SAND2007-7193C

Rheology of Nanoparticle-Polymer Mixtures

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Sandia National Laboratories

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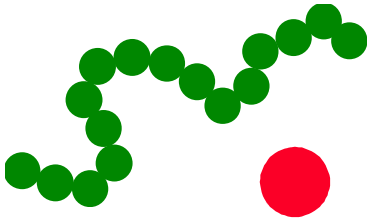
Outline



- overview of suspension viscosity
- data on NP/polymer rheology
- review of polymer melt rheology
- some theoretical speculations

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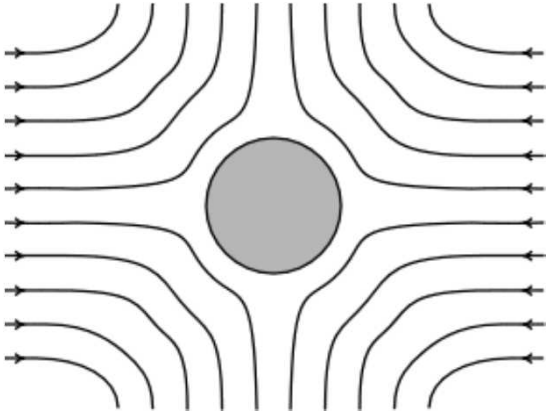
How do NPs affect viscosity?

behavior of dilute suspensions



Einstein (1906):

$$\eta = \eta_s\left(1+\frac{5}{2}\phi\right)$$ good for $\phi < 0.03$

intrinisic viscosity: $$[\eta] = \lim_{\phi\to 0}\left(\frac{\eta-\eta_s}{\phi\eta_s}\right) = \frac{5}{2}$$

two-body interactions
(Batchelor, 1977)

$$\eta = \eta_s\left(1+2.5\phi+6.2\phi^2\right)$$ good for $\phi < 0.10$

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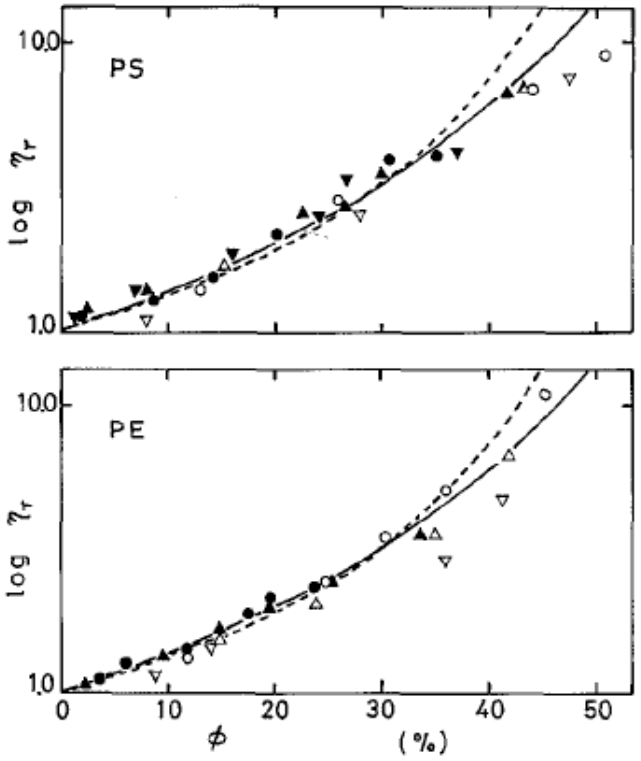
Conventional Filled Polymers

> micron-sized particles

modulus $$\frac{G_c}{G_o} = \left[1 + 1.25\phi/\left(1 - \phi/\phi_m\right)\right]^2$$

$$= 1 + \frac{5}{2}\phi + 4.94\phi^2 + O\left(\phi^3\right)$$

viscosity $$\frac{\eta}{\eta_0} = 1 + \frac{5}{2}\phi + 6.25 k_H \phi^2 + O\left(\phi^3\right)$$



Kitano et al., Rheol. Acta **17**, 149 207 (1978)

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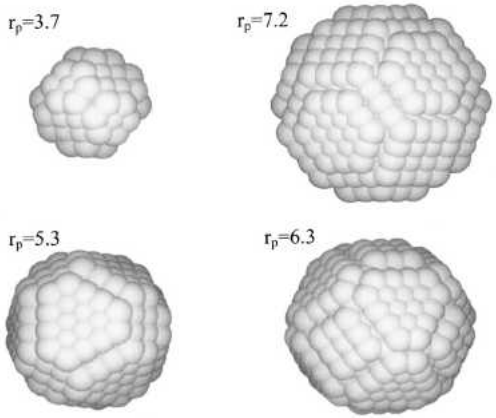
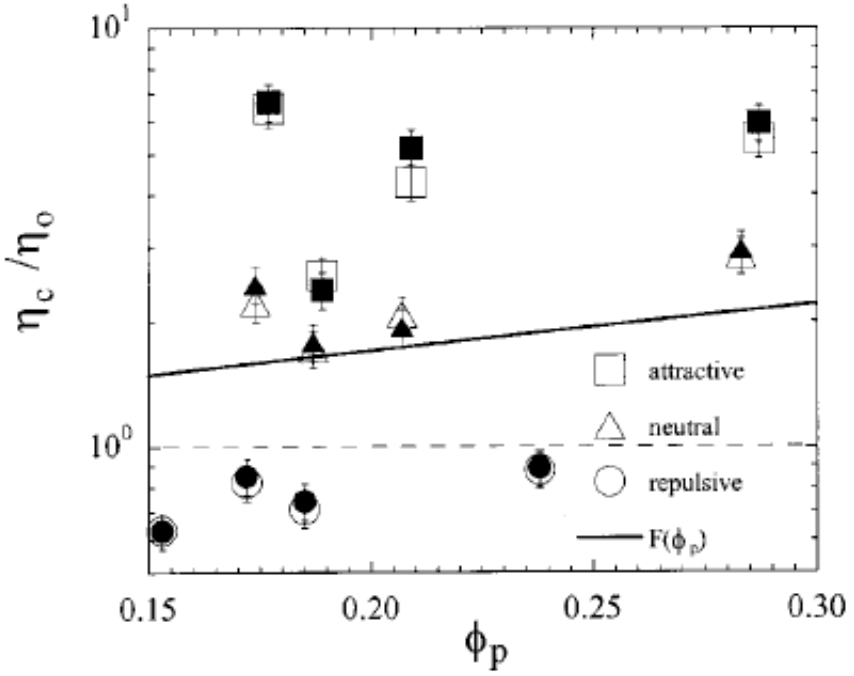
Nanocomposite Simulations



chain length 20
R_g = 2.1



Smith et al., J Chem Phys 117, 9478 (2002)

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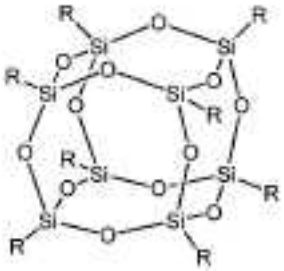
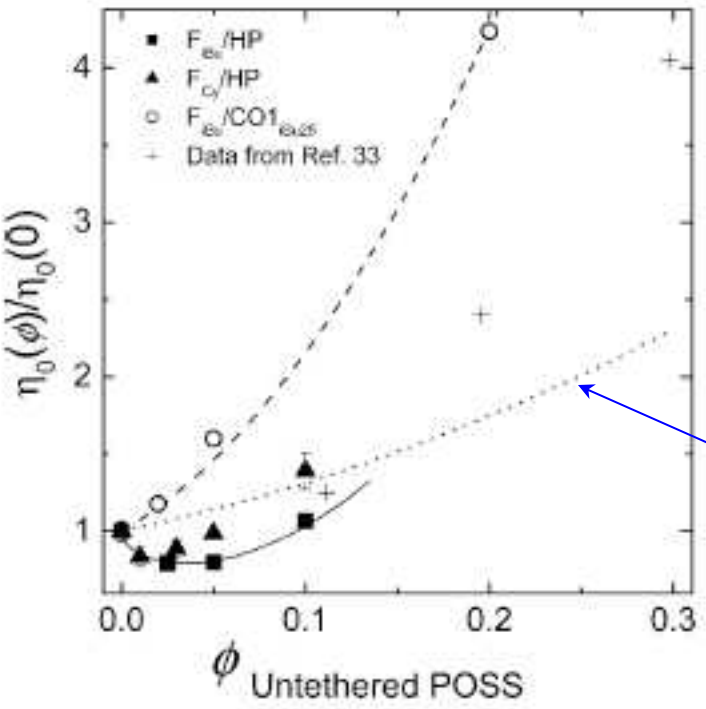
POSS in PMMA



~1.5 nm



$N/N_e = 43$

Einstein-Batchelor

Kopesky et al., Macromolecules 37, 8992 (2004)

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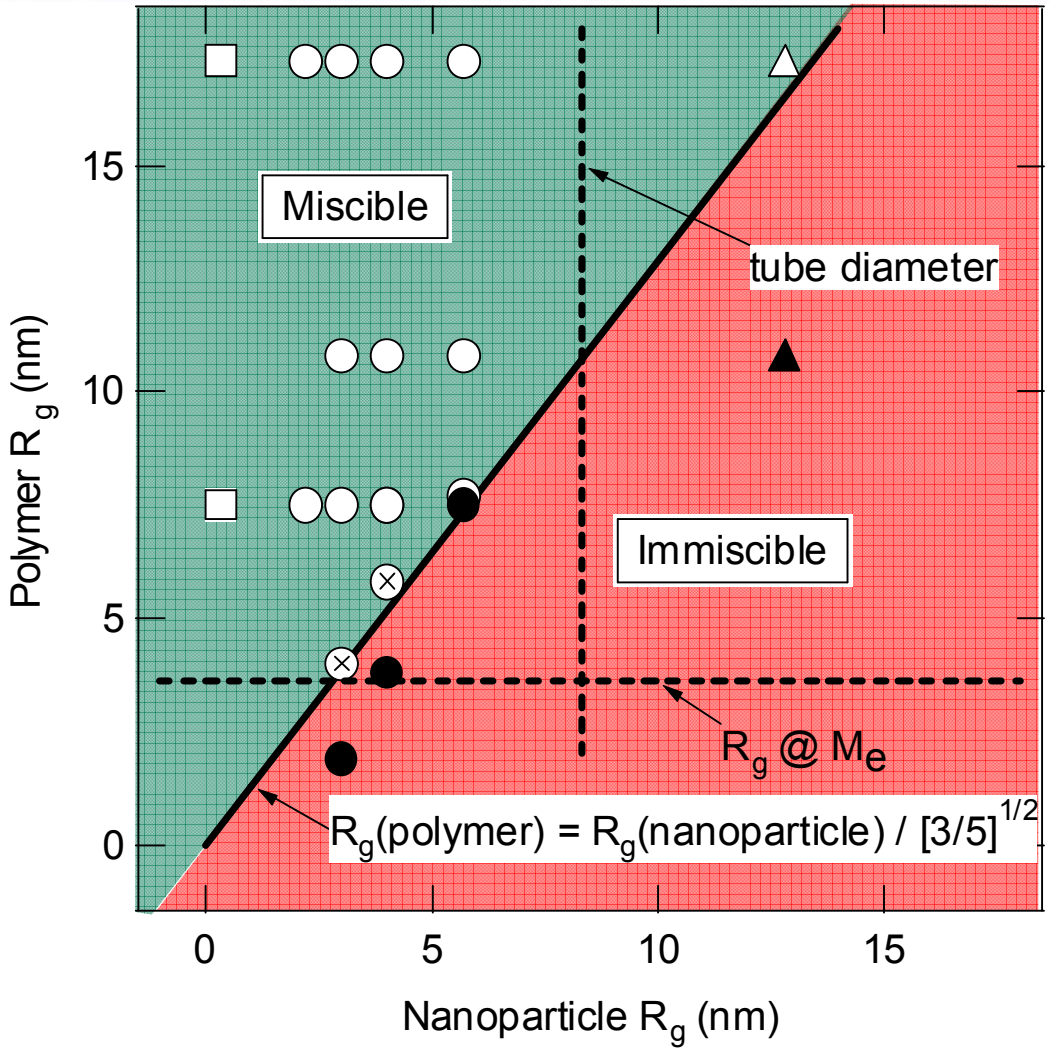
Miscible Polymer/Nanoparticle Blends



linear polystyrene with:

- C60
- polystyrene
- PE dendrimers

Mackay et al., Science 311, 1740 (2006)

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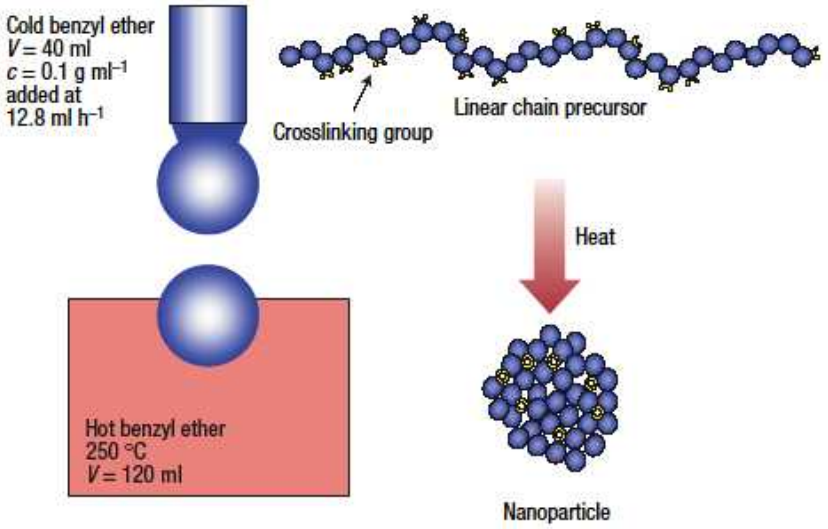
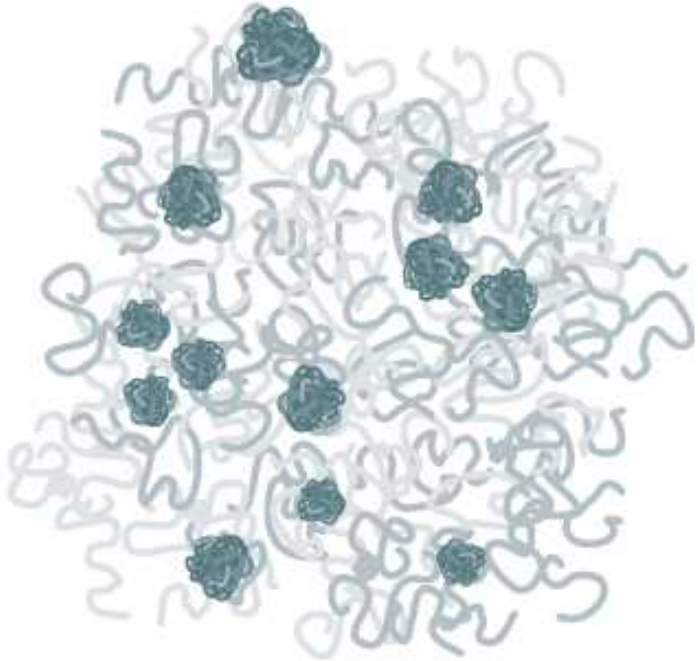
A Model Athermal System: PS NPs in PS

hard-sphere like nanoparticles



mix in melt PS



NPs stay dispersed!
(for $R_{NP} < R_g$)

MICHIGAN STATE UNIVERSITY

Mackay et al., Nature Mat., 2003
E. Harth, J. Am. Chem. Soc., 2002

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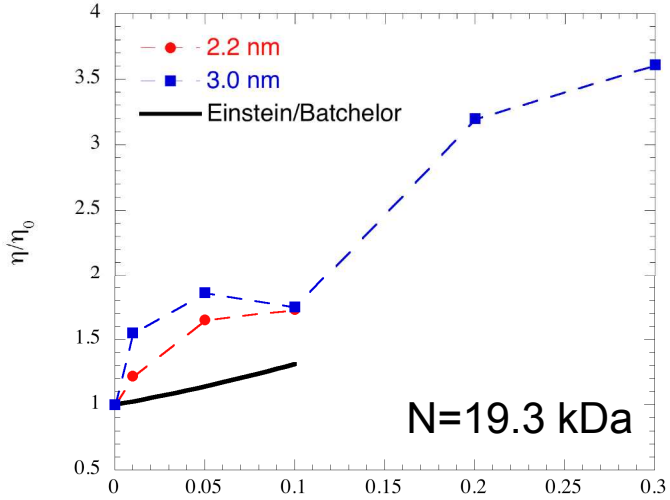
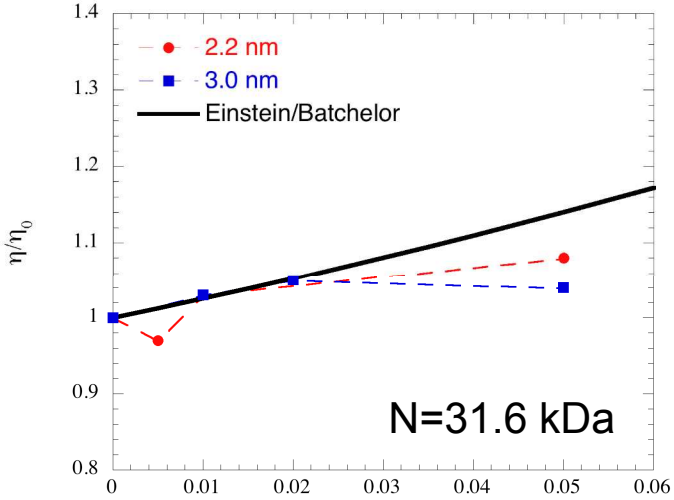
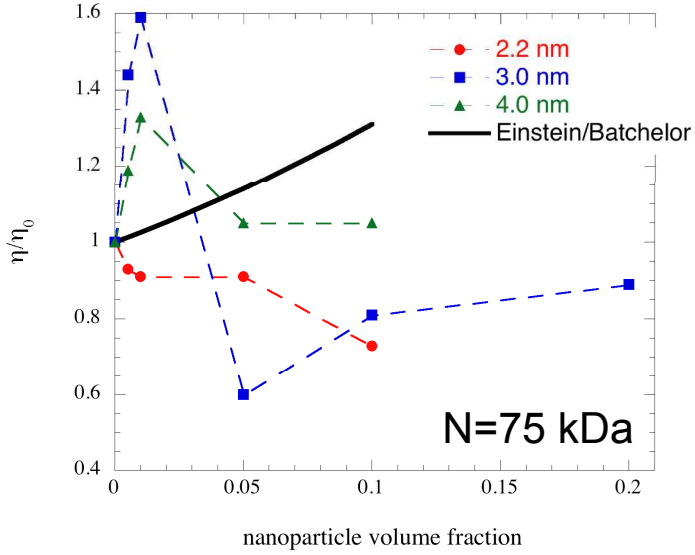
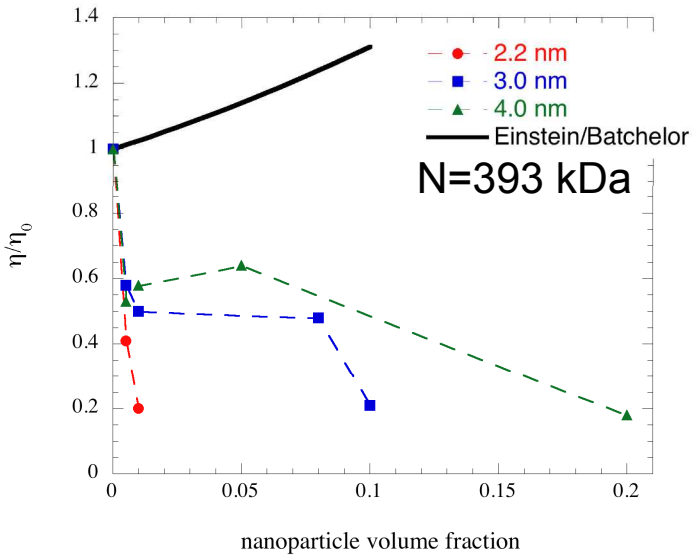
Data: PS Nanoparticles in PS









Tuteja et al., Macromolecules, 38, 8000 (2005).

how can intrinsic viscosity change sign?

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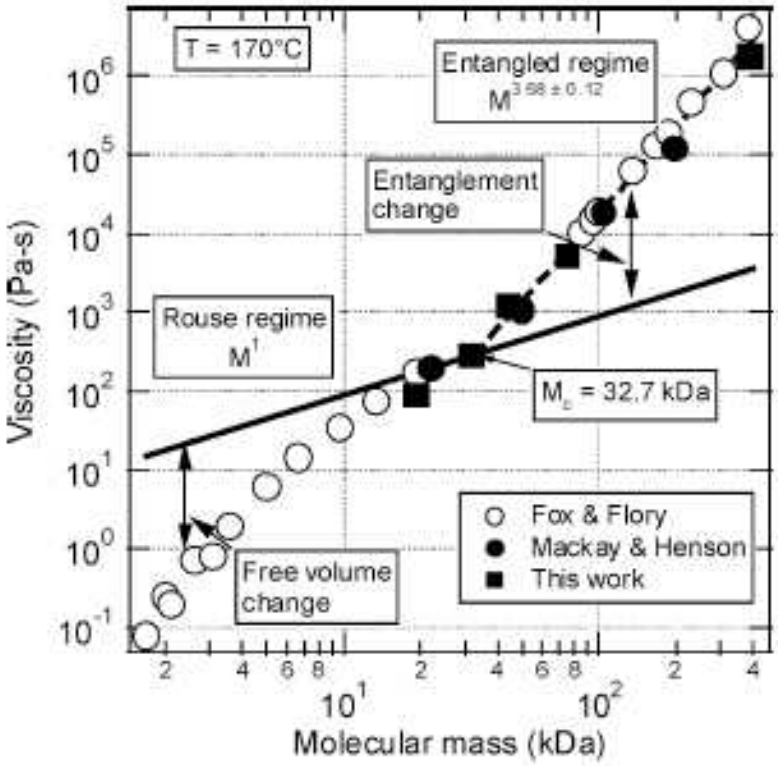
Polymer Viscosity



distinct change in scaling at crossover molecular weight

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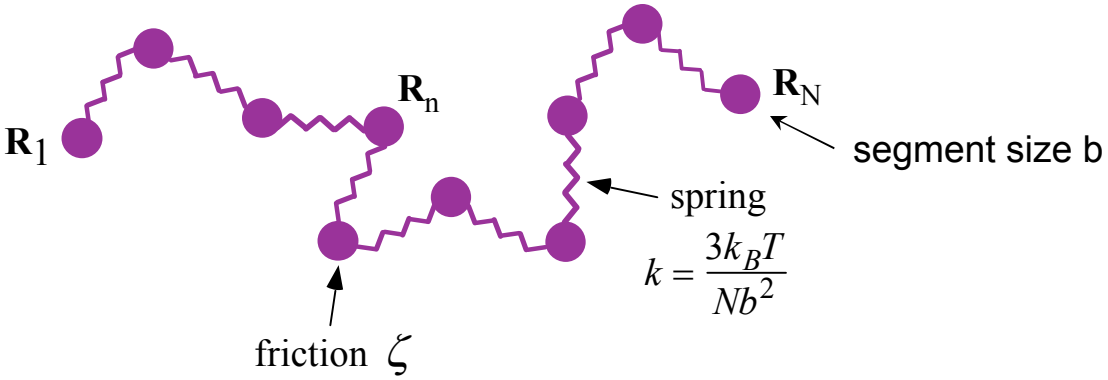
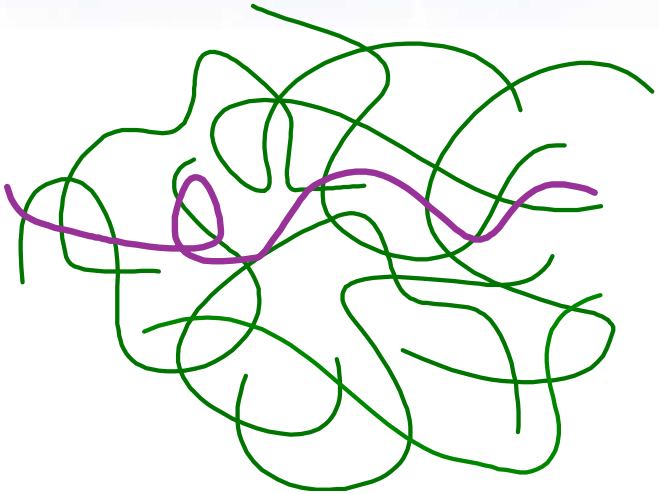
Short Chains: Rouse Model



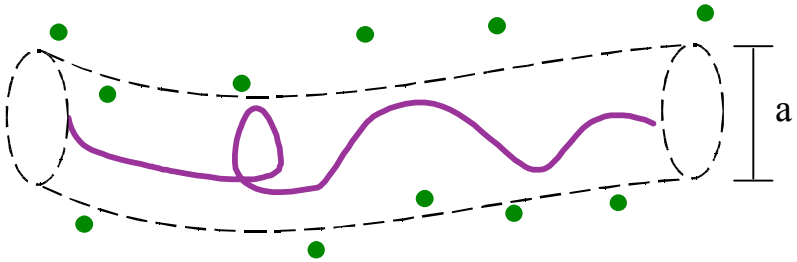
longest relaxation time $$\tau_R = \frac{\zeta N^2 b^2}{3\pi^2 k_B T}$$

viscosity $$\eta \approx G_N^0 \tau_R = \frac{c\zeta b^2}{36} N$$

Entangled Chains: Reptation



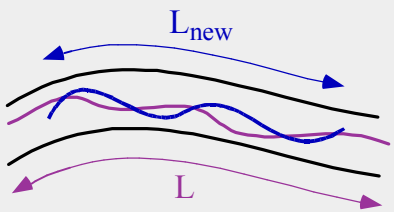
chain confined
in tube



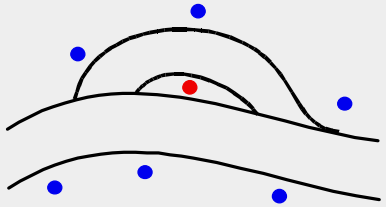
$$D_R = \frac{k_B T}{N\zeta} \qquad \tau_{rep} \approx \frac{L^2}{D_R} \approx \left(\frac{N}{N_e}\right)^3, \quad \eta \approx \left(\frac{N}{N_e}\right)^3$$

reptation is missing:

contour-length
fluctuations



constraint-release effects



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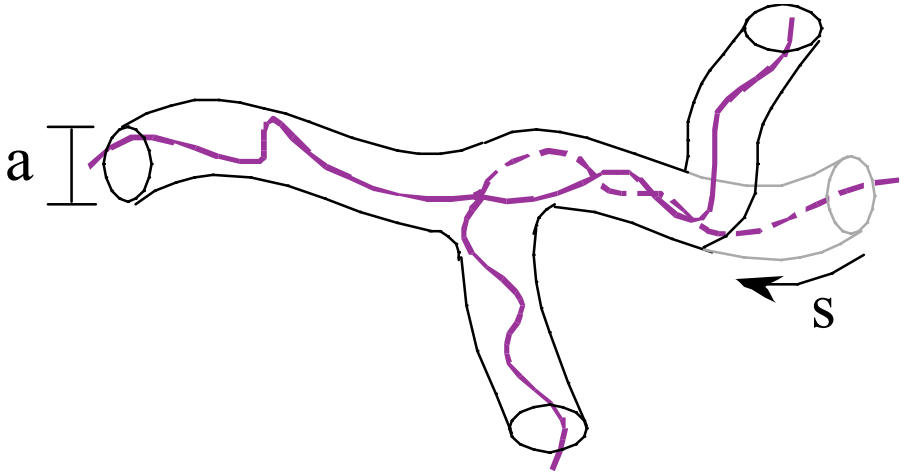
Digression: Star Polymers

arms constrained in tubes

move by arm retraction



moves in potential: $U(s) = \frac{15Ns^2}{8N_e}$ (fixed network)

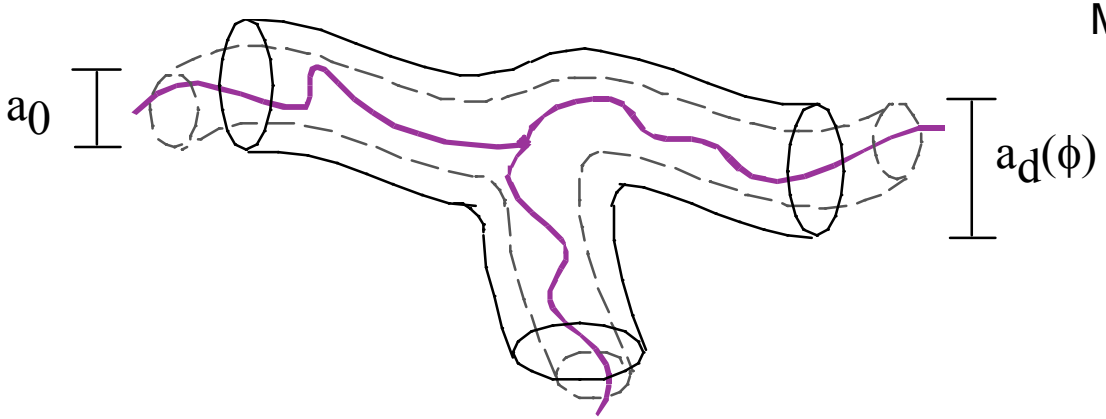
Pearson-Helfand

relaxation time: $\tau(s) = \tau_0 e^{U(s)}$

$\tau(s) \approx \exp\left(\gamma N s^2\right) \Rightarrow$ wide separation in time scales

Dynamic Dilution

Ball and McLeish
Milner and McLeish



at $\tau(s)$: segments with s'<s completely relaxed
segments with s'>s not relaxed

entanglement network dilutes
tube diameter dilates

$$N_e = N_e \big/ (1-s)^{4/3}, \quad a_d = a_0 \big/ (1-s)^{8/3}$$

dd gives new effective potential

$$\tau_a(s) \approx f(N/N_e)\tau_e \exp\left(U_{eff}(N/N_e, s)\right)$$

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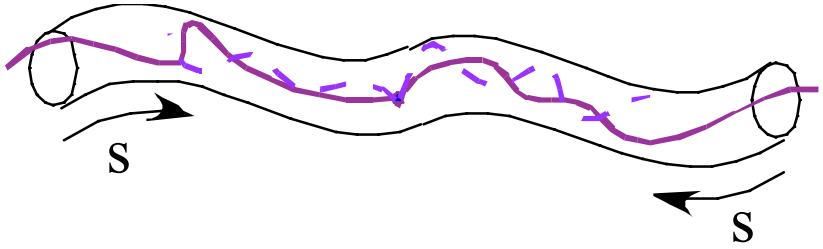
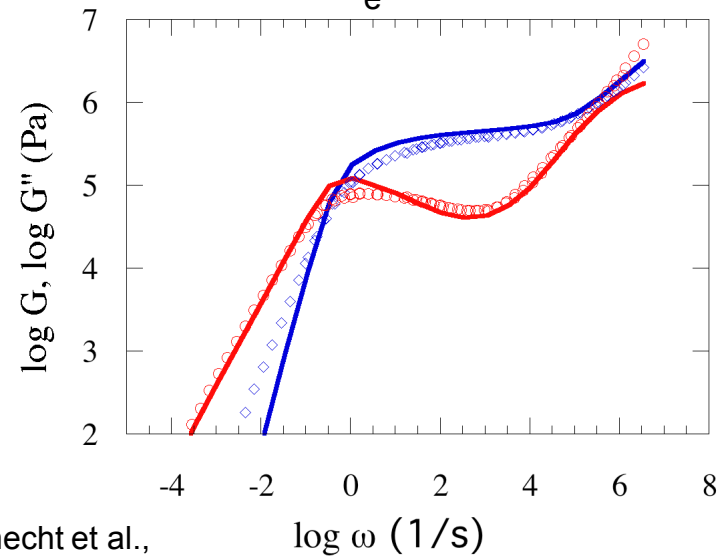
Linear Polymers

contour-length fluctuations:
treat linear chain as 2-armed star

Milner and McLeish



linear PI
$N/N_e = 24.6$



Frischknecht et al.,
Macromolecules (2002)

- ends retract until td, then chain reptates
- fractional distance retracted by τ_d is s_d:

$$\tau_a(s_d) = \tau_d$$

from star theory

- reptation time shorter due to CLF:

$$\tau_d \propto \frac{L^2}{D_R} \propto \frac{\left(N(1-s_d)\right)^2}{1/N} \propto \left(\frac{N}{N_e}\right)^3 (1-s_d)^2$$

- with Doi-Edwards spectrum + Rouse mode get good agreement with experiment

$$\eta \propto (N/N_e)^{3.4}$$

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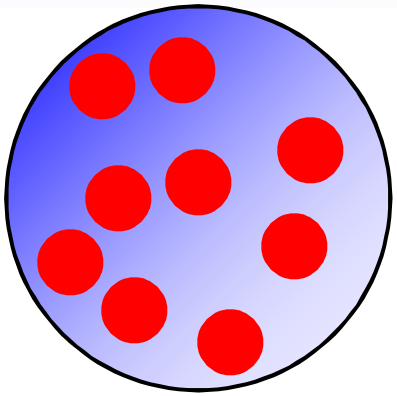
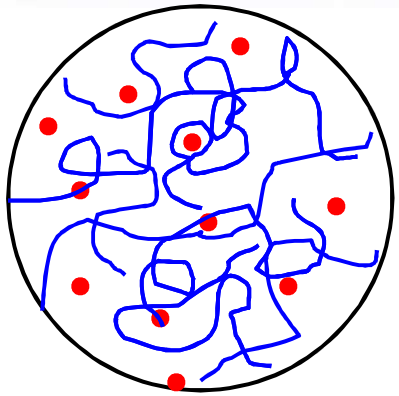
Proposed Mechanism for NP Effects



large particles
low MW matrix

Classical Suspension



small particles
high MW matrix

Nanoparticles dilute entanglements in linear polymer

Idea: *Crossover in* $[\eta]$ *occurs when the viscosity increase due to particles is offset by a decrease in the matrix viscosity due to dilution*

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Dilution of Entangled Chains

assume nanoparticles are like theta solvent
take up space → dilute entanglement network

tube diameter increases:

$$a(\phi) = a_0[1-\phi]^{-2/3}, \quad N_e(\phi) = N_e[1-\phi]^{4/3}$$

reptation time lower
(fewer entanglements)

$$\tau_d = \frac{\zeta b^4 N^3}{\pi^2 kTa^2} = \frac{\zeta b^4 N^3}{\pi^2 kTa_0{}^2}(1-\phi)^{4/3}$$

plateau modulus

$$G_N^0(\phi) = G_N^0(\phi=0)[1-\phi]^{7/3}$$

viscosity:

$$\eta \approx G_N^0 \tau_d$$

$$\eta_0(\phi) = \frac{5\pi^2}{16} G_N^0 \tau_e \left(\frac{N}{N_e}\right)^3 (1-\phi)^{11/3} \qquad N >> N_e$$

Colby & Rubinstein *Macromolecules* **23**, 2753 (1990)

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Simplest Theory

combine dilution + Einstein result

$$\eta = \eta_p(\phi)\left(1+\frac{5}{2}\phi\right)$$

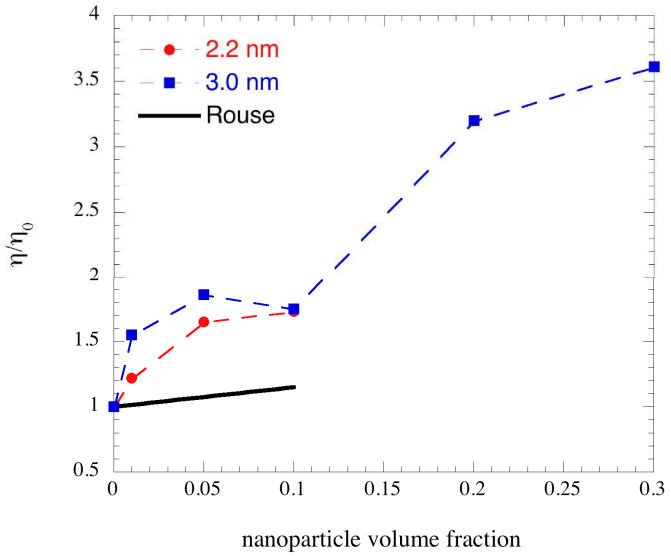
Rouse

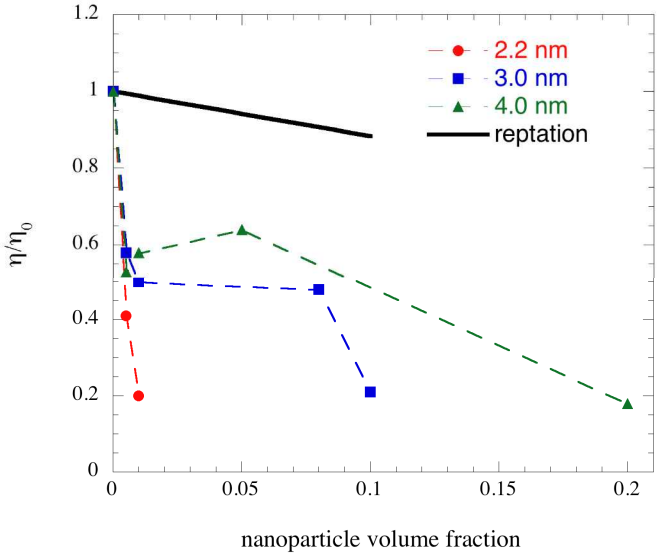
$$\frac{\eta}{\eta_0} = (1-\phi)\left(1+\frac{5}{2}\phi\right) \approx 1+\frac{3}{2}\phi, \quad N < N_e$$

reptation

$$\frac{\eta}{\eta_0} = (1-\phi)^{11/3}\left(1+\frac{5}{2}\phi\right) \approx 1-\frac{7}{6}\phi, \quad N >> N_e$$

change in sign: dilution vs. suspension contribution





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What do the NPs contribute?

can we treat the mixture as a miscible blend?

$$\eta \stackrel{?}{=} \phi\eta_{part} + \eta_0(\phi)$$

low MW - Rouse model

$$\eta_0(\phi) = \frac{\pi^2}{15} G_N^0 \tau_e \left(\frac{N}{N_e}\right)(1-\phi) \qquad N << N_e$$

High MW - Reptation

$$\eta_0(\phi) = \frac{5\pi^2}{16} G_N^0 \tau_e \left(\frac{N}{N_e}\right)^3 (1-\phi)^{11/3} \qquad N >> N_e$$

η_{part} is the viscosity of the nanoparticles at a liquid-like packing fraction

Viscosity of Nanoparticle Mixture

$$\frac{\eta}{\eta_0} = 1 + \phi\left(\frac{\eta_{part}}{\eta_0} - 1\right) + \cdots \qquad N << N_e$$

$$[\eta] = \left(\frac{\eta_{part}}{\eta_0} - 1\right)$$

$$\frac{\eta}{\eta_0} = \frac{\eta_{part}}{\eta_0}\phi + (1-\phi)^{11/3}$$

$$= 1 + \phi\left(\frac{\eta_{part}}{\eta_0} - \frac{11}{3}\right) + \cdots \qquad N >> N_e$$

$$[\eta] = \left(\frac{\eta_{part}}{\eta_0} - \frac{11}{3}\right)$$

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Polymeric Nanoparticles

$$\eta_{part} = \int_0^\infty G(t)dt = G_b \tau_b N_b^{2/D}$$

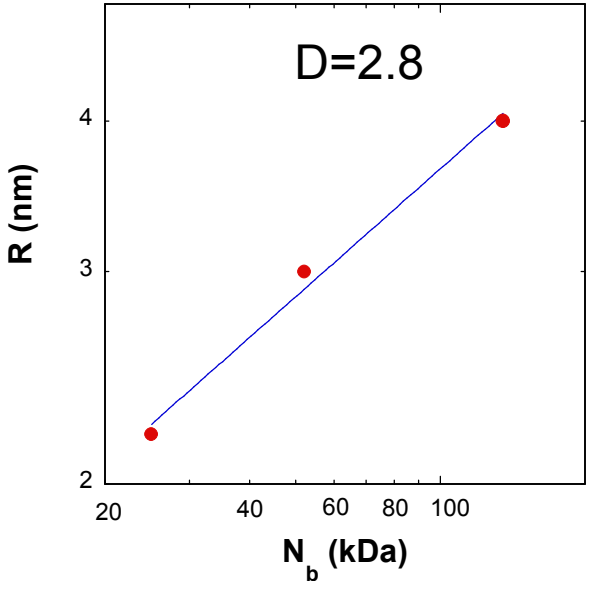
Single chain cluster
D = fractal dimension

Martin, Adolf, Wilcoxon, *Phys. Rev. A* **39**, 1325 (1989)

$$\frac{\eta}{\eta_0} = 1 + \phi\left[\frac{\left(N_b/N_b^*\right)^{2/D}}{\left(N/N_e\right)} - 1\right] \qquad N << N_e$$

$$\frac{\eta}{\eta_0} = \frac{16\left(N_b/N_b^*\right)^{2/D}}{75\left(N/N_e\right)^3}\phi + \left(1-\phi\right)^{11/3}$$

$$= 1 + \phi\left[\frac{16\left(N_b/N_b^*\right)^{2/D}}{75\left(N/N_e\right)^3} - \frac{11}{3}\right] + \cdots \qquad N >> N_e$$



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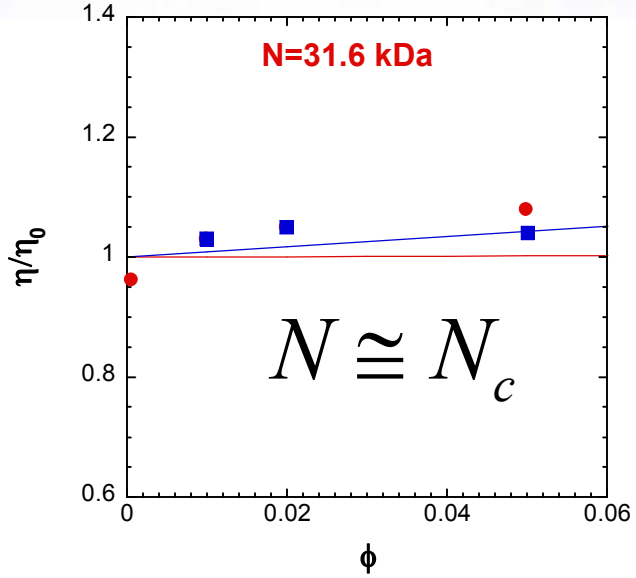
Comparison with Experiments of Tuteja et. al.

N_e=18.1 kDa
N_c= 37 kDa

N_b* =25 kDa

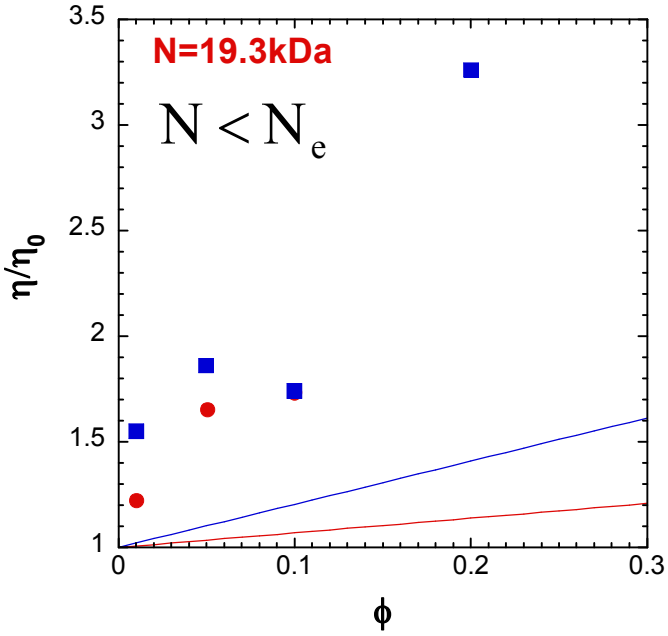
D=2.8

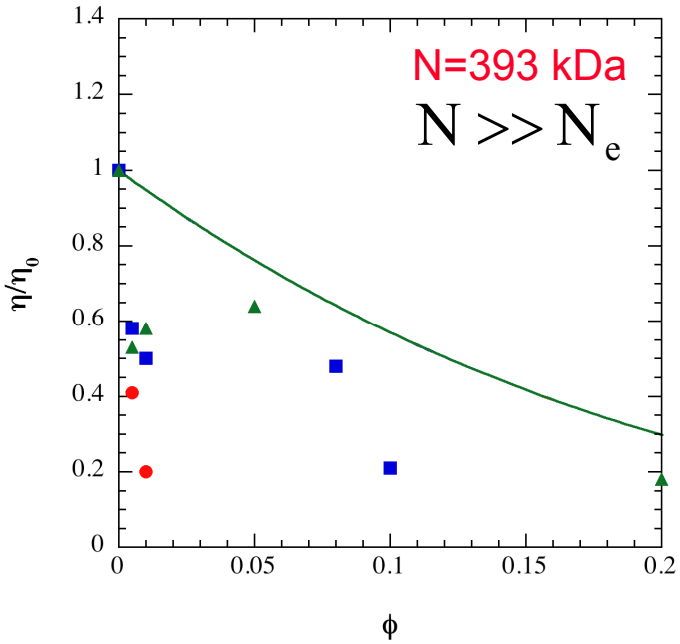


lines - theory

points - experiment

2.2 nm, 3.0 nm, 4.0 nm





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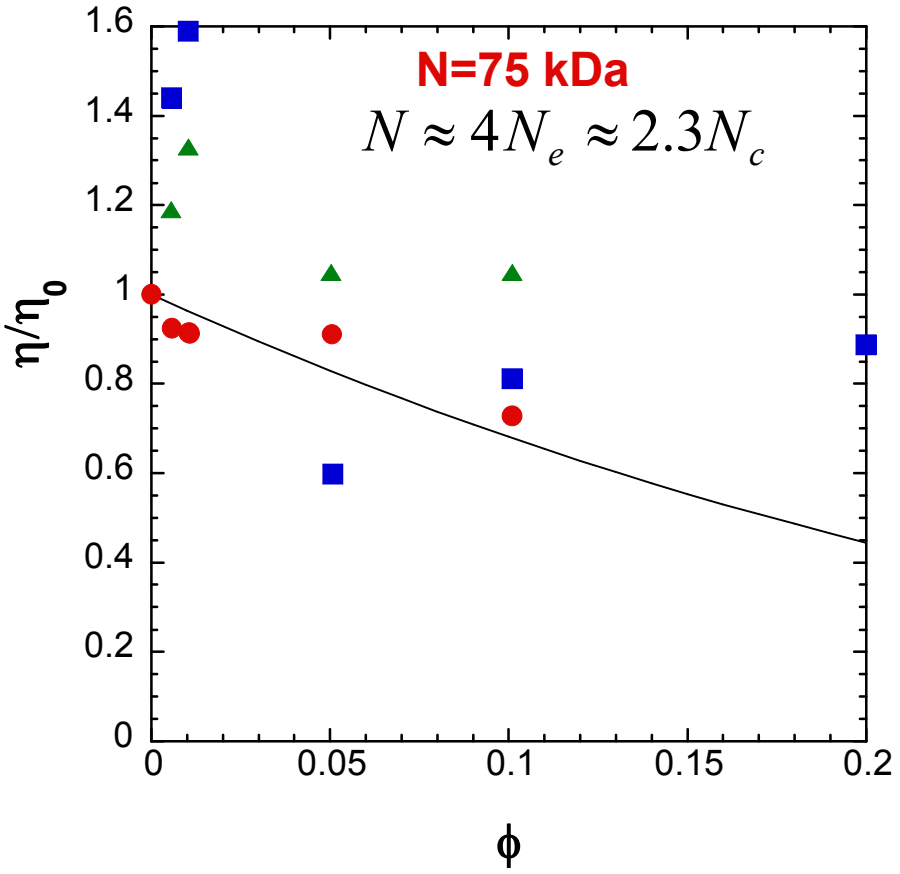
Crossover Regime

Experiments are non-monotonic

Theory predicts monotonically decreasing viscosity



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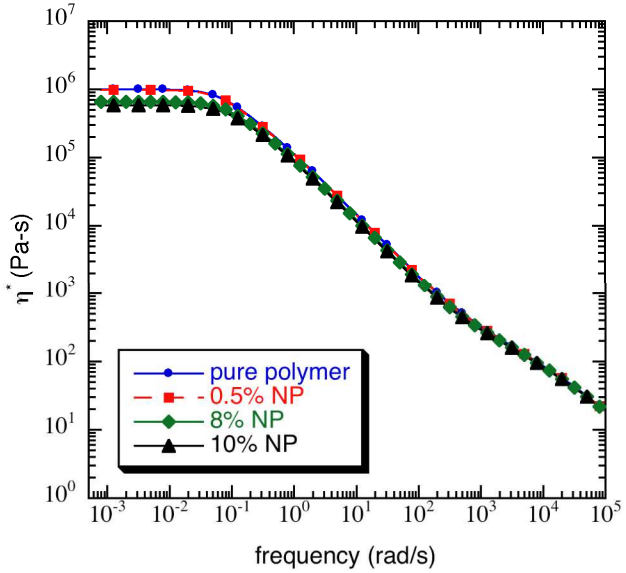
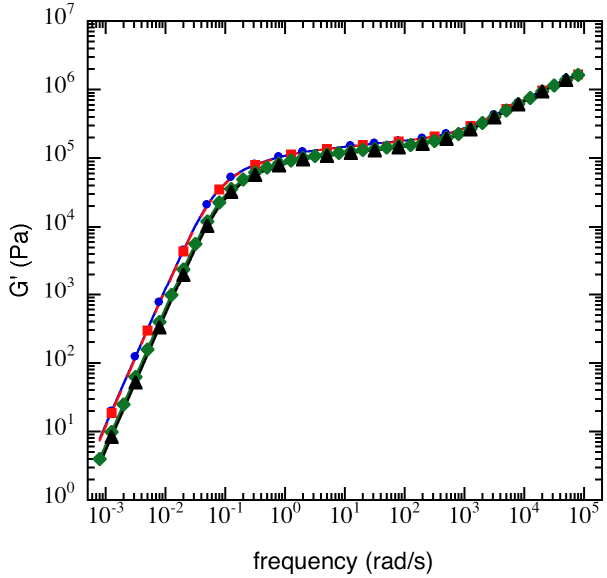
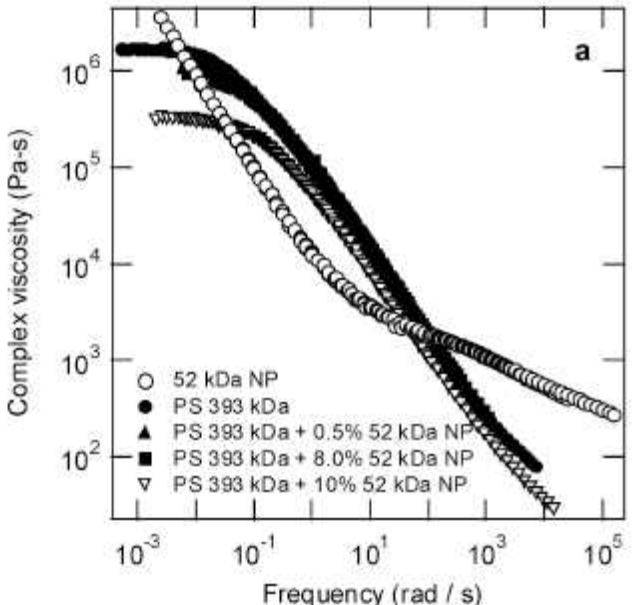
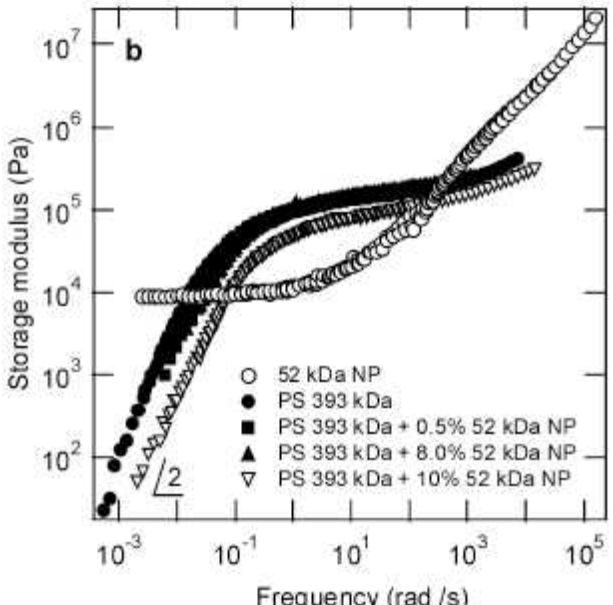
Viscoelasticity









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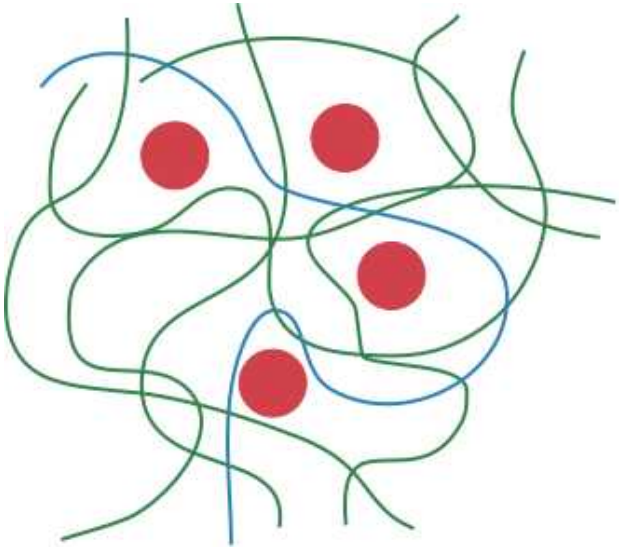
What do the NPs experience?



R < a

to move, nanoparticle doesn't need to move whole chain

feel viscosity of $n = R^2/b^2$ monomers

$$\eta_{Rouse} \cong \eta_1 n \cong \eta_1 \frac{R^2}{b^2}$$

$$drag = R\eta_{Rouse} = \zeta \frac{R^3}{b^3}$$

drag depends on particle size for small particles

Brochard Wyart and de Gennes, Eur. Phys. J. E, 1, 93 (2000)

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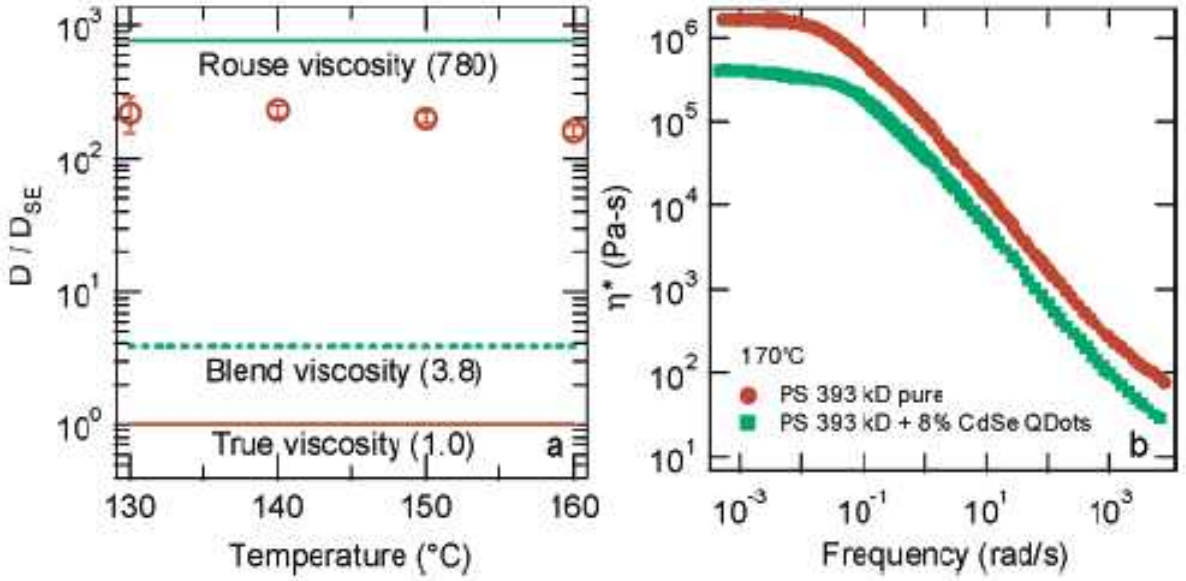
Nanoparticle Diffusion: Data

CdSe quantum dots in PS



$$D_{SE} = k_B T / 6\pi\eta R$$

NPs don't feel macroscopic viscosity

Tuteja et al., Nano Lett **7**,1276 (2007)

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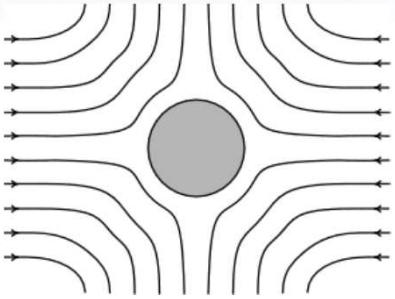
Dilute Limit Hydrodynamics



length-scale dependent polymer viscosity

$$\eta(q) \approx \eta_0 \frac{1}{1+(qR_g)^2}$$

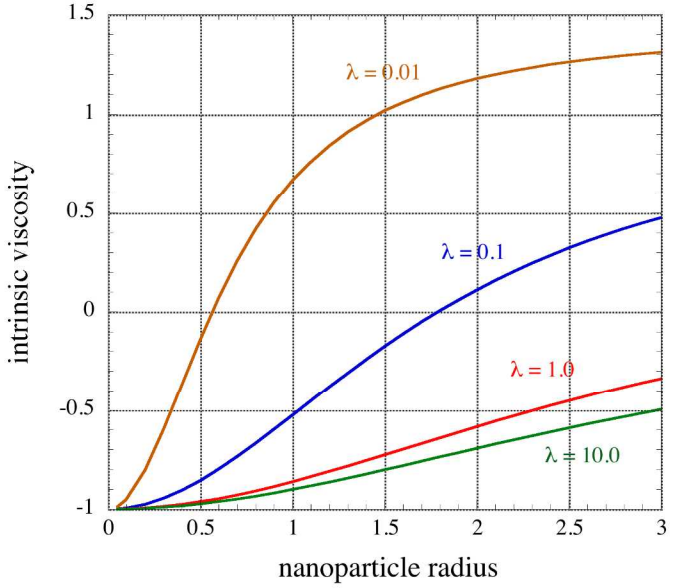
solve hydrodynamics of NP in melt

intrinsic viscosity $$[\eta] = \frac{\eta - \eta_0}{\phi \eta_0(\phi)} = \frac{5+10\lambda}{2\left(1+5\lambda+48\lambda(R_g/R)^2\right)}$$

λ = slip length

Rouse $$[\eta] = \frac{3-96\lambda(R_g/R)^2}{2\left(1+5\lambda+48\lambda(R_g/R)^2\right)}$$

$$[\eta] \to -1 \quad \text{for } R << R_g$$



Ganesan et al., J. Chem. Phys. 124, 221102 (2006)

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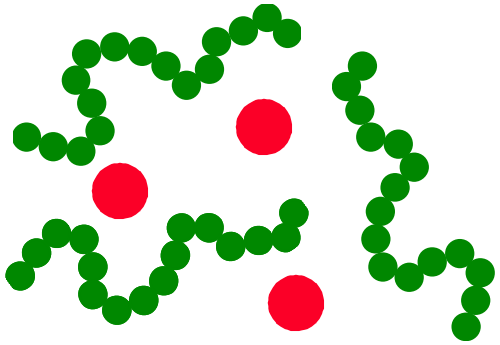
A better mixing rule?

mixing rule for friction coefficient at Rouse level?



drag on NPs $R\eta_{Rouse} = \zeta \frac{R^3}{b^3}$

drag per Rouse bead $\zeta \frac{R}{b}$

$$\zeta(\phi) \stackrel{?}{=} \zeta_0(1-\phi) + \zeta_0 \frac{R}{b}$$

Rouse scaling $[\eta] = \frac{R}{b} - 2$

reptation scaling $[\eta] = \frac{R}{b} - \frac{14}{3}$

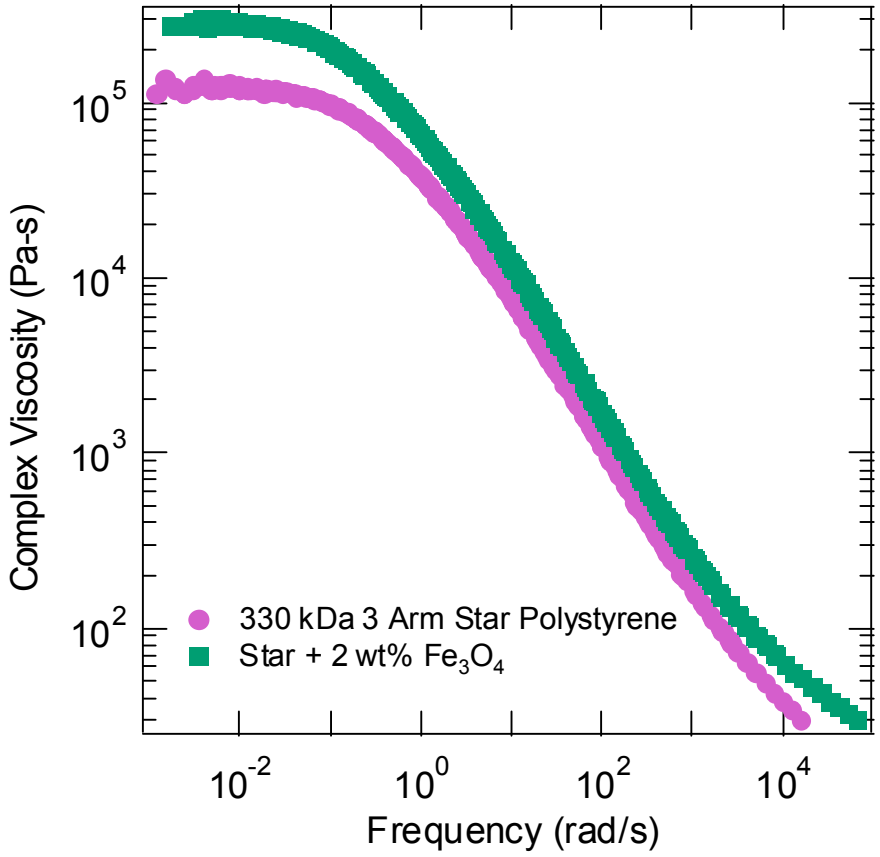
depend on NP size

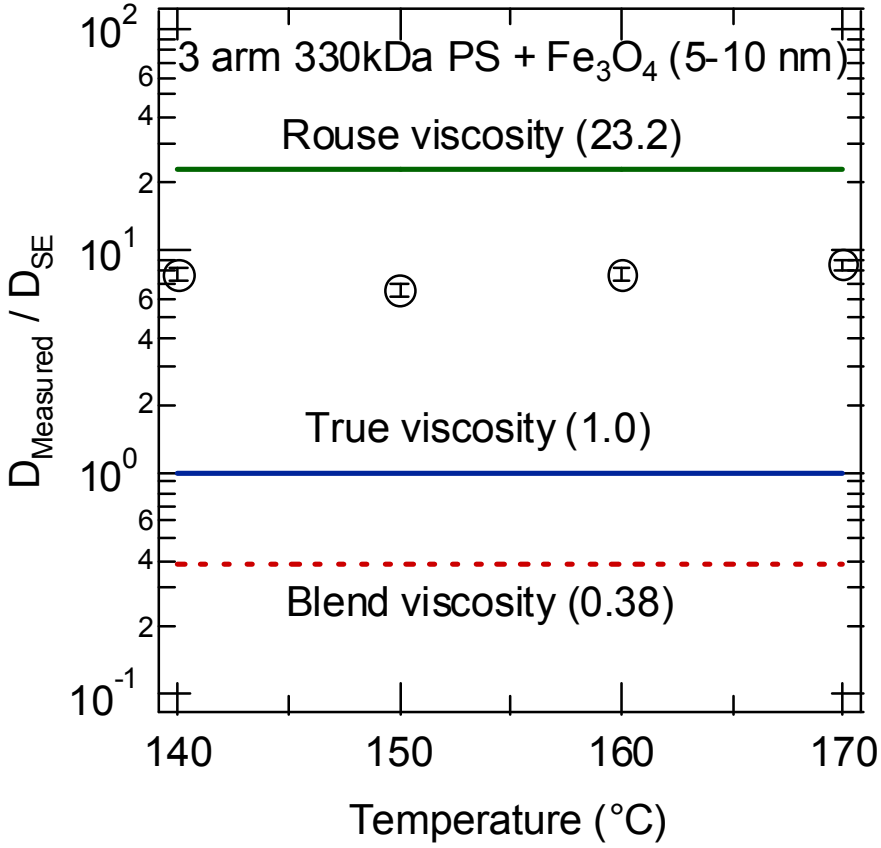
slows down Rouse relaxation
still have dilution effect in engtangled chains

how incorporate in detailed molecular model?

A further puzzle: star polymers

magnetite NPs, R ≈ 5-10 nm
in 3-arm PS star, N_a = 110 kDa





but viscosity goes down for 110kDa linear!

Mackay et al., 2007

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What's happening?

how can viscosity go down for linears, up for stars??

recall: for stars $\eta \propto \tau_a \propto \exp(\nu N / N_e)$

if NPs dilute entanglement network
(or release constraints) $N_e(\phi) = N_e(1-\phi)^{-4/3}$

then NPs should also speed up star dynamics

BUT:

star arms fairly short:

110 kDa: $N_a/N_e = 6$

dilution mechanism different somehow?

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Summary

- small NPs dramatically alter polymer viscosity
  - $[\eta] < 0$ for N>>Ne
  - seems particle-size dependent
- can get change in sign of $[\eta]$ from simple theories
  - dilution of entanglement network
  - NPs only feel local viscosity
- something different in stars?
- quantitative theory still elusive

Thanks

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