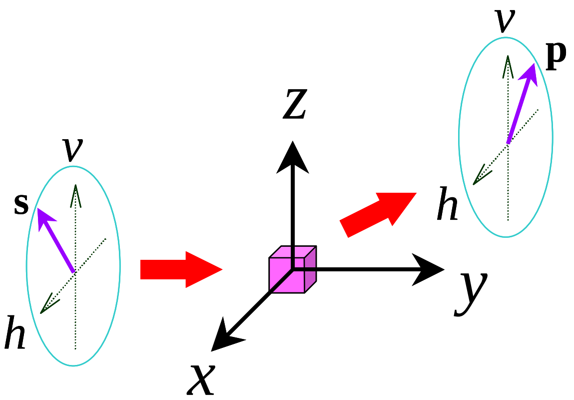
Small-Angle Light Scattering from MWNT Suspensions

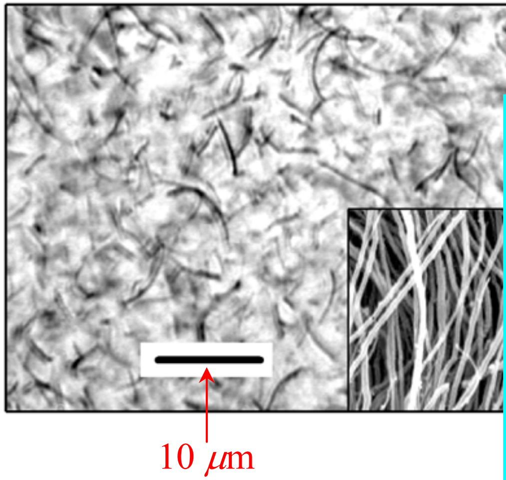


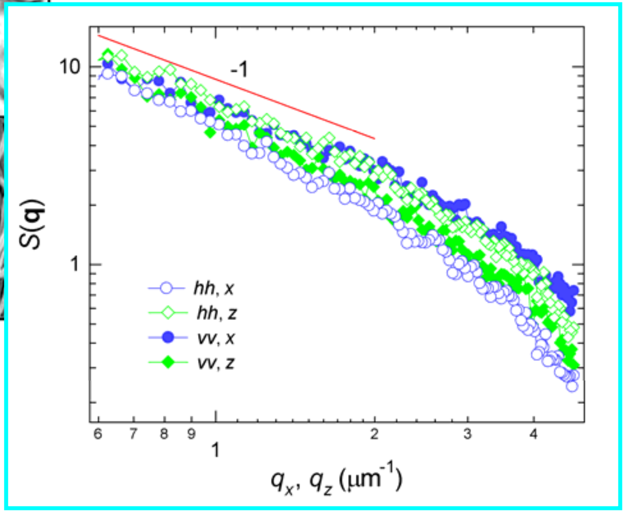


SWNTs and MWNTs are optically active, so ‘depolarized’ light scattering is needed …

… polarization and absorption are *both* anisotropic along and normal to the symmetry axis of the tube



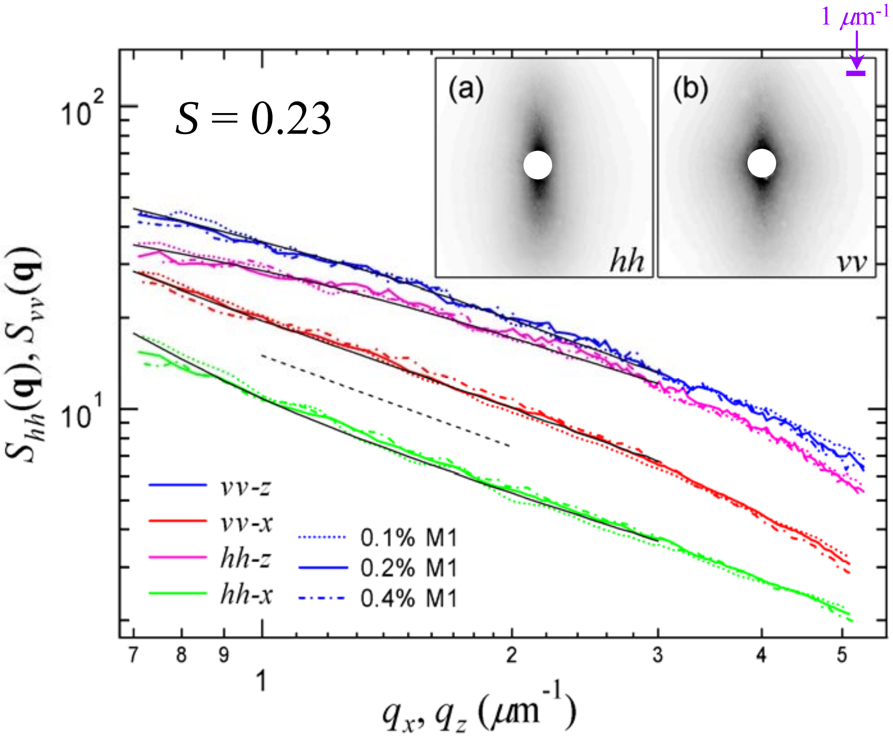


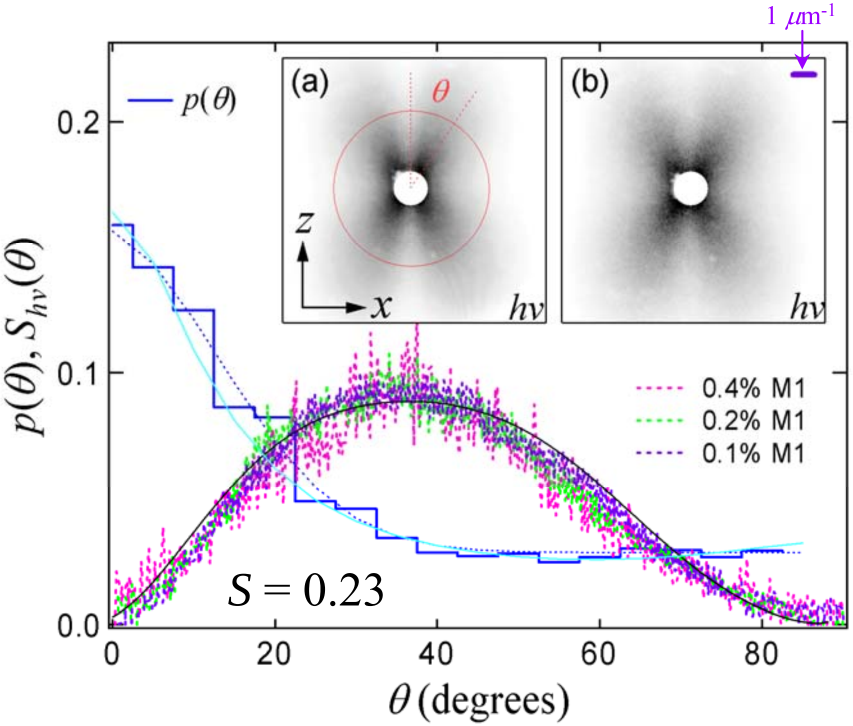


E. K. Hobbie *et al*, *RSI* **74**, 1244 (2003)

Good MWNT dispersion

Shear-Induced Orientation in Suspensions -
Scaling of SALS in the Semi-dilute Regime





Scaling of depolarized light scattering data corroborates the scaling observed in the dichroism and the birefringence, and a zero^th^-order fitting scheme describes all of the data with only one adjustable parameter, a small back ground in a Gaussian ODF, *p*(*θ*). Fitting trends consistent with modest to minimal tube deformation.

D. Fry, *et. al. Phys. Rev. Lett*. **95**, 0383304 (2005)

Orientation in Sheared Suspensions - Scaling of Birefringence and Dichroism

$$\Delta n' \approx \frac{1}{2n_s}\phi(\alpha'_\parallel - \alpha'_\perp)S + \ldots$$

$$\Delta n'' \approx \frac{1}{2n_s}\phi(\alpha''_\parallel - \alpha''_\perp)S + \ldots$$

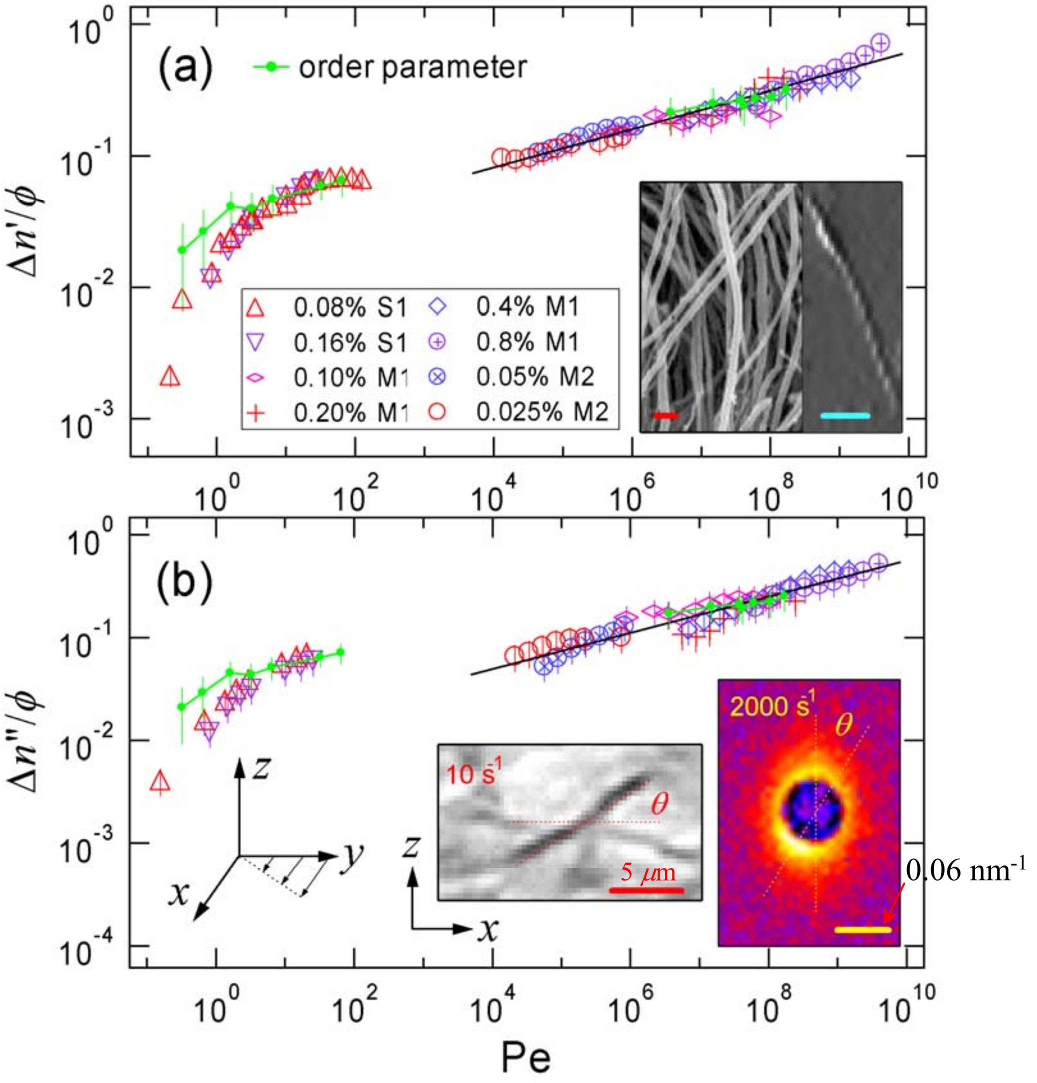
$$S = \frac{1}{2}(3\langle\cos^2\theta\rangle - 1)$$

$$\mathrm{Pe} = \frac{\dot{\gamma}}{D}$$ (rotational Peclet number)

$$D = D_o = \frac{3k_BT[\ln(L/d) - 0.8]}{\pi\eta L^3}$$ **(dilute)**

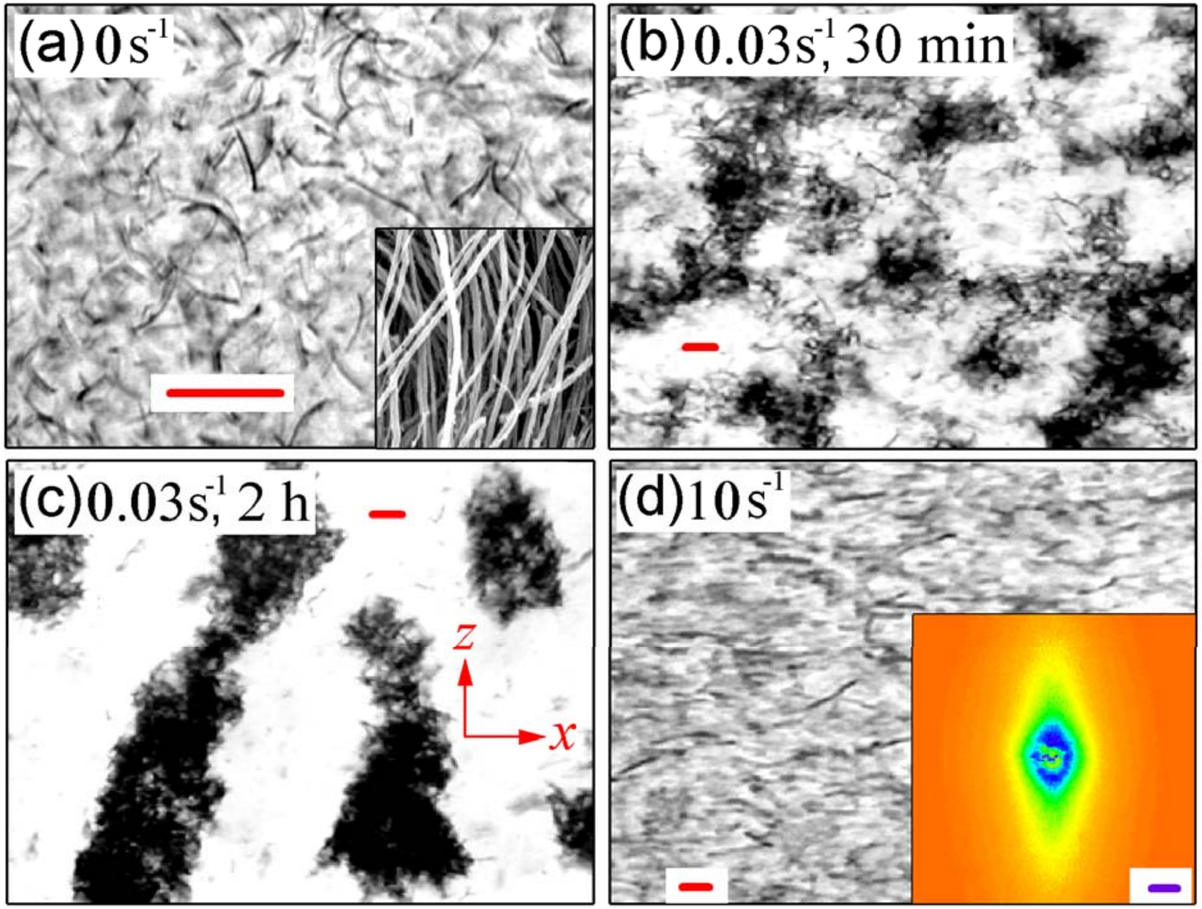
$$D \propto D_o\phi^{-2}$$ **(semi-dilute - Doi and Edwards)**

$$\boxed{S \propto \mathrm{Pe}^{0.16} \propto \phi^{1/3}}$$



D. Fry, *et. al. Phys. Rev. Lett.* **95**, 0383304 (2005)

Flow-Induced Aggregation - Banding in Weak Shear?



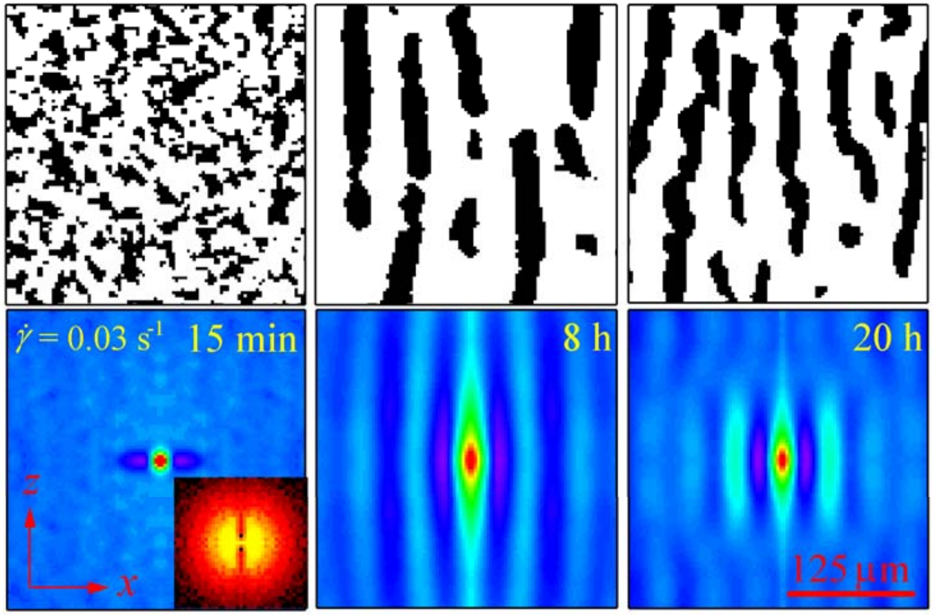
MWNTs
$d \approx 50$ nm
$L \approx 10\ \mu$m
dispersed in PIB
($M_n = 800$)
$\eta = 10$ Pa-s at 25 °C
0.17 wt. % MWNT
$nL^3 \approx 54$
$nL^2d \approx 0.23$

S. Lin-Gibson *et al*, *Phys. Rev. Lett.* **92**, 048302 (2004)

Schmid & Klingenberg, *Phys. Rev. Lett.* **84**, 290-293 (2000)

Shear-Induced Aggregation and Coarsening

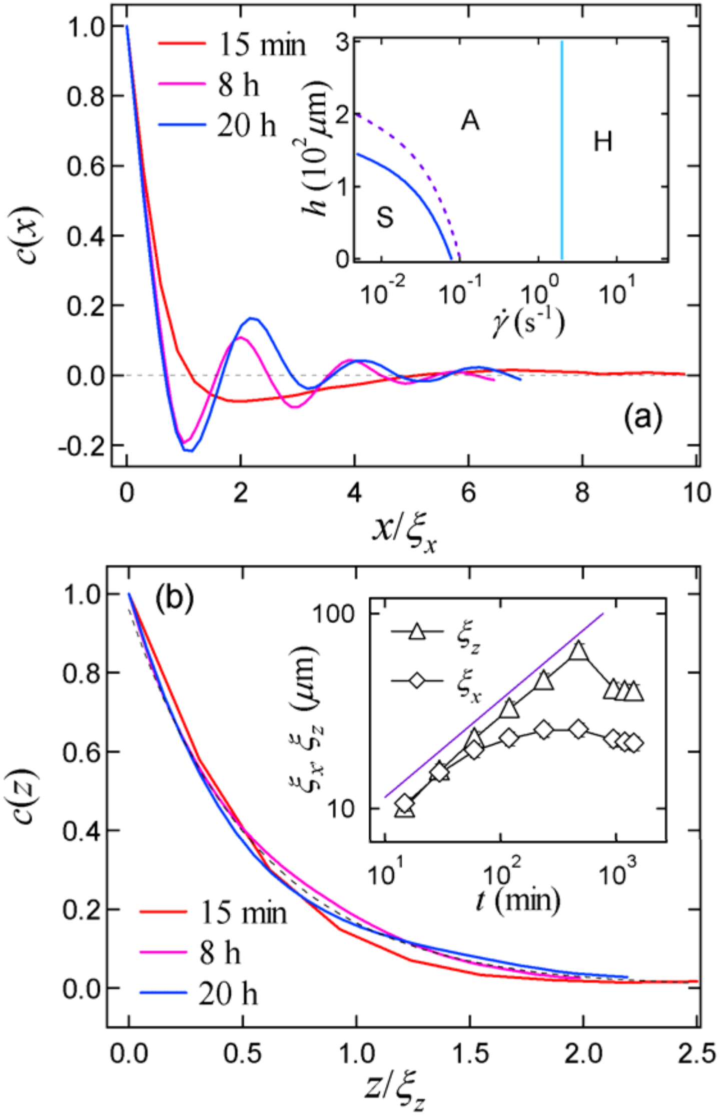
Generic pattern at early time
exaggerated by confinement effects
at late time …



ψ = area fraction

$$c(\mathbf{r}) = \langle \psi(\mathbf{r})\psi(0) \rangle$$

[width of FFT = 1.2 μm^{-1}]

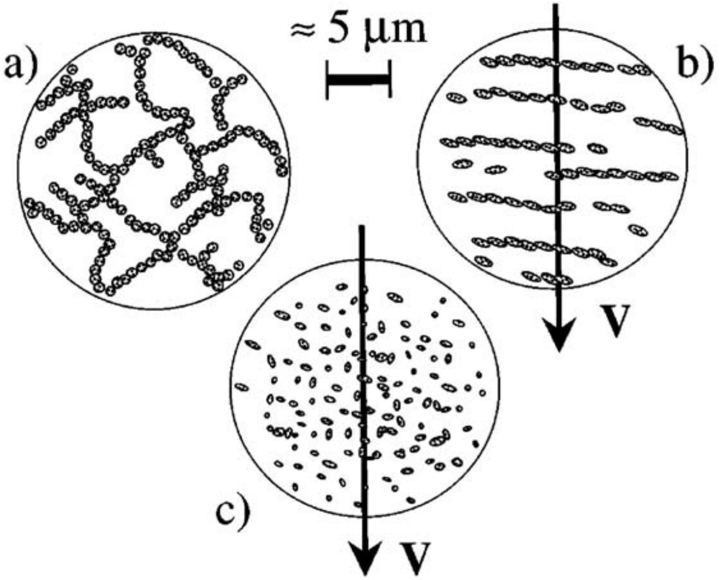


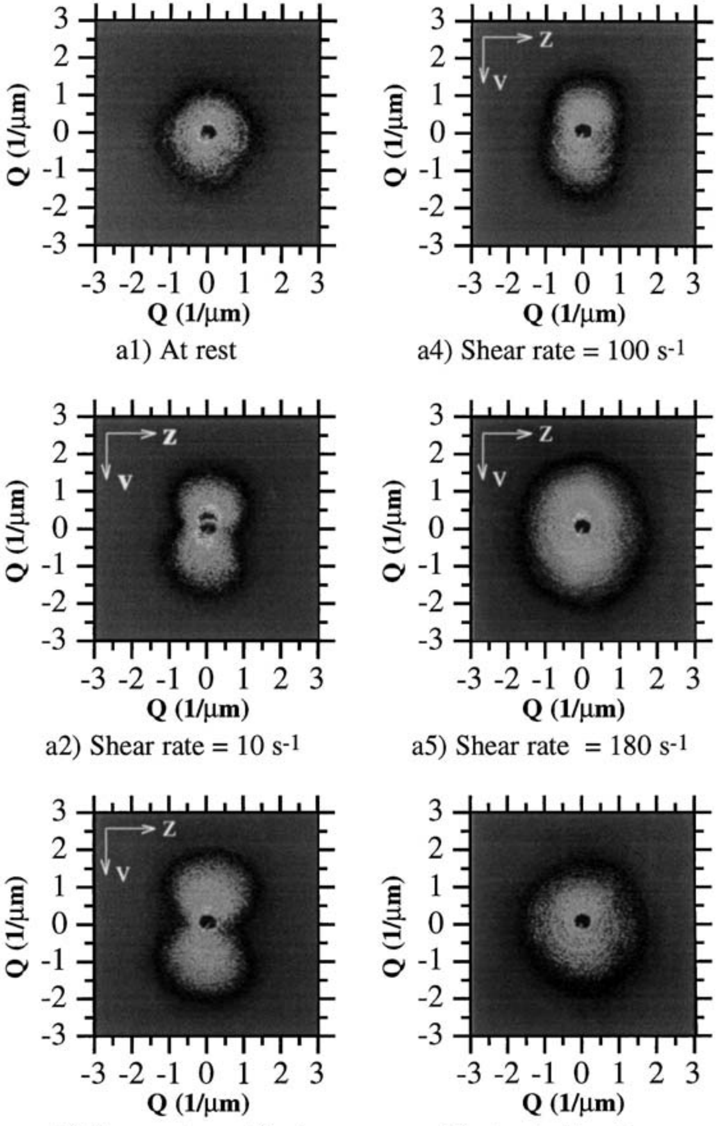
S. Lin-Gibson *et al*, *Phys. Rev. Lett.* **92**, 048302 (2004)

Many Other Systems …

Clay gels under simple shear flow

Gel of 0.56 % XLG
in water (25 ^oC)





a1) At rest

a4) Shear rate = 100 s^{-1}

a2) Shear rate = 10 s^{-1}

a5) Shear rate = 180 s^{-1}

a3) Shear rate = 40 s^{-1}

a6) at rest after shear

Pignon, Magnin, & Piau, *Phys. Rev. Lett.* **79**, 4689 (1997)

Macroscopic Voriticty Rolls (0.1 s^{-1} – sped up x10)

Banding Movie

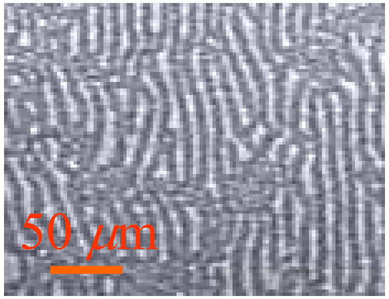
(vorticityrolls.avi)

Width of image = 1 mm

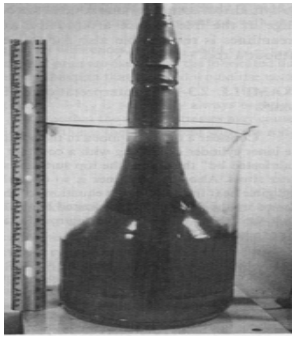
NIST

A Simple Cartoon of a Flow Induced Instability

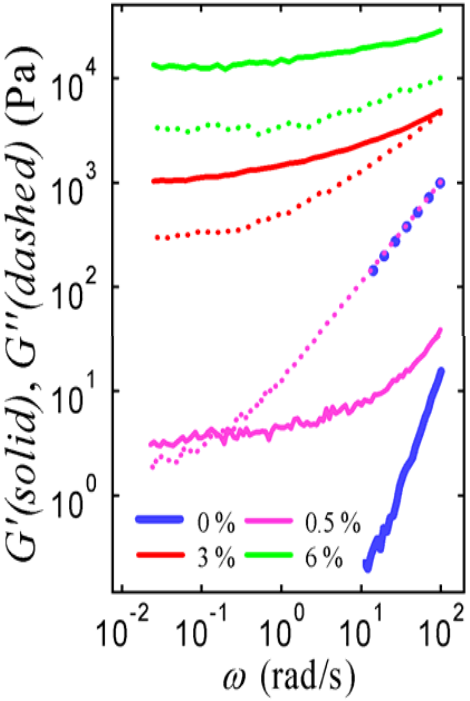
A number of vastly different systems exhibit the same shear-induced pattern because they each represent *elastic* droplets suspended in a *viscous* fluid

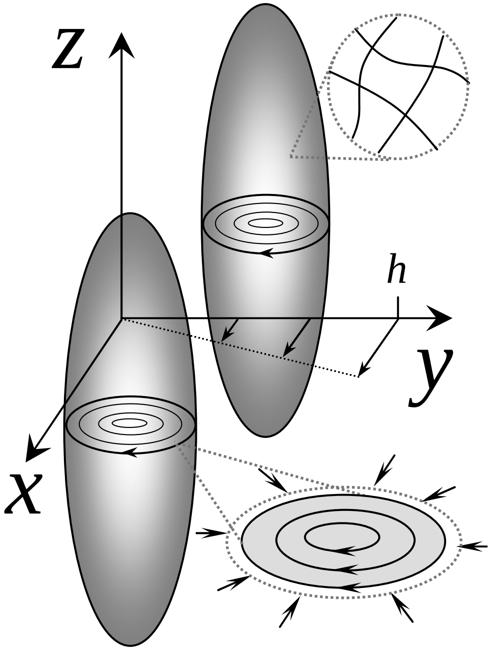


Montesi, Pena, & Pasquali

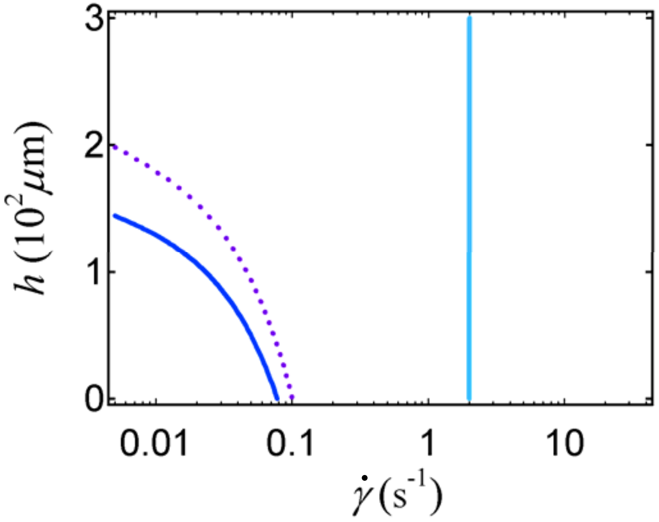


Bird, Armstrong, & Hassager





‘phase diagram’



Generic phase diagram for shear-induced aggregation in semi-dilute non-Brownian MWNT suspensions

Unusual Rheological Signal

$$N_1 = \sigma_{xx} - \sigma_{yy} \qquad N = \sigma_{xx} - \sigma_{zz}$$

[J. M. Dealy, *J. Rheol.* **39**, 253 (1995)]

Growth Cycle

Negative normal stress

Large intrinsic viscosity

Decreasing ϕ

Confinement effects

Vorticity elongation

$Re \approx 10^{-5}$, $Wi \approx 10$

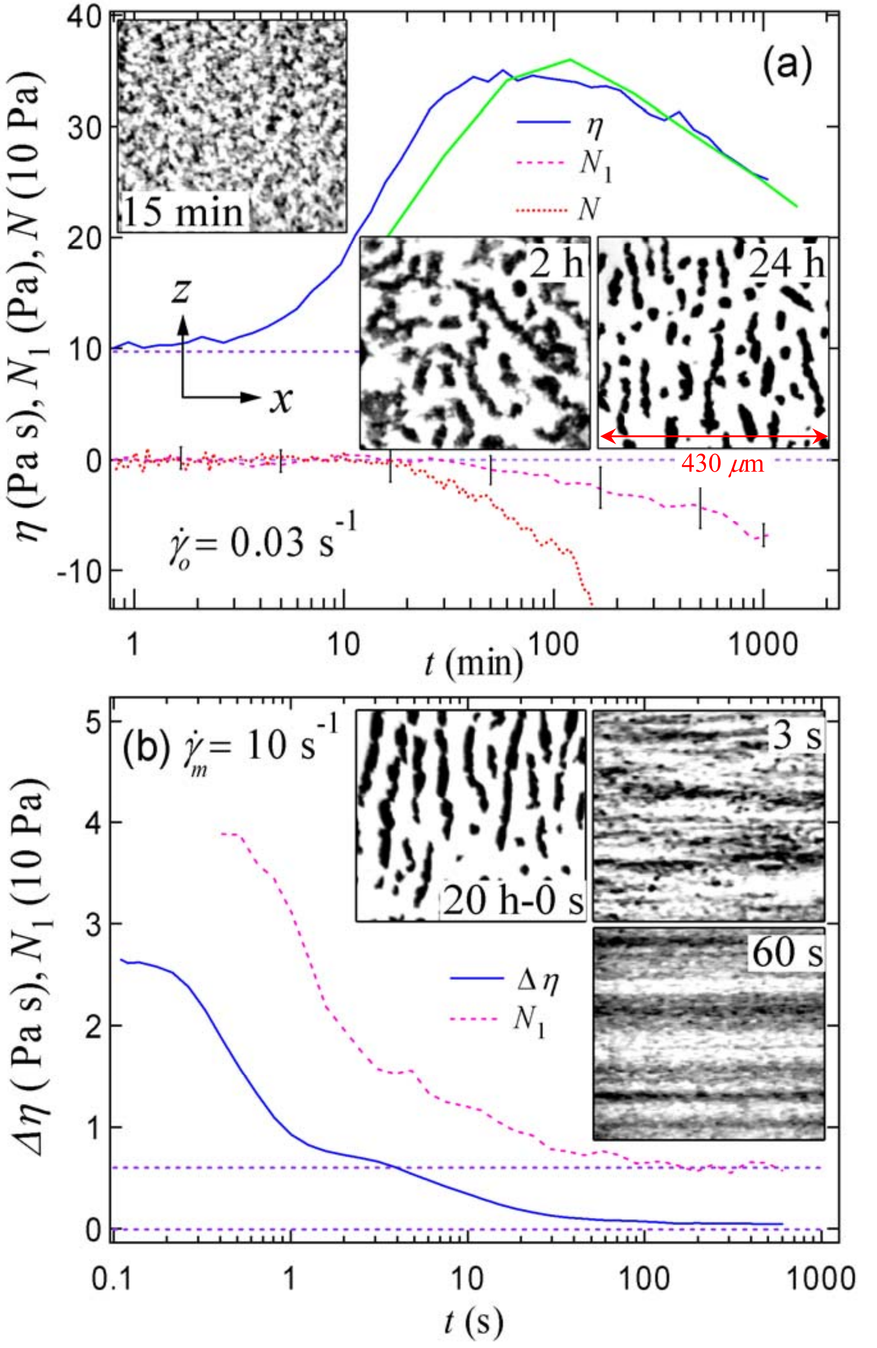
Dissolution Cycle

Flow orientation

Positive normal stress

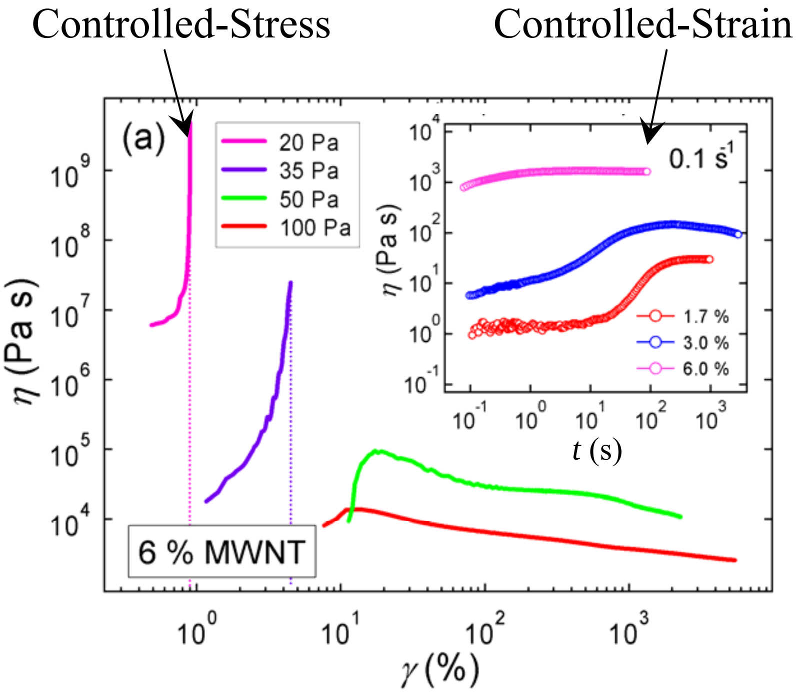
Multi-step process

$Re \approx 10^{-3}$, $Wi < 1$



S. Lin-Gibson *et al*, *Phys. Rev. Lett.* **92**, 048302 (2004)

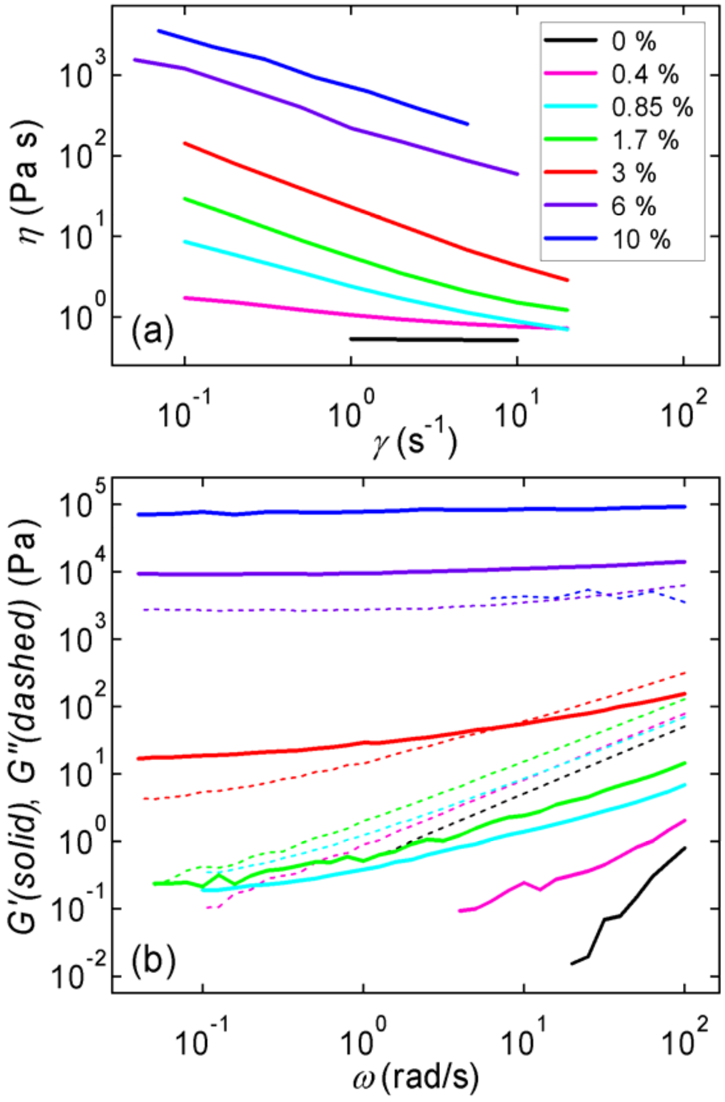
Rheology of Semi-Dilute to Concentrated Suspensions



Controlled-Stress

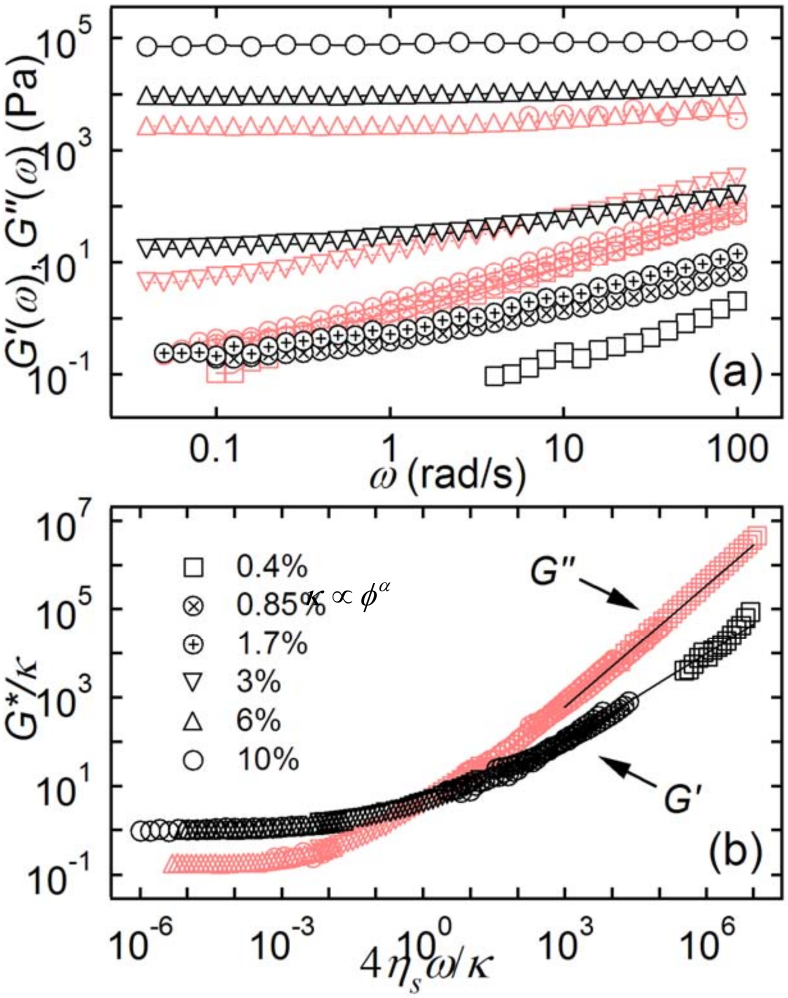
Controlled-Strain

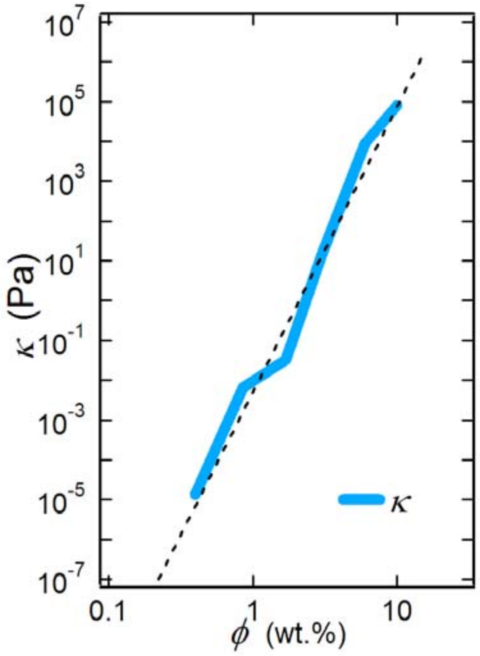
Controlled-Strain



MWNTs in 500 PIB
Cone-and-plate geometry

Scaling of Linear Viscoelasticity with Concentration





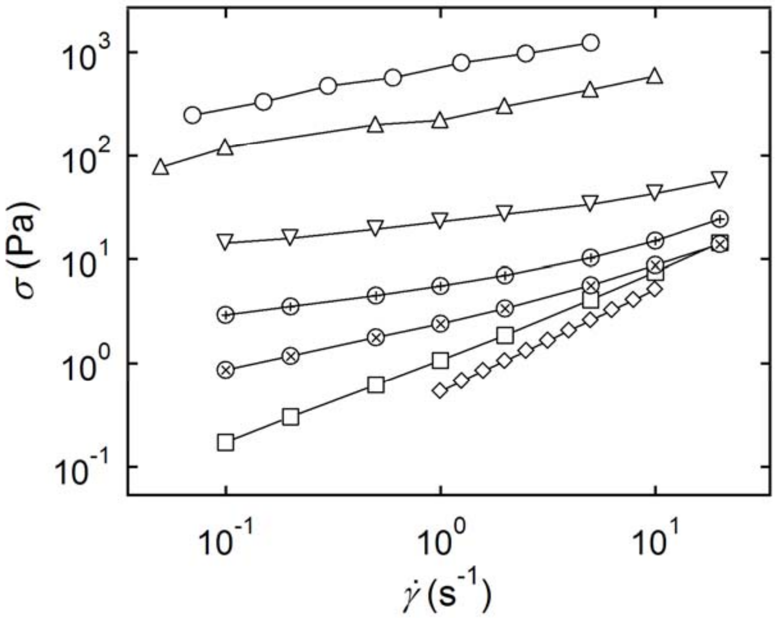
$$\kappa \propto \phi^\alpha$$

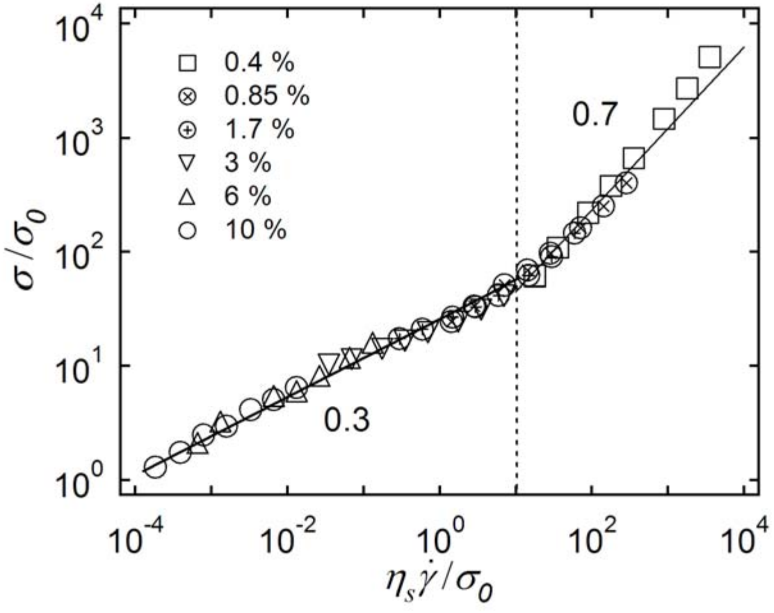
$$\alpha = 7.1$$

E. K. Hobbie and D. J. Fry, *Phys. Rev. Lett.* **97**, 036101 (2006)

Network Yield Stress

Controlled Strain

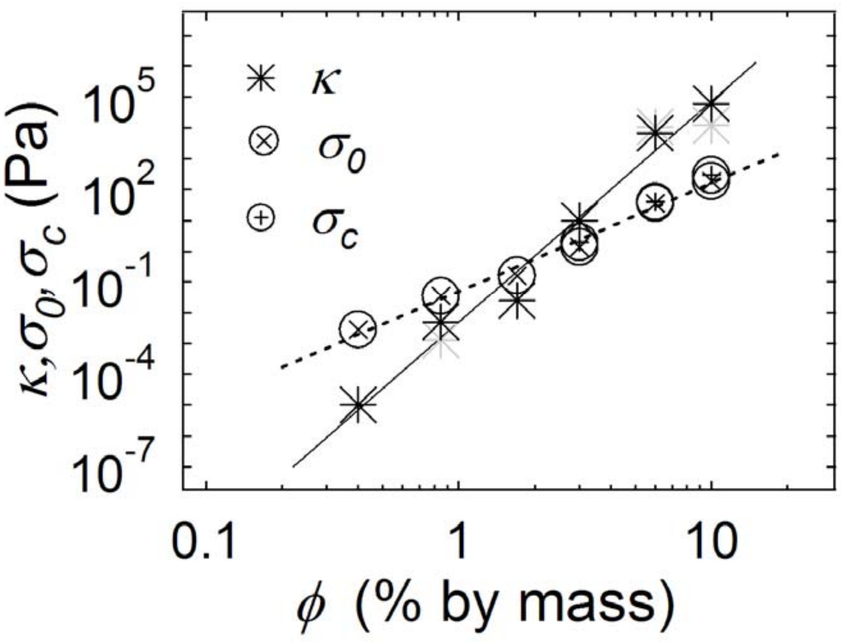




E. K. Hobbie and D. J. Fry, *J. Chem. Phys.* **126**, 124907 (2007)

Relating Shear Modulus and Yield Stress to Network Morphology

W.-H. Shih et al., *Phys. Rev. A* **42**, 4772 (1990).



$$\kappa \propto \phi^{\alpha} \quad \alpha = 7.1$$

$$\sigma_0 \propto \phi^{\beta} \quad \beta = 3.5$$

$$\alpha = \frac{(3+d_b)}{(3-d_f)} \quad \beta = \frac{2}{(3-d_f)}$$

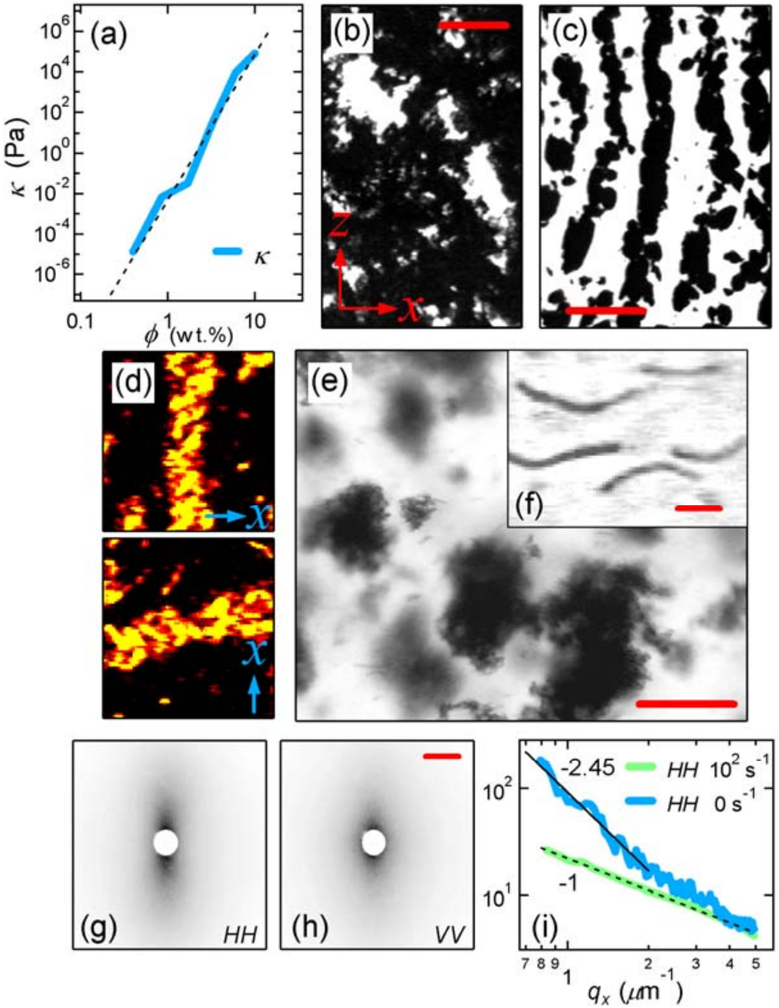
$$d_f \approx 2.45$$
$$d_b \approx 1$$

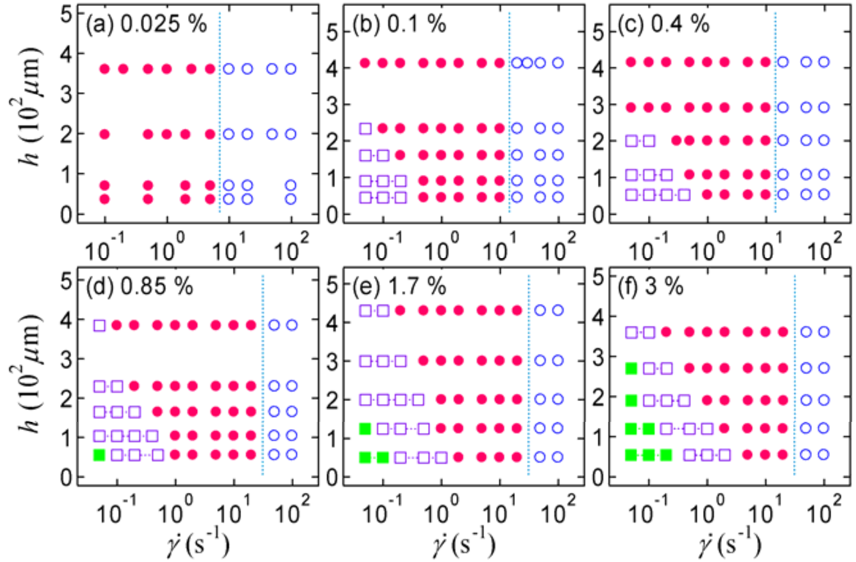
E. K. Hobbie and D. J. Fry, *Phys. Rev. Lett.* **97**, 036101 (2006)

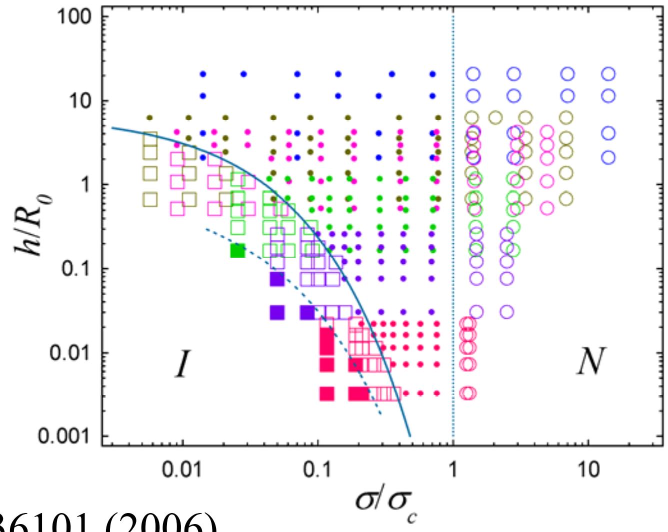
E. K. Hobbie and D. J. Fry, *J. Chem. Phys.* **126**, 124907 (2007)

Processing Phase Diagram

Morphology as a function of concentration, confinement, and strain rate for MWNTs in 500 PIB - controlled strain measurements:

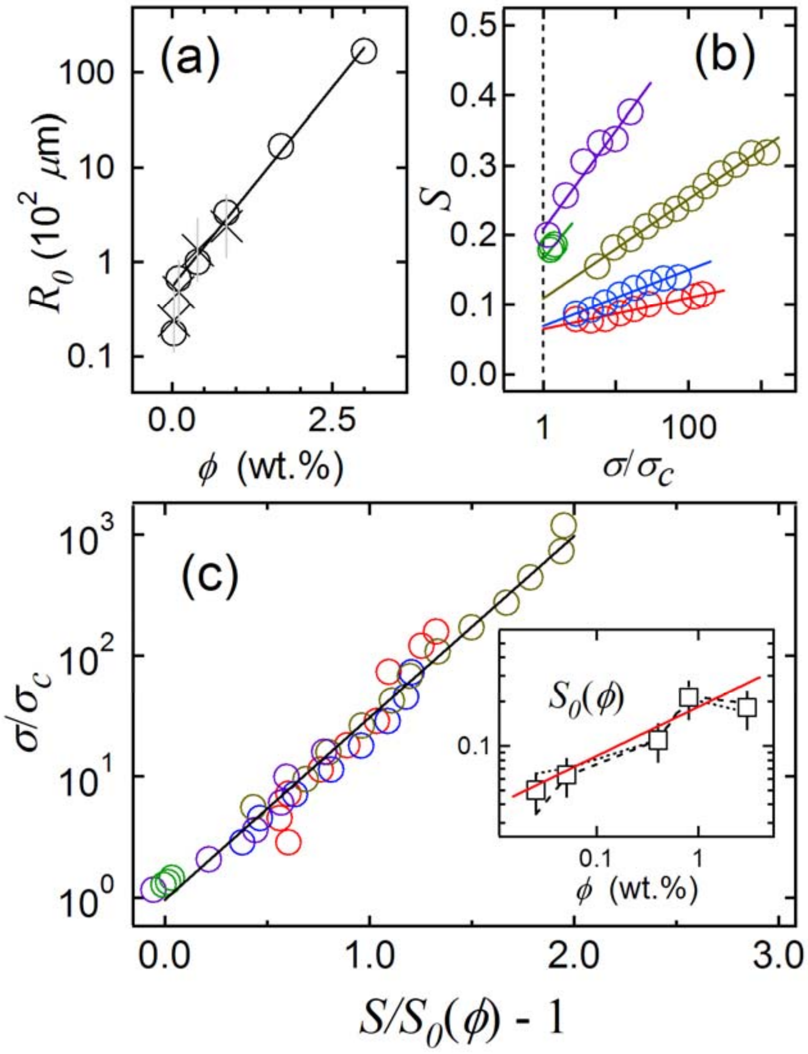






E. K. Hobbie and D. J. Fry, *Phys. Rev. Lett.* **97**, 036101 (2006)

Universal Phase Diagram – Critical Parameters

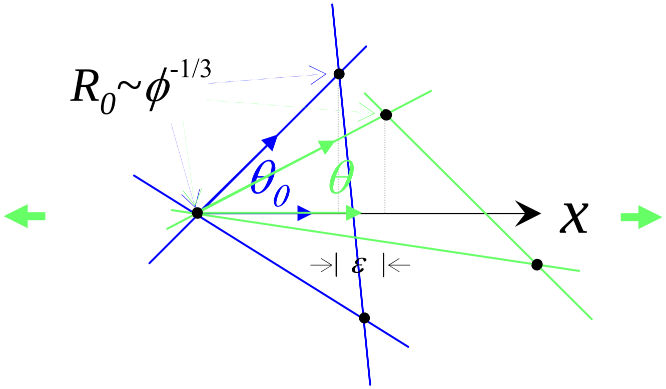


$$\delta R_0 / \delta\phi \propto R_0$$

$$S = \left\langle P_2(\cos\theta) \right\rangle$$

$$\delta S / \delta\dot{\gamma} \propto \tau \propto \dot{\gamma}^{-1}$$

$$\sigma / \sigma_c = \exp\left[a(S - S_0)/S_0\right]$$



$$S \propto \frac{\langle \varepsilon \rangle}{R_0} \propto \phi^{1/3}$$

E. K. Hobbie and D. J. Fry, *Phys. Rev. Lett.* **97**, 036101 (2006)

Thanks!!

D. Fry (NIST – NRC now at JPL)
H. Wang (NIST – now at SUNY)
B. Langhorst (SURF)
S. Lin-Gibson (NIST),
J. Pathak (NIST, now at NRL)
H. Kim (Kyunghee U)
E. Grulke (U Kentucky)
S. Hudson (NIST)