Department of Chemical Engineering
University of Texas@Austin

Origins of Mechanical and Rheological Properties of Polymer Nanocomposites

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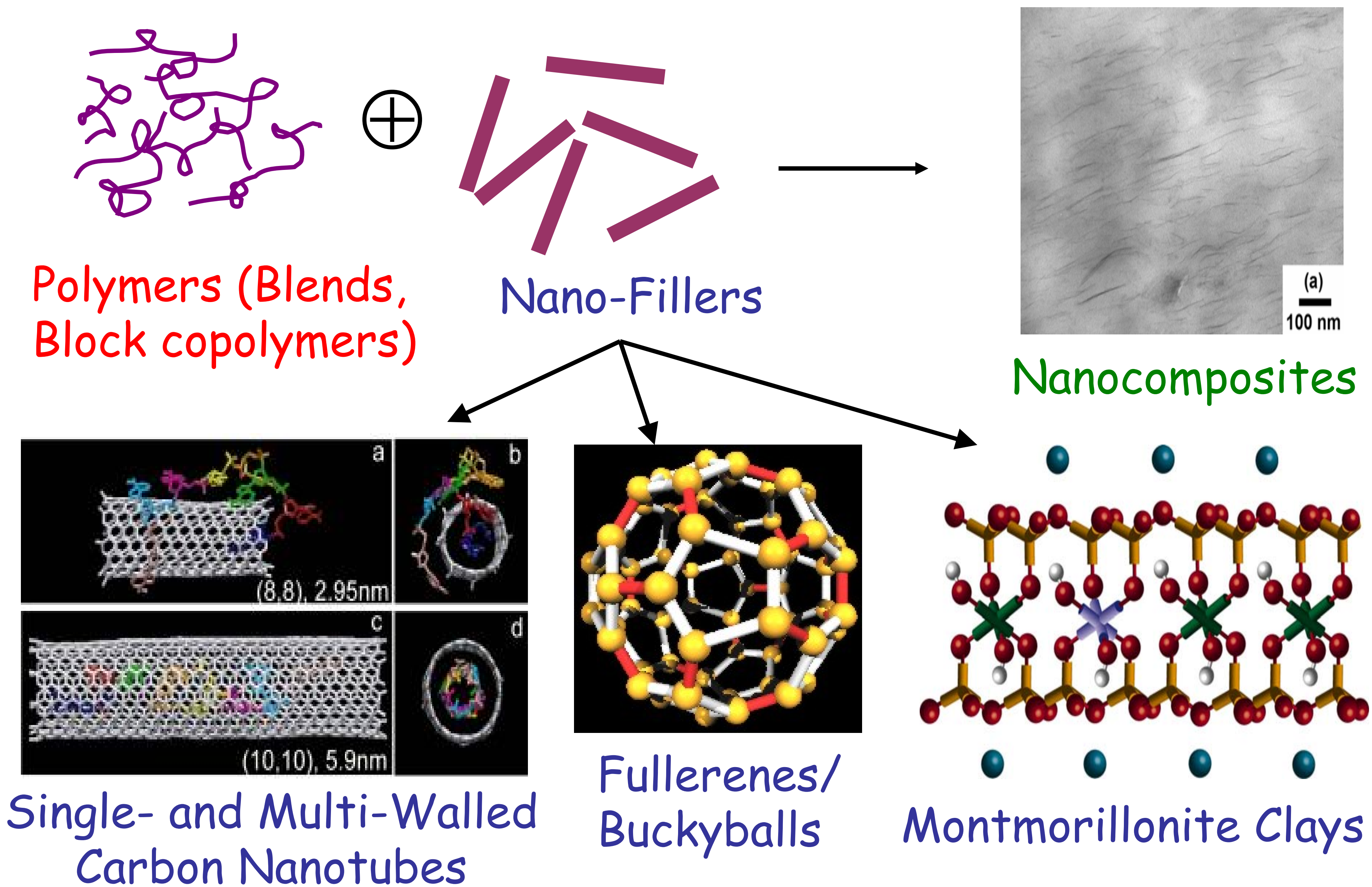
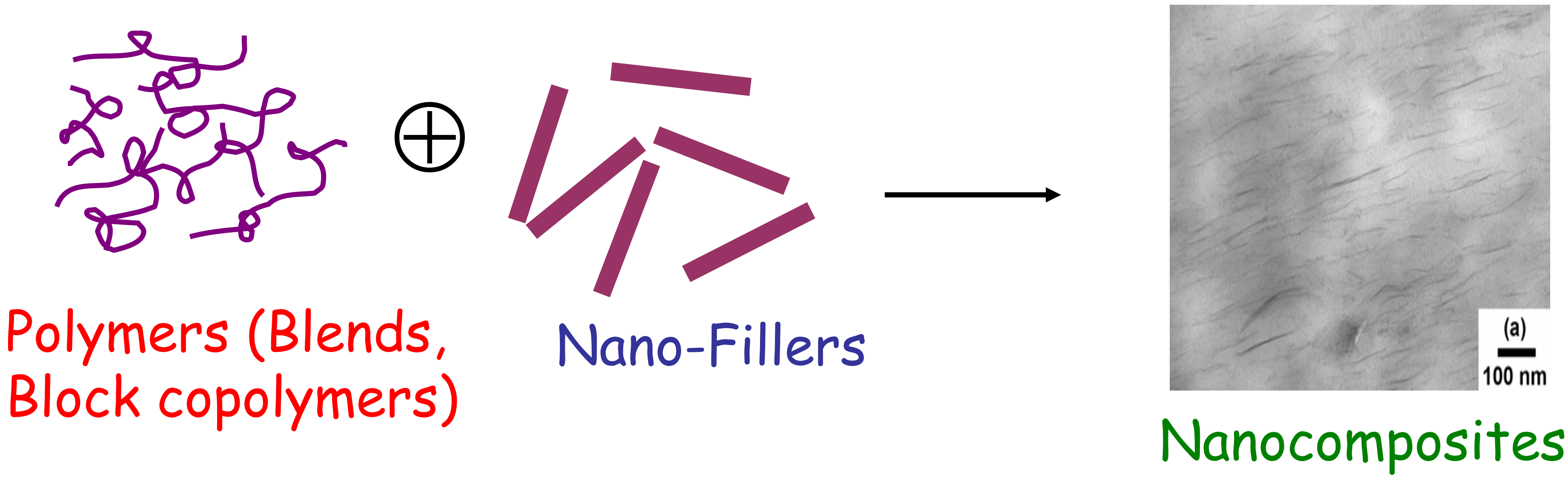
$$$: NSF DMR, Welch Foundation

Megha Surve, Victor Pryamitsyn

Polymer Nanocomposites



Polymer Nanocomposites



- Processing nanocomposites requires understanding their flow behavior.

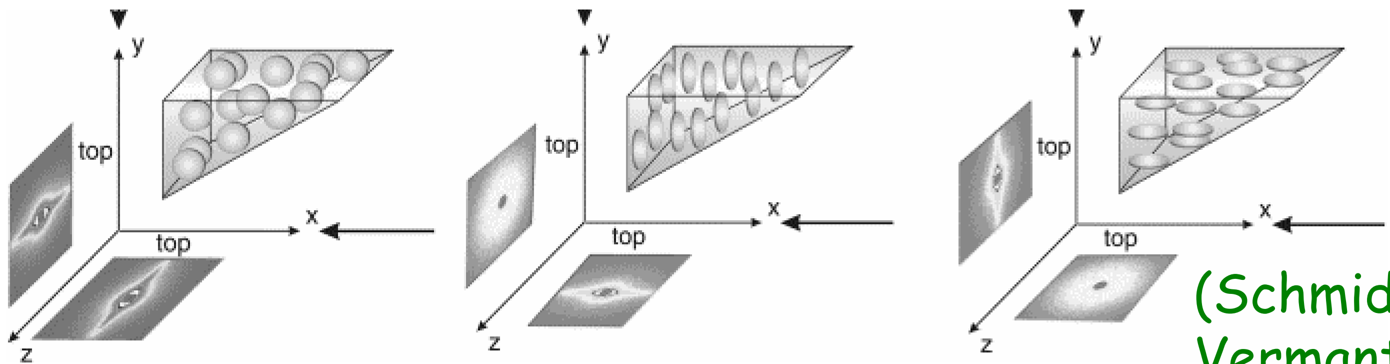
- Flow fields provide a versatile approach for controlling dispersions of nanocomposites.

Challenges

• Objective: To model the flow dynamics and structure of nanoparticle-polymer mixtures.

Interplay of hydrodynamics and friction in a viscoelastic medium

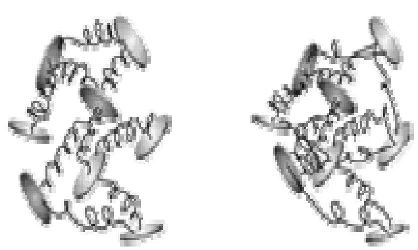
Flow-induced orientation



(Schmidt Vermant)

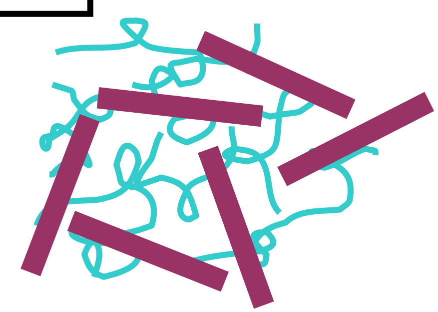
Effect of molecular interactions

Flow-induced gelation



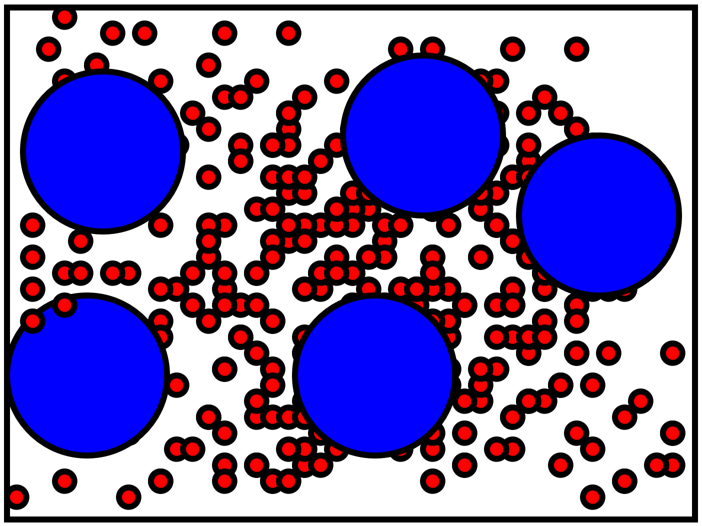
(Schmidt)

Flow-induced Jamming



(Galgali)

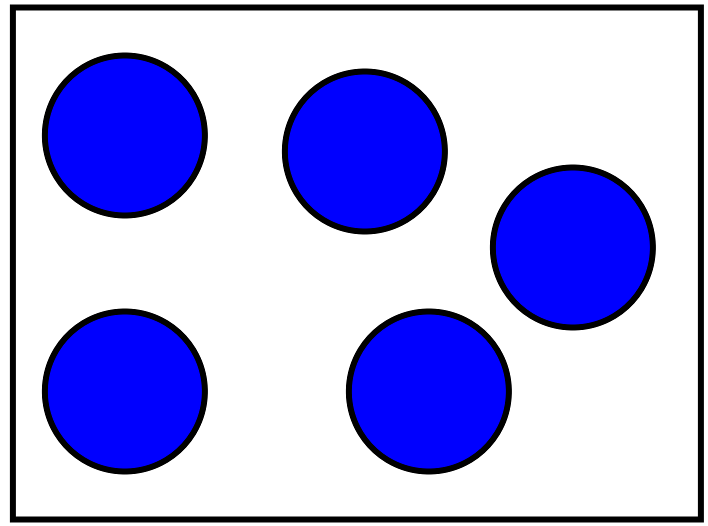
The Approach



Explicit Solvent Method

(Molecular dynamics)

- Captures hydrodynamics and other interactions.
- Due to size asymmetry, is computationally expensive.



Continuum Methods

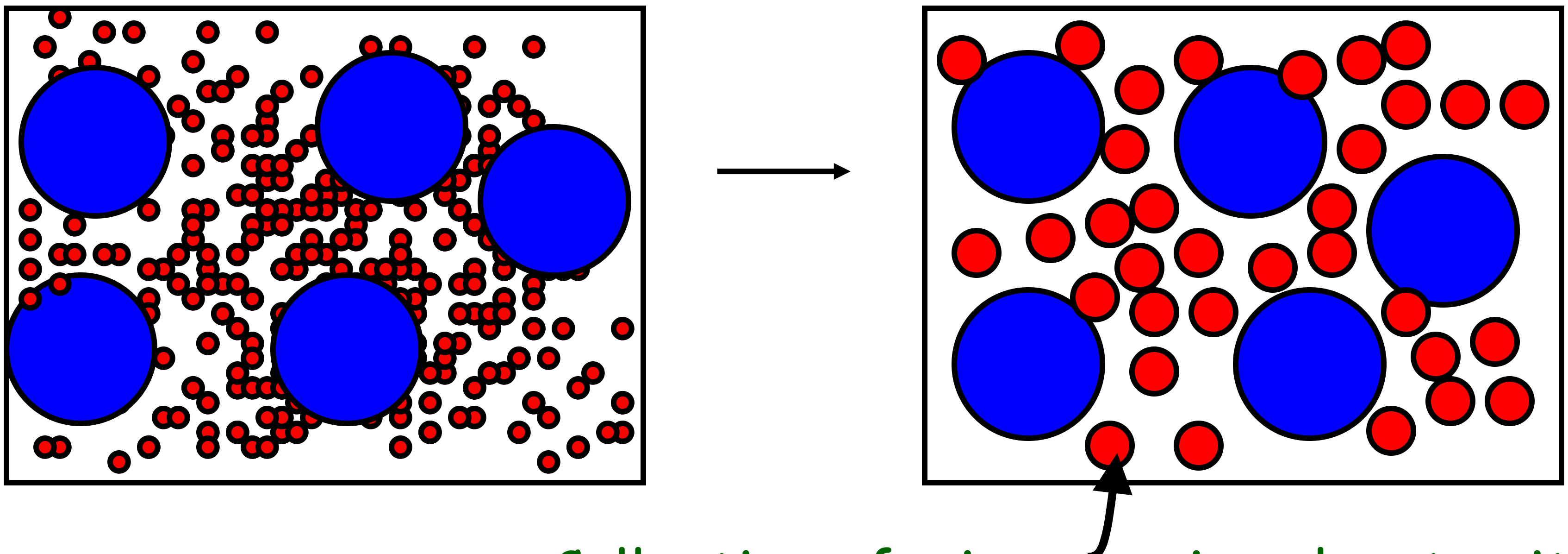
(Stokesian dynamics, Lattice-Boltzmann)

- Captures hydrodynamics and is computationally tractable.
- Can't include interactions with the solvent.
- Not developed for Non-Newtonian flows.

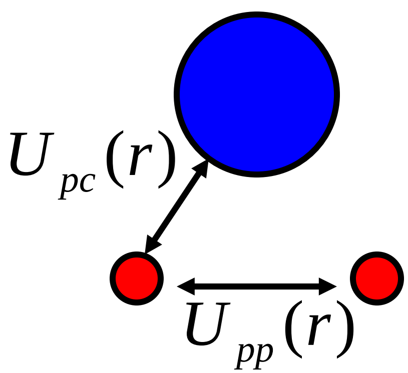
The Approach

Explicit Solvent Method

Coarse-Grained Explicit Solvent Method



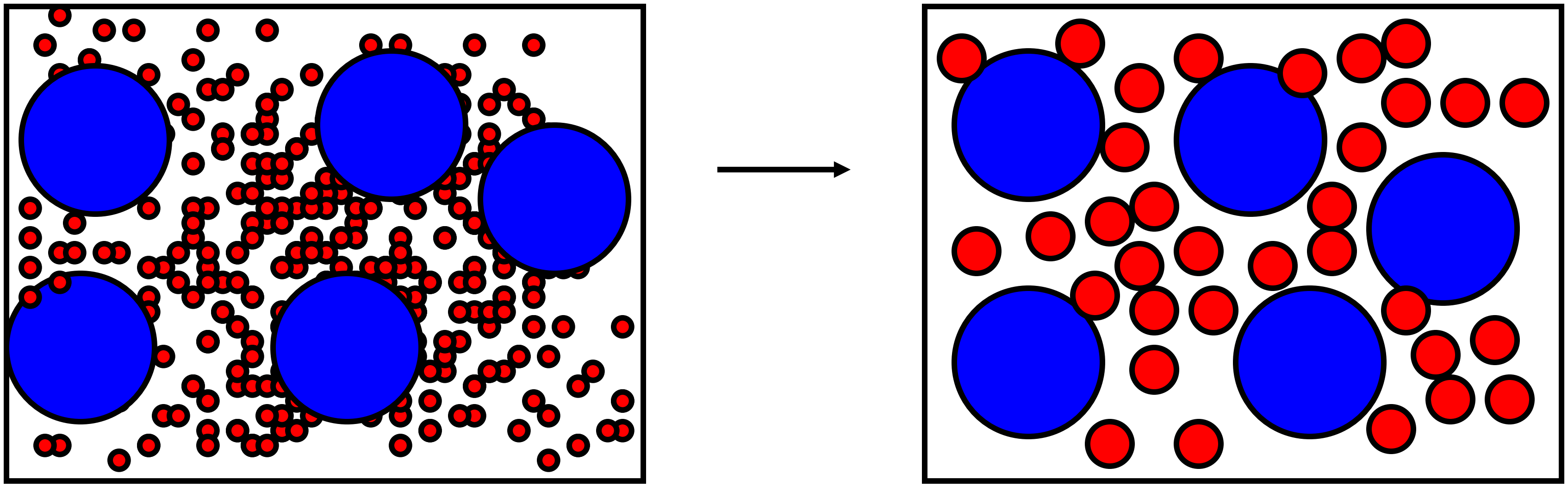
Collection of microscopic solvent units

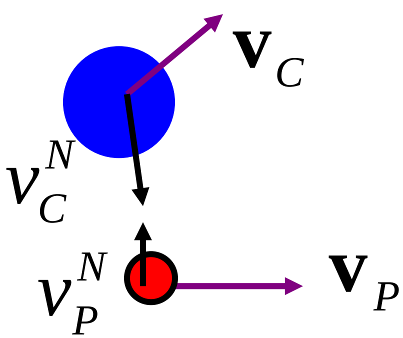


- Particle and solvent units interact by coarse-grained potentials.
- $U_{pc}(r), U_{pp}(r)$ are derivable from more atomistic representations.

The Approach

Explicit Solvent Method → **Coarse-Grained Explicit Solvent Method**



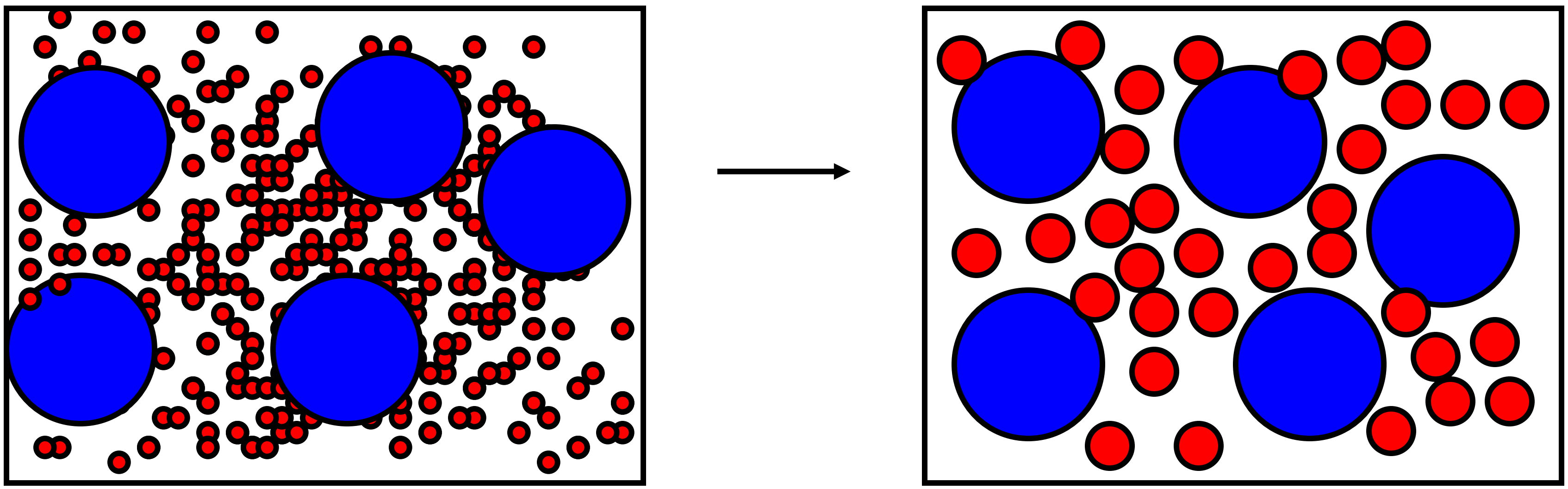


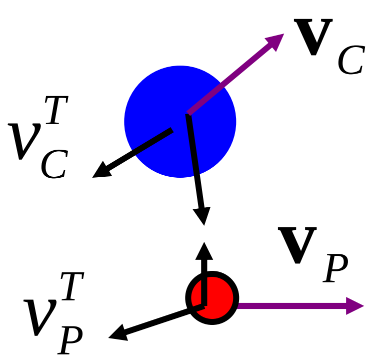
$$F_D^N \propto v_P^N - v_C^N$$

- Particles interact by momentum conserving thermostat (preserves hydrodynamics).
- Involves (central) dissipative forces dependent upon the normal component of the velocity differences.
- Similar to Dissipative Particle Dynamics.

The Approach

Explicit Solvent Method → **Coarse-Grained Explicit Solvent Method**





No-Slip

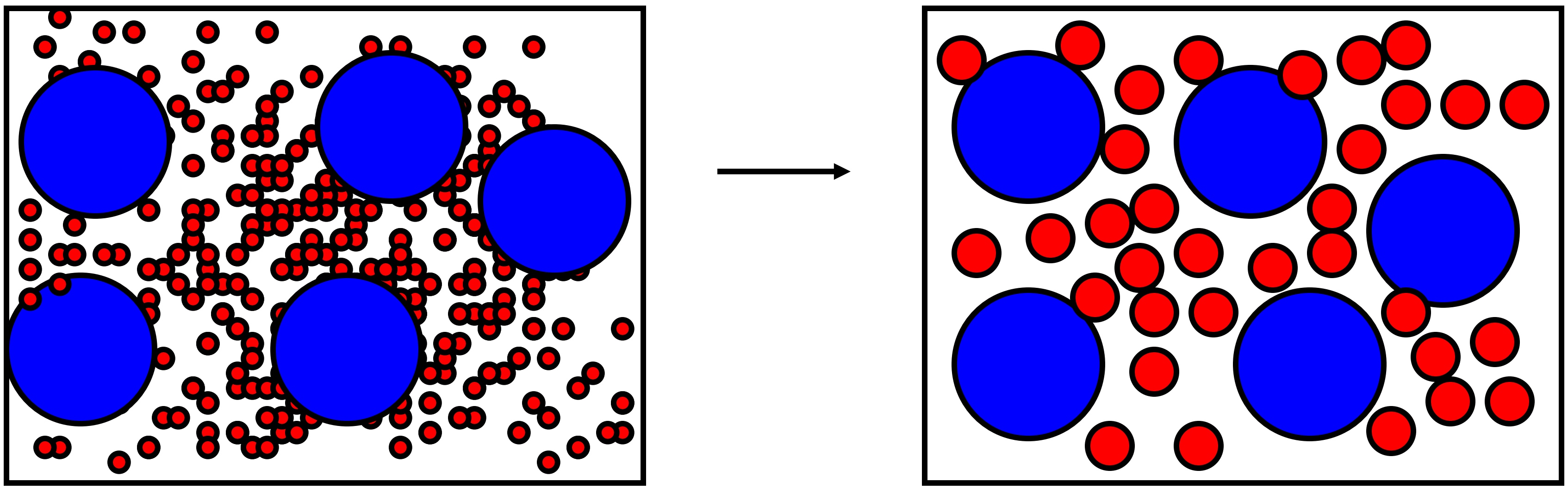
$$F_D^T \propto v_P^T - v_C^T$$

- Does not capture local hydrodynamics.
- Requires tangential (not central) velocity-dependent forces.

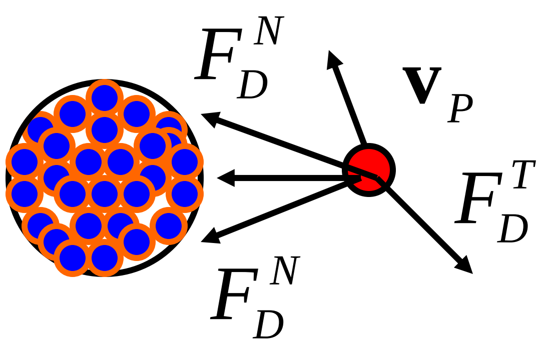
The Approach

Explicit Solvent Method

Coarse-Grained
Explicit Solvent Method



Composite Particles

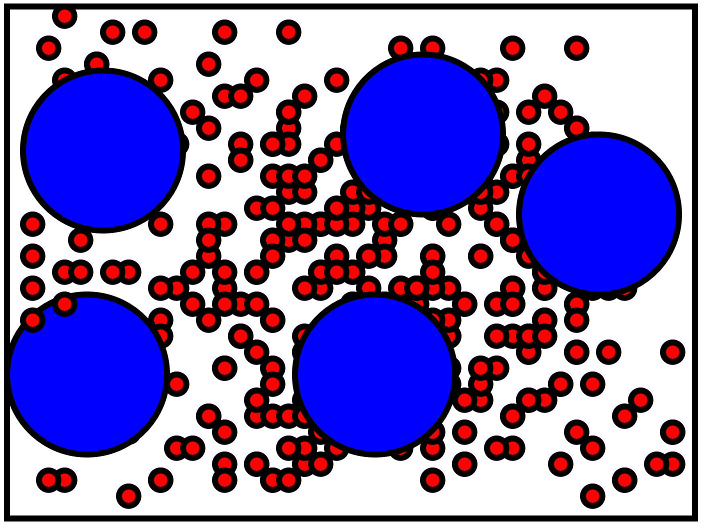


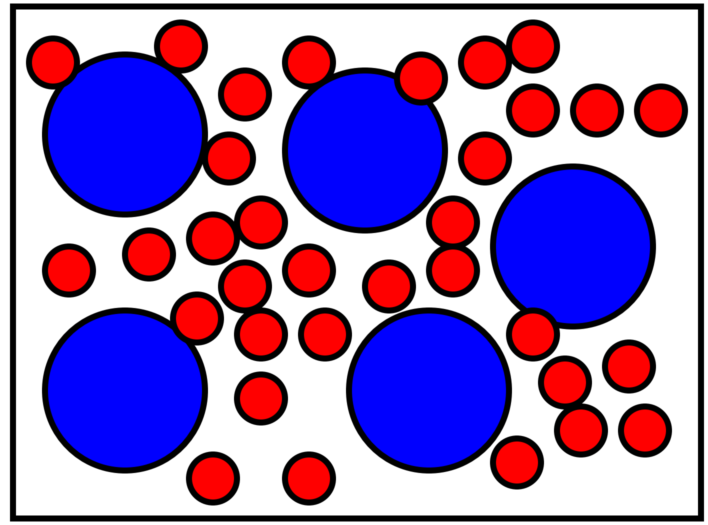
- Does not capture local hydrodynamics.
- Requires tangential (not central) velocity-dependent forces.

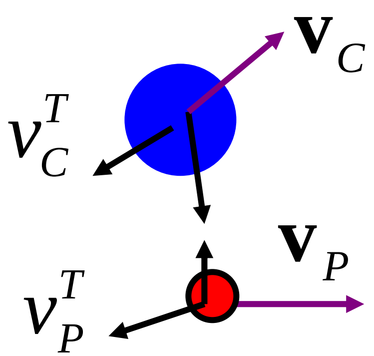
The Approach

Explicit Solvent Method

Coarse-Grained Explicit Solvent Method





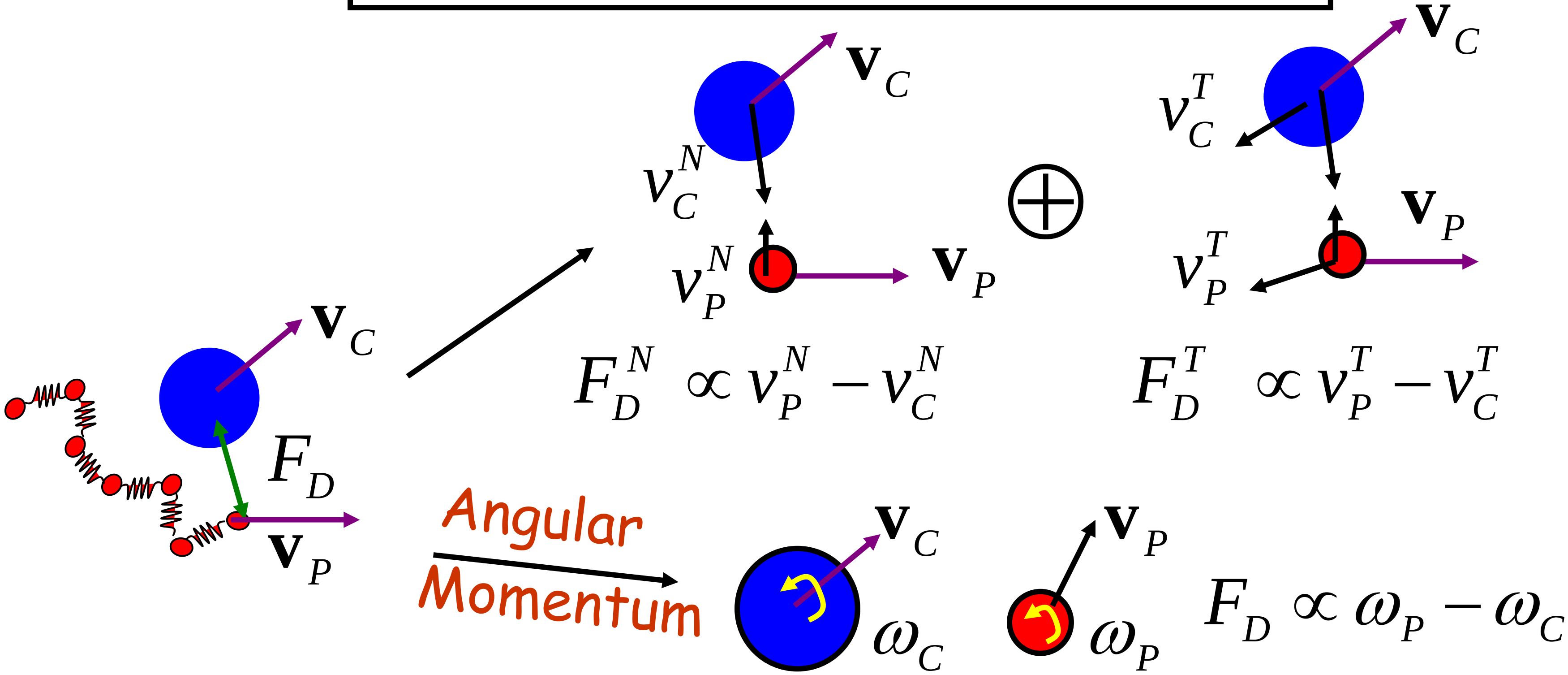


$$F_D^T \propto v_P^T - v_C^T$$

Our proposal

- Directly incorporate tangential velocity-dependent forces.

Hydrodynamic Friction Forces



- Conserves linear and angular momentum
- Preserves hydrodynamical phenomena
- Includes tangential friction
- Brownian dynamics + Dissipative forces
- Computationally tractable (for size asymmetric systems)

U_{ij} Conservative

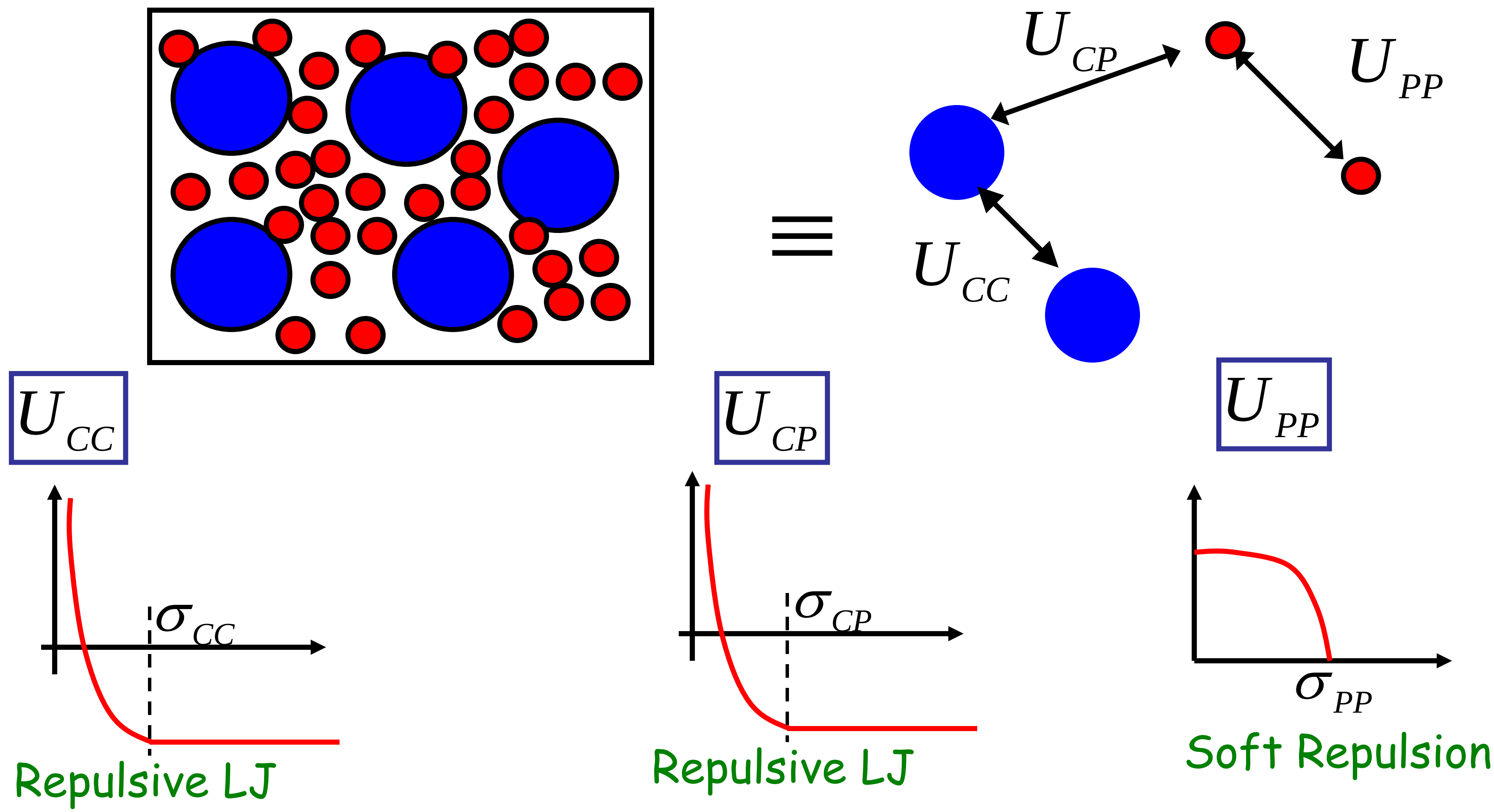
F_D^T Dissipative

F_R Random forces

(Espanol, 1998; Pryamitsyn and Ganesan, JCP, 2005)

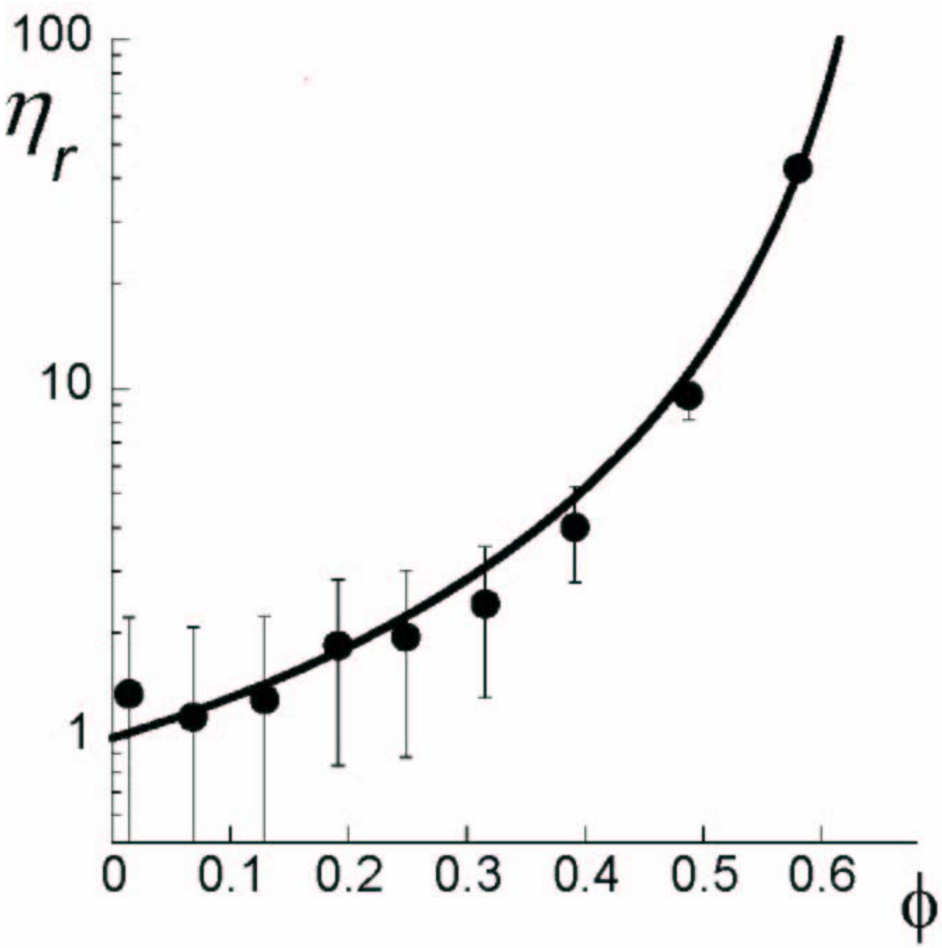
Coarse-Grained Colloidal Suspension

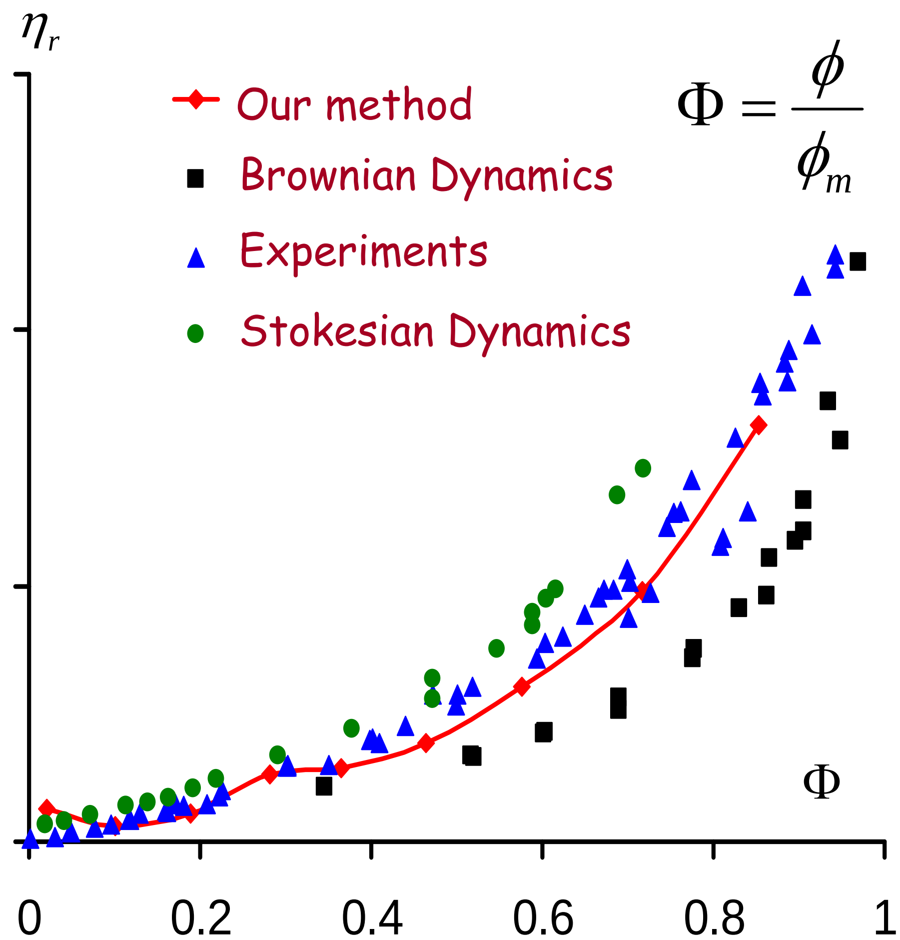
- Mixture of colloid and solvent
- Colloid:Solvent Radius = 5:1.



(Pryamitsyn and Ganesan, JCP, 2005)

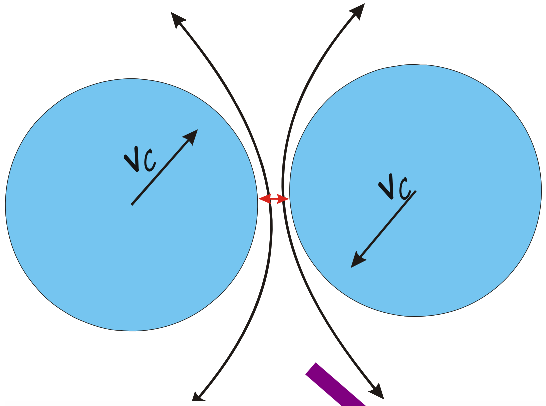
Hydrodynamic Interactions: Zero-Shear Viscosity





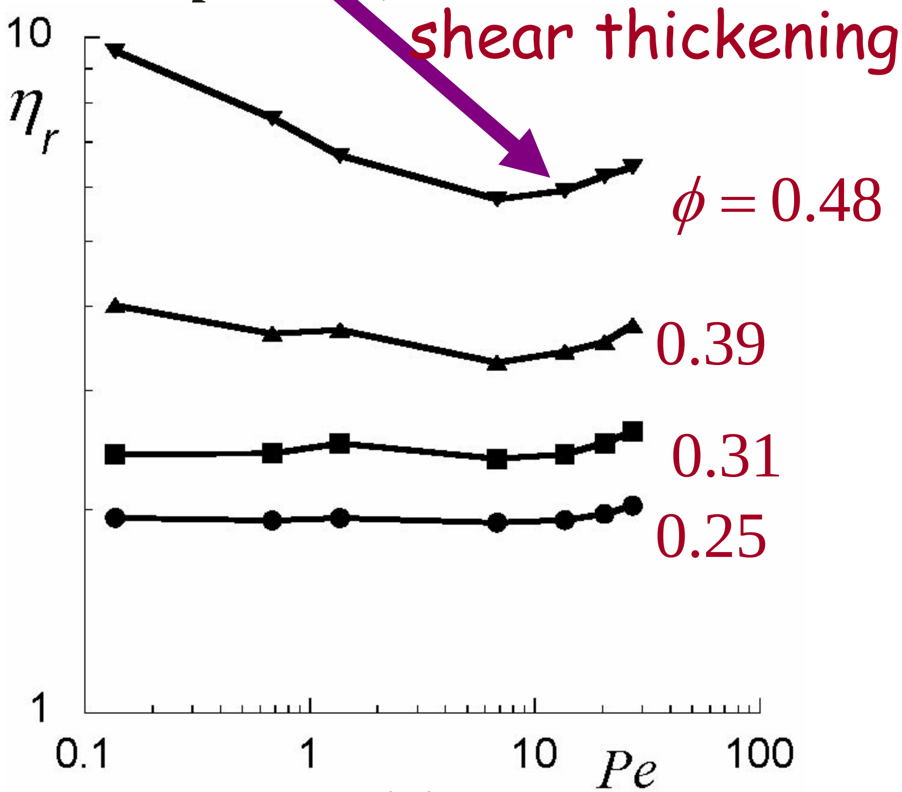
- Coarse-Grained solvent method captures hydrodynamical interactions

Shear Rheology

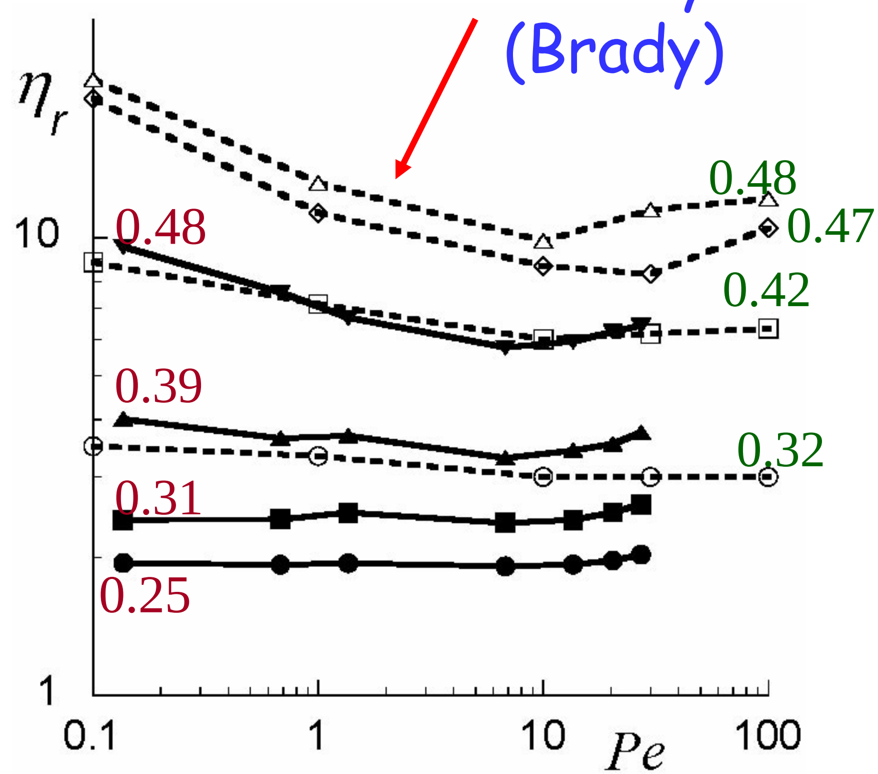


Rheology is sensitive to lubrication forces

Provides a sensitive test of explicit solvent model.



Stokesian Dynamics (Brady)



Agrees to within 20% of Stokesian dynamics results

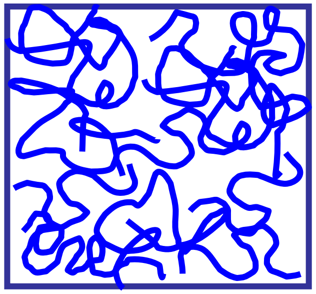
Summary So Far..

- Outlined a coarse-grained explicit solvent method to simulate hydrodynamical phenomena involving particles in complex fluids.

- Provided evidence that both hydrodynamical and other interactions can be faithfully captured.

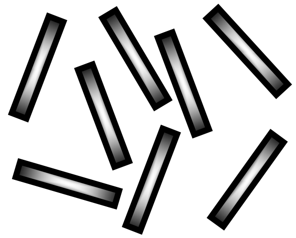
- Results on hard sphere suspensions provided new insights into the interplay between glass transition, hydrodynamics and rheology.

Why Polymer Nanocomposites ?



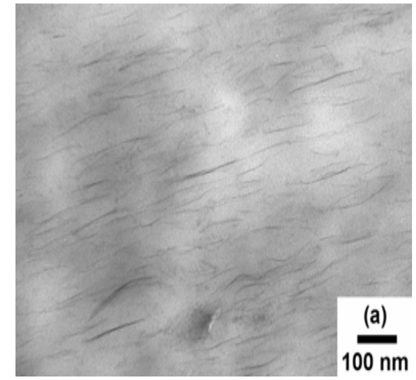
Polymers
(Solutions, Blends)

⊕



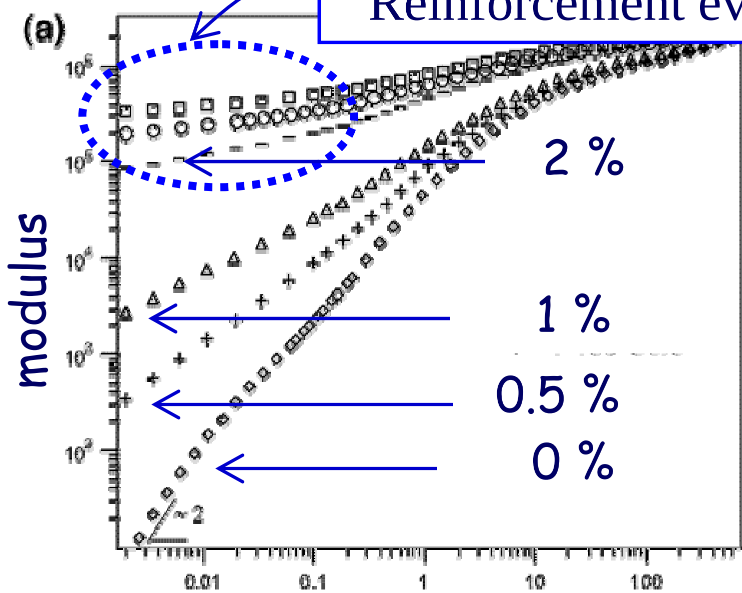
Nano-fillers (Clay, Nanotubes, Fullerenes)

⇒



Nanocomposites

Reinforcement even at η ~ 2%



Silica + PEO#

Elastic modulus doubles

Viscosity increases by an order of magnitude

Microsized particles vol ~ 30%

Nanoparticles vol ~ 1 -5 %

Zhang and Archer, Langmuir, 2002

✓Addition of small particles – Significant property enhancement!!

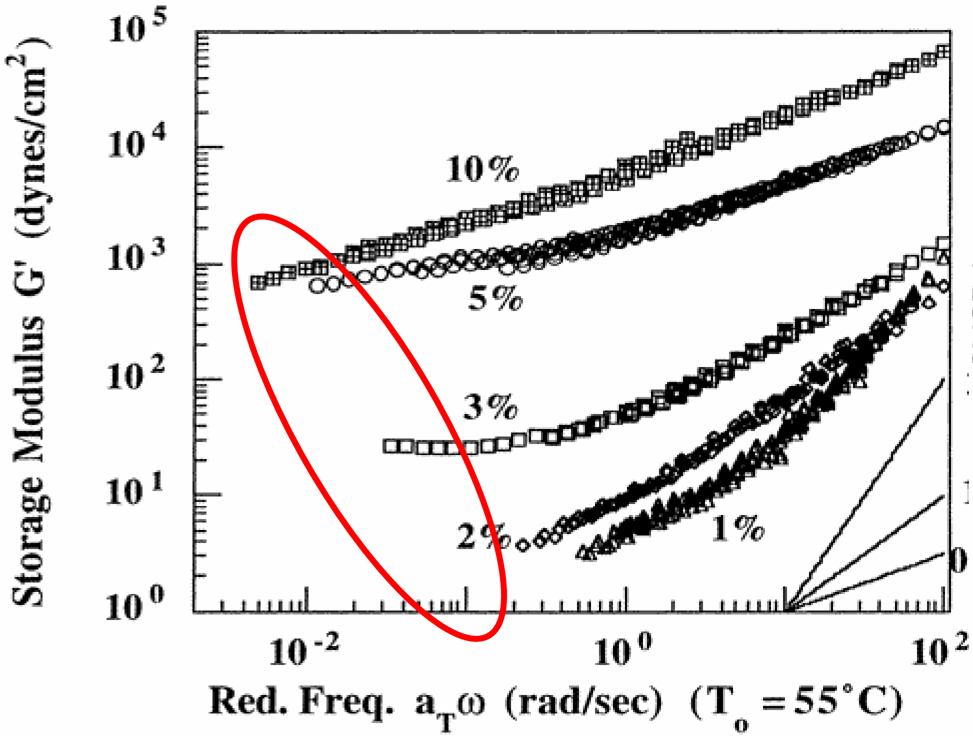
Issues and Questions

- How do nanoparticles modify the mechanical properties of polymer matrices ?

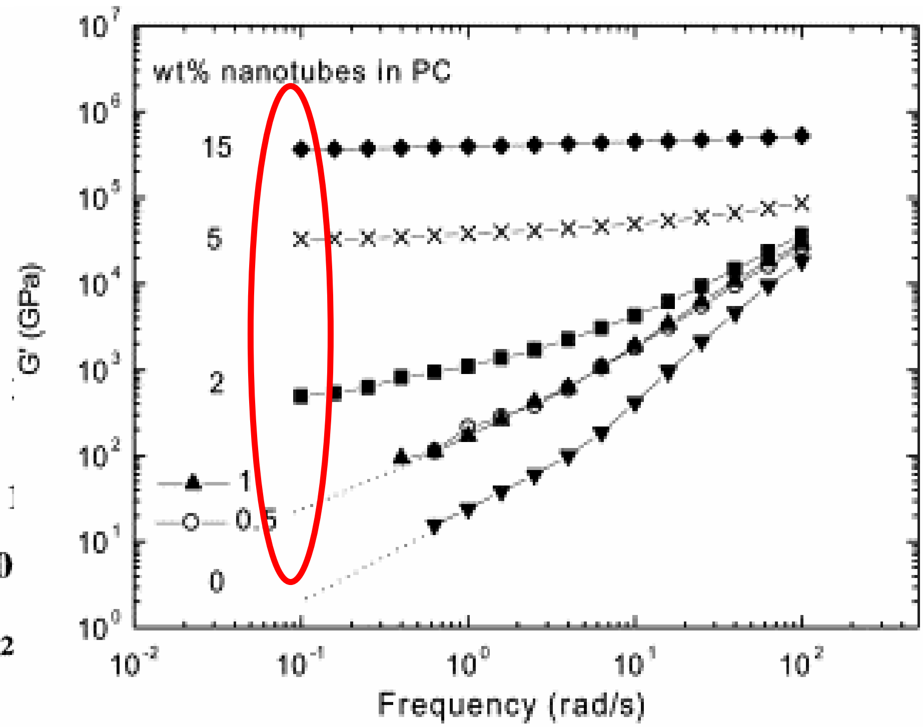
- What are the mechanisms underlying the above effects ?

- What are the parameters governing the mechanisms ?

Rheology of PNCs: Linear Viscoelasticity



Polycaprolactone + Montmorillonite Clays*



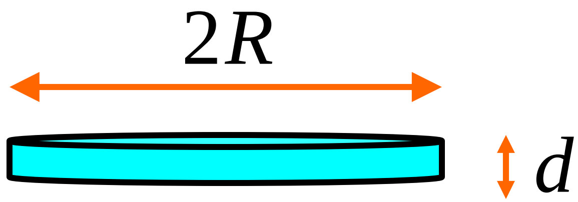
PC + Nanotubes**

- Significant enhancements in elasticity at extremely low loadings
- Change of viscoelastic response to “solid-like” behavior.

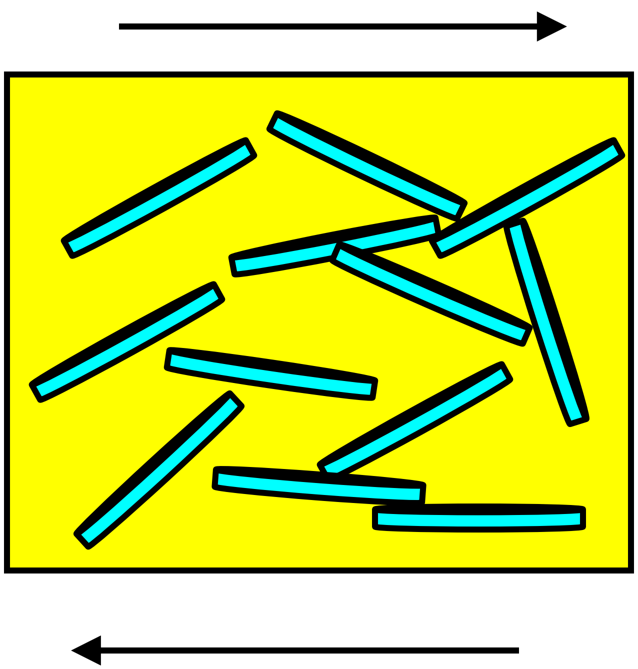
*:Krishnamoorti and Giannelis; **: Fornes and Paul

Rheology: Explanations

Particle Jamming/Percolation (Krishnamoorti)



$$2R >> d$$



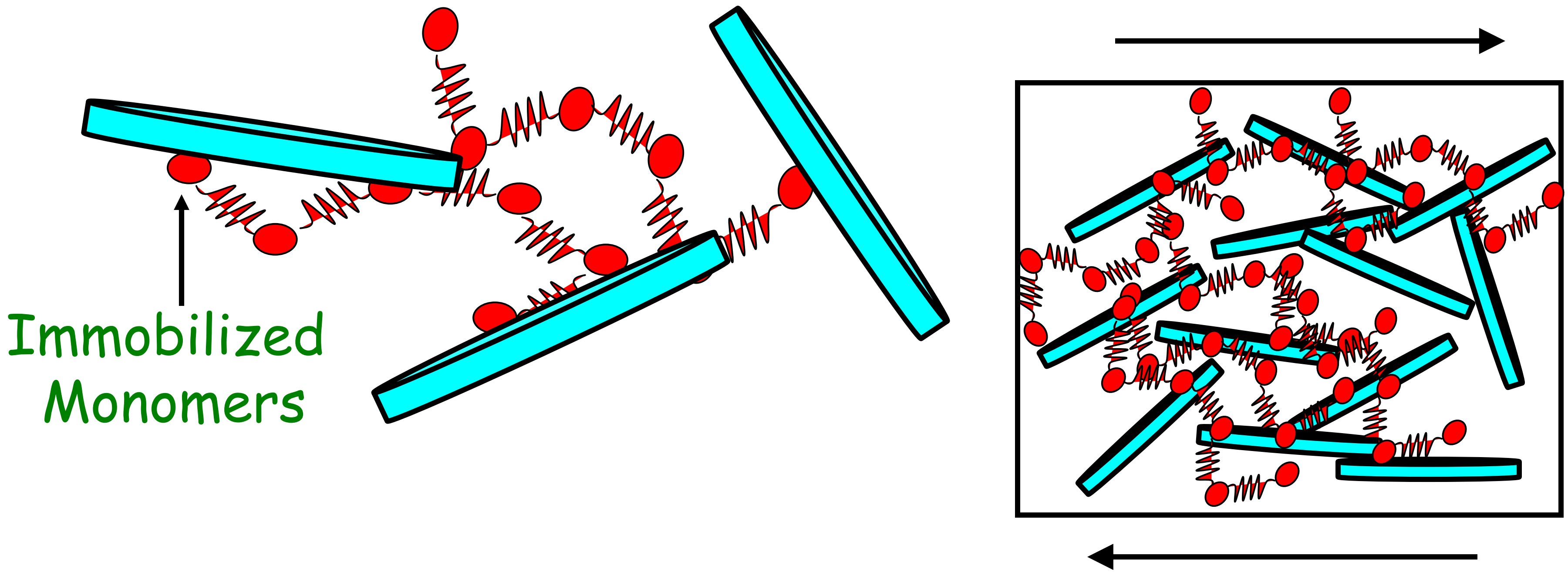
- Jamming/percolation occurs at low ϕ

$$\phi R^3 \approx 1$$

- Leads to solid behavior and the enhancements in modulus.

Rheology: Explanations

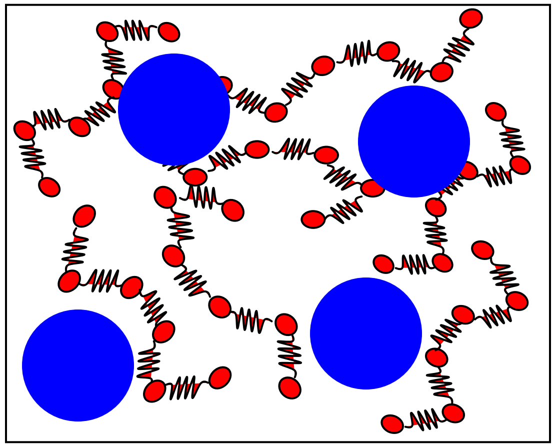
Polymer Network Mechanism (Kumar and Douglas)



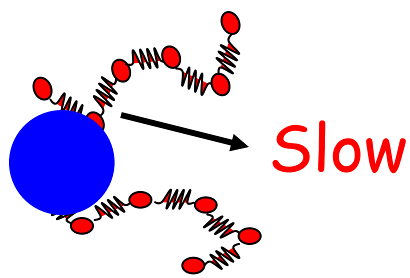
- Elasticity due to transient network formation.
- Plateau modulus due to bridges.

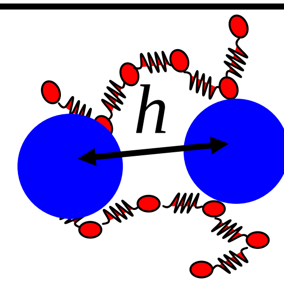
Rheology of PNCs: Model System

- Mixture of spherical nanoparticles in polymer matrices



$$\frac{2R_g^P}{\sigma_{CC}} \approx O(1)$$



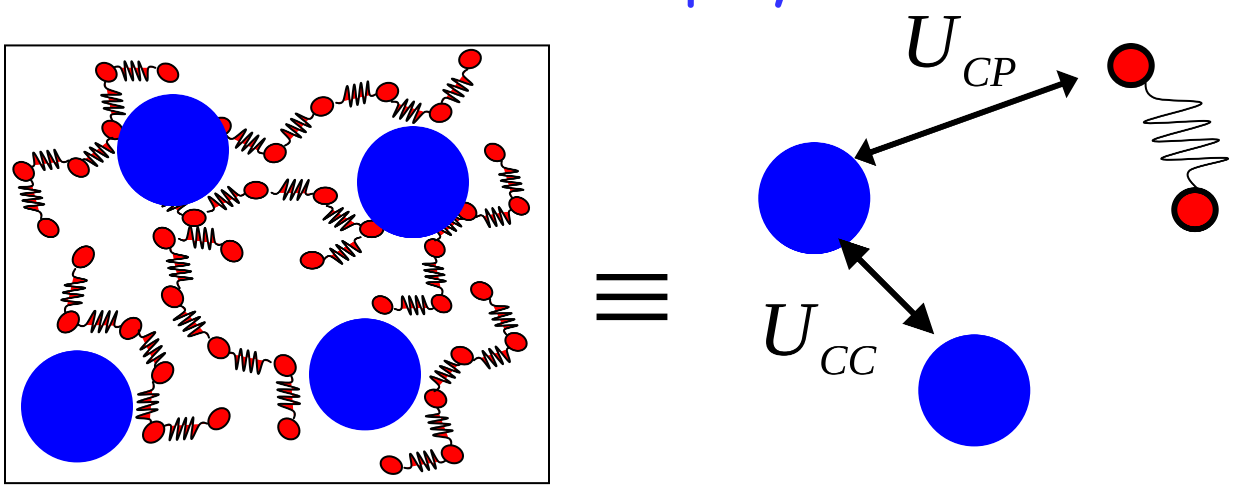


$$\frac{h}{R_g} \approx O(1)$$

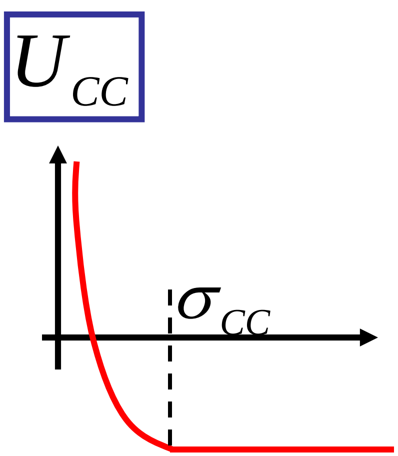
- Advantage: A lot is known about spherical colloidal dispersions
- Disadvantanges: Orientational effects are absent.
  Need much higher loadings.

Model of Polymer Nanocomposites

- Mixture of colloid and polymeric melt

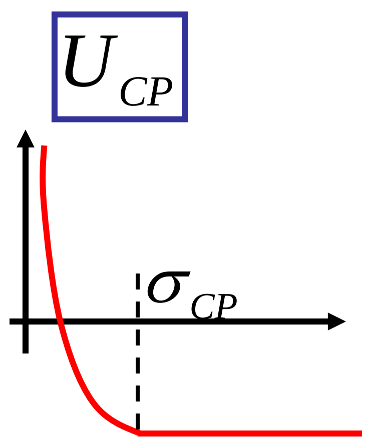


N_P	$\frac{2R_g^P}{\sigma_{CC}}$
4 → 48	0.45 → 1.6



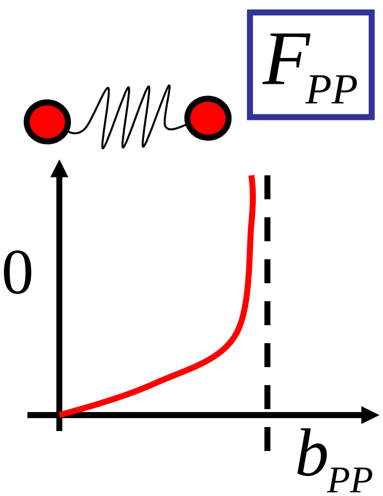
Repulsive LJ

$$\frac{\sigma_{CC}}{\sigma_{PP}} = 5.0$$



Repulsive LJ

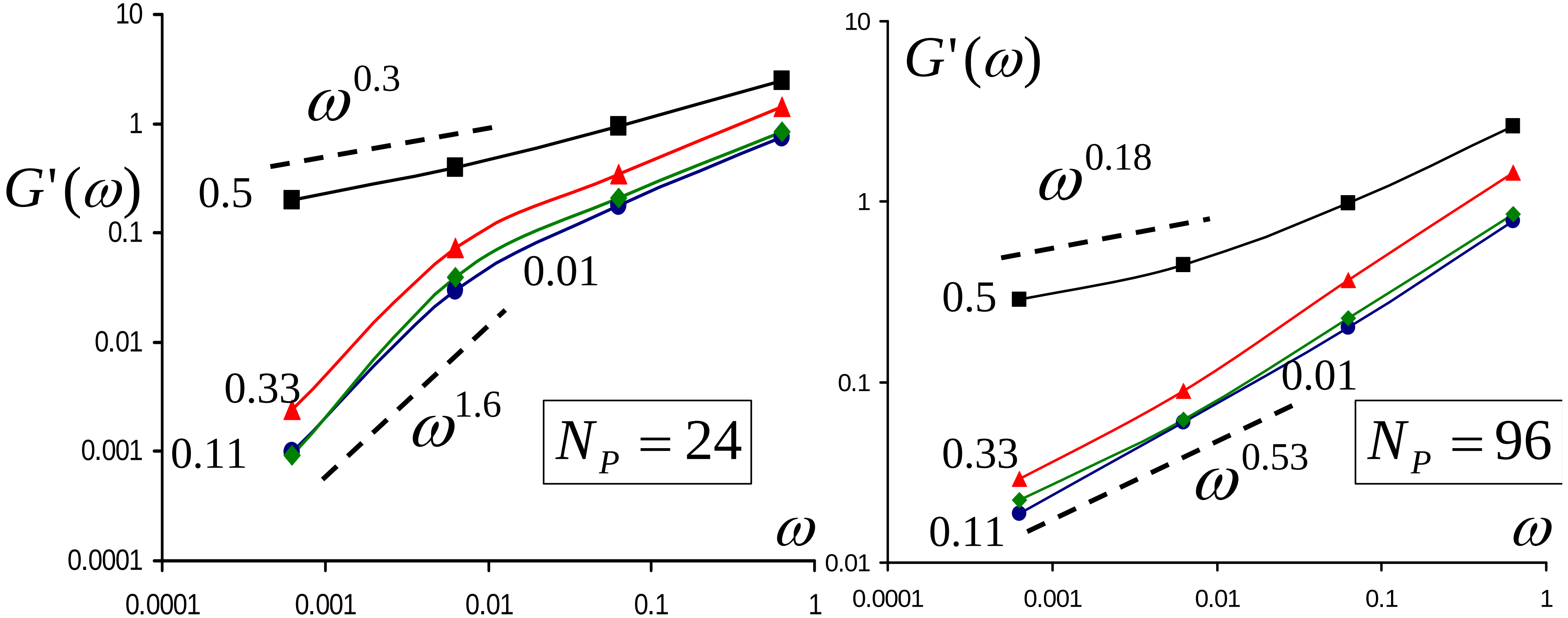
$$\frac{b_{PP}}{\sigma_{PP}} = 3.0$$



FENE Springs

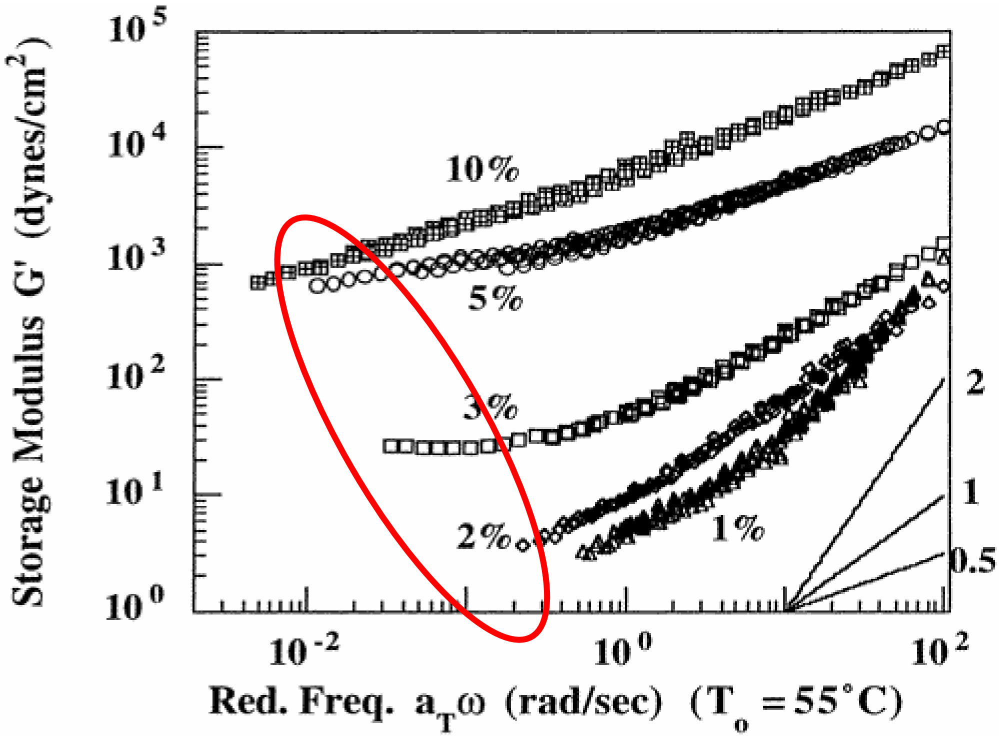
(VP & VG: Macromolecules, 2006; J. of Rheology)

Rheology of PNCs: Linear Viscoelasticity

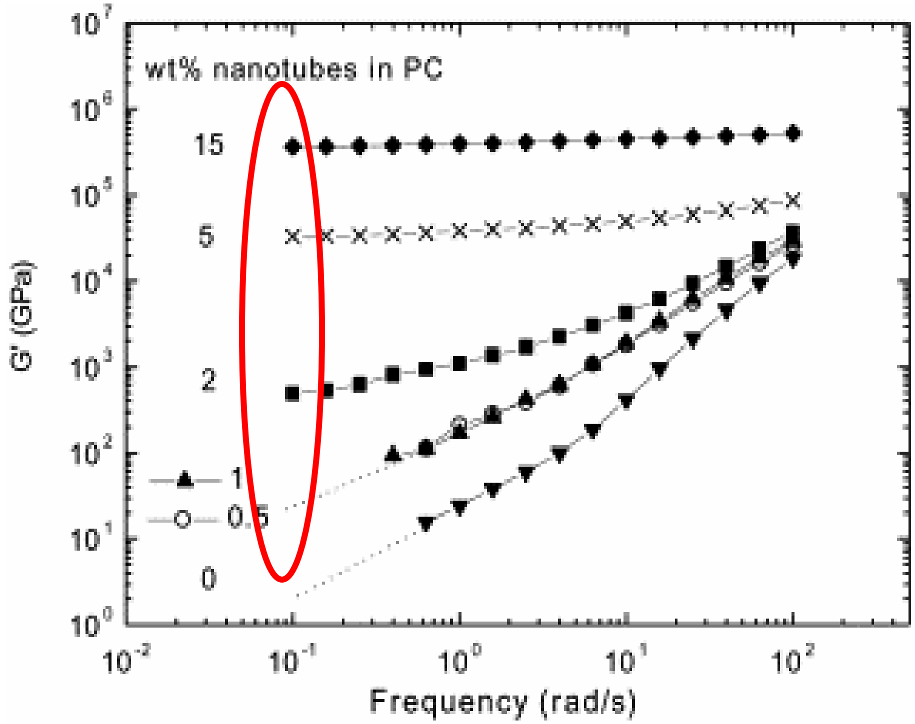


- Lower Loadings: Enhancement in modulus but no apparent change in relaxation behavior.
- Higher Loadings: Significant enhancement in modulus and a solid-like behavior.

Rheology of PNCs: Linear Viscoelasticity



Polycaprolactone + Montmorillonite Clays*



PC + Nanotubes**

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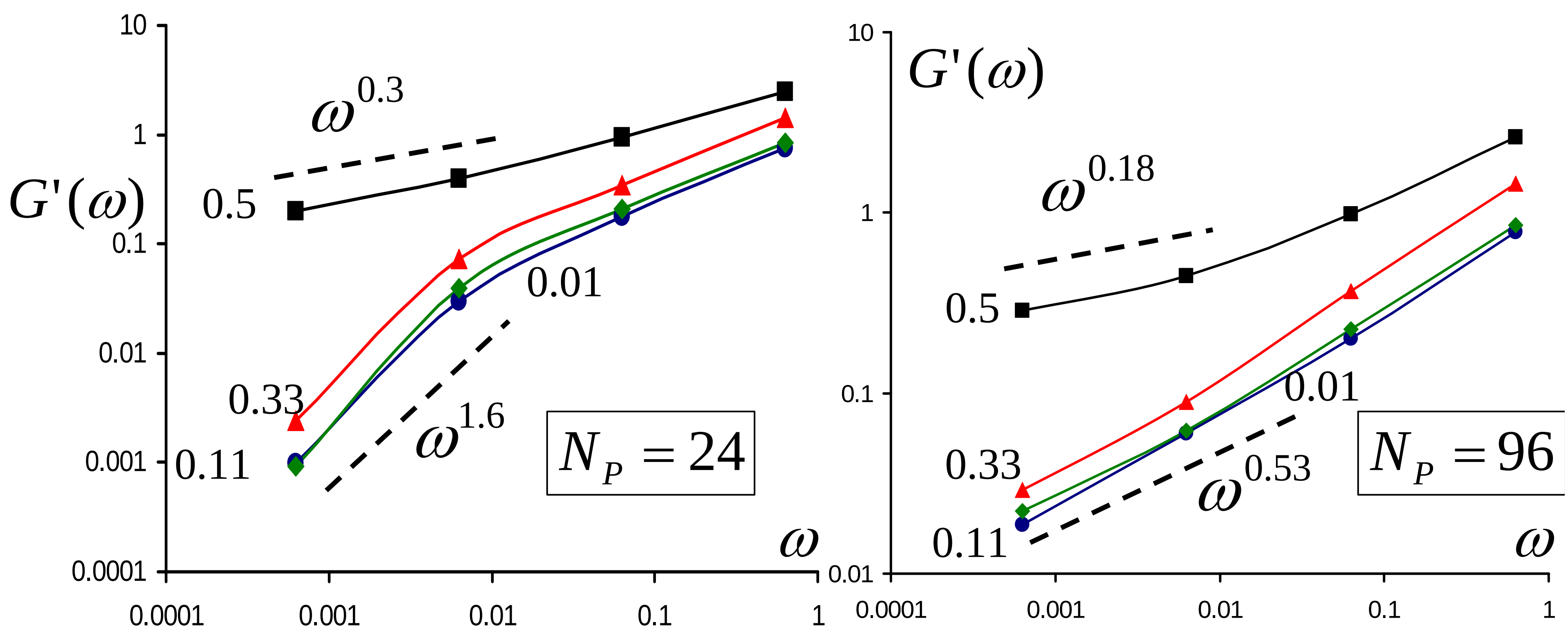
Rheology of PNCs: Linear Viscoelasticity

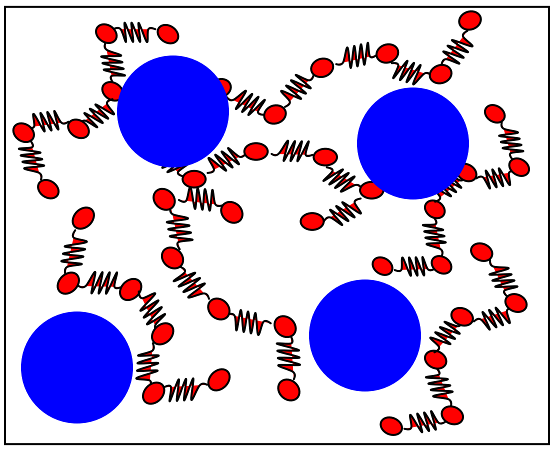


- Enhancement in modulus but no apparent change in relaxation behavior at lower loadings: Why ?
- Significant enhancement in modulus and a solid-like behavior at higher loadings: Why ? (Not in this talk)

Impact on Polymer Dynamics

- Significant impact upon glass transition temperature and polymer dynamics on adding nanoparticles.#

How does the polymer dynamics change due to addition of nanoparticles ?



$$R(t) \xrightarrow[\text{modes}]{\text{Normal}} X_m(t)$$

$$\downarrow$$

$$\langle X_m(t) X_m(0) \rangle$$

Simulation Features
No glass transition
Coarse-grained model

For unentangled polymers,

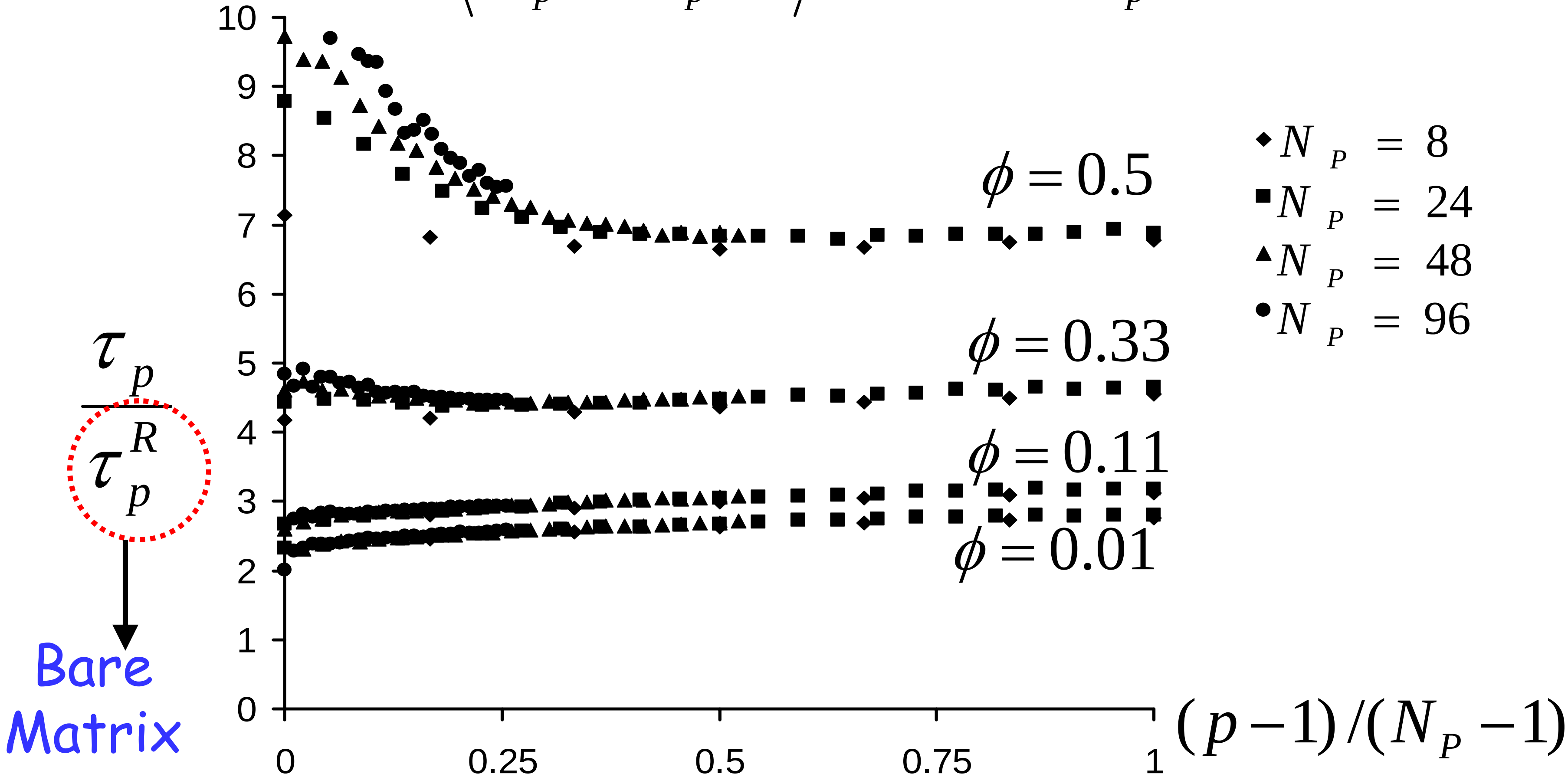
$$\langle X_m(t) X_m(0) \rangle \approx \exp(-t/\tau_m)$$

$$\tau_m \propto m^{-2} \qquad \tau_1 N_p^{-2} \propto \xi$$ Related to viscosity of media

#: Giannelis, Adv. Pol. Sci, 138, 107

Effect of Particles on Polymer Dynamics

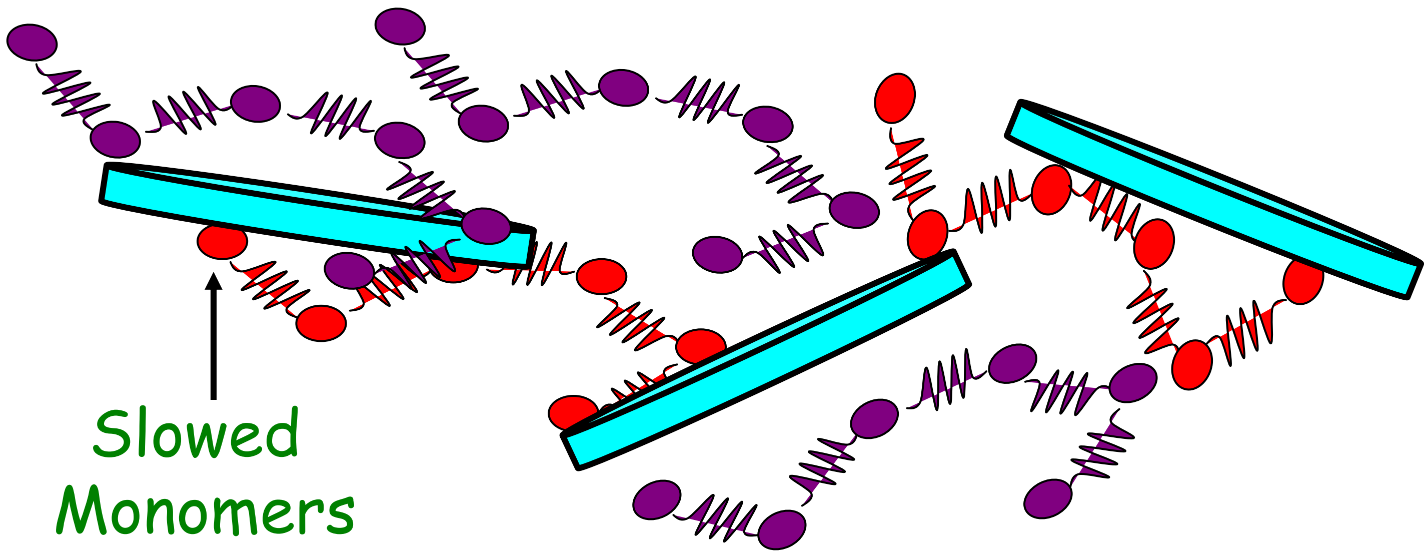
$$\left\langle X_p(t) X_p(0) \right\rangle \approx \exp(-t/\tau_p)$$



Overall Slowing of Polymer Relaxations

Effect of Particles on Polymer Dynamics

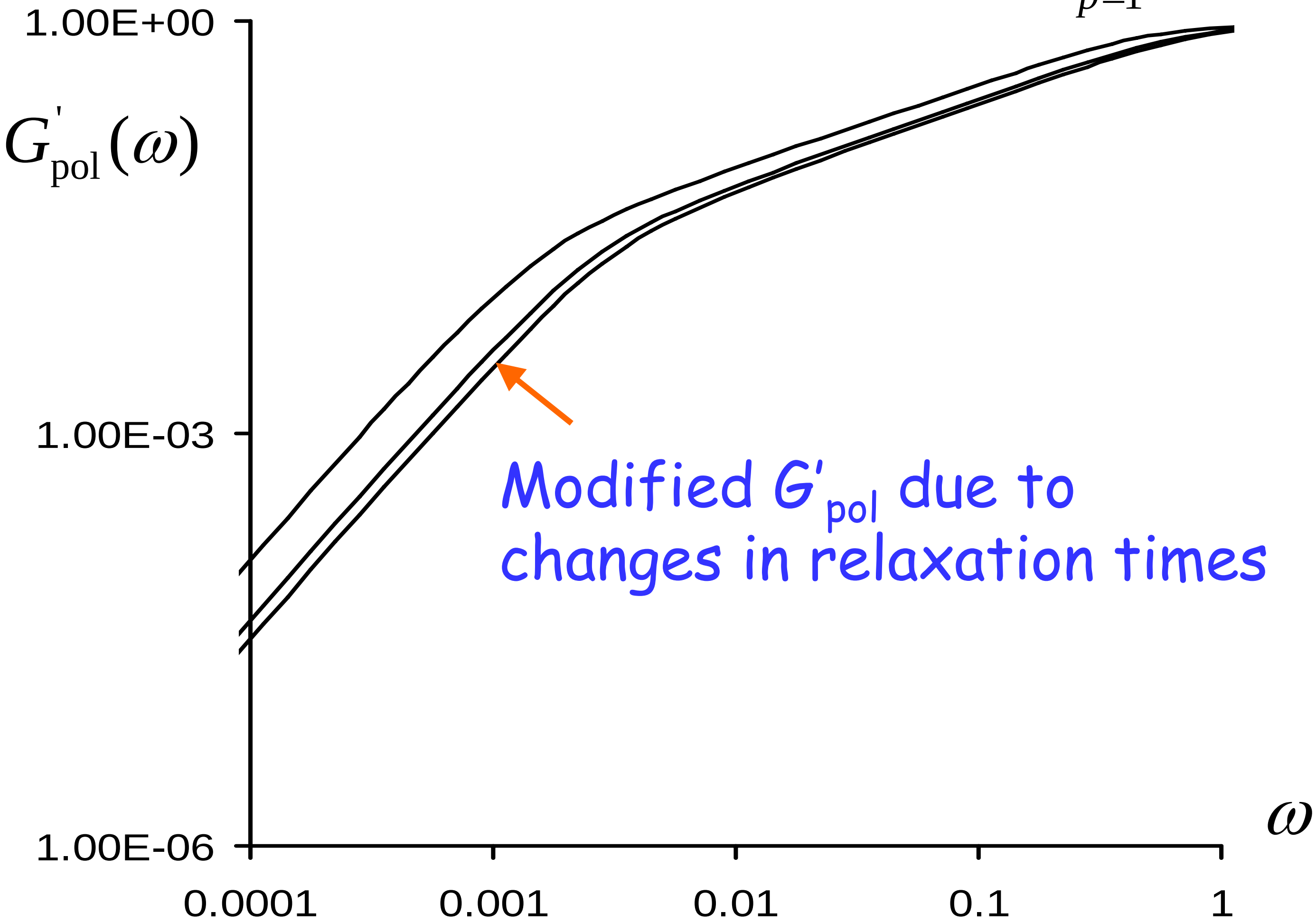
$$\left\langle X_p(t) X_p(0) \right\rangle \approx \exp(-t/\tau_p)$$



- Simulations of Grant Smith: Attractions lead to only a weak slowing down in melts.
- Different monomers of a chain access the slower regions: Overall slowing down of the polymers

Effect of Particles on Polymer Viscoelasticity

$$\langle X_p(t) X_p(0) \rangle \approx \exp(-t/\tau_p) \Rightarrow G(t) \propto \sum_{p=1}^{N_P} \exp(-2t/\tau_p)$$



Effect of Particles on Polymer Viscoelasticity

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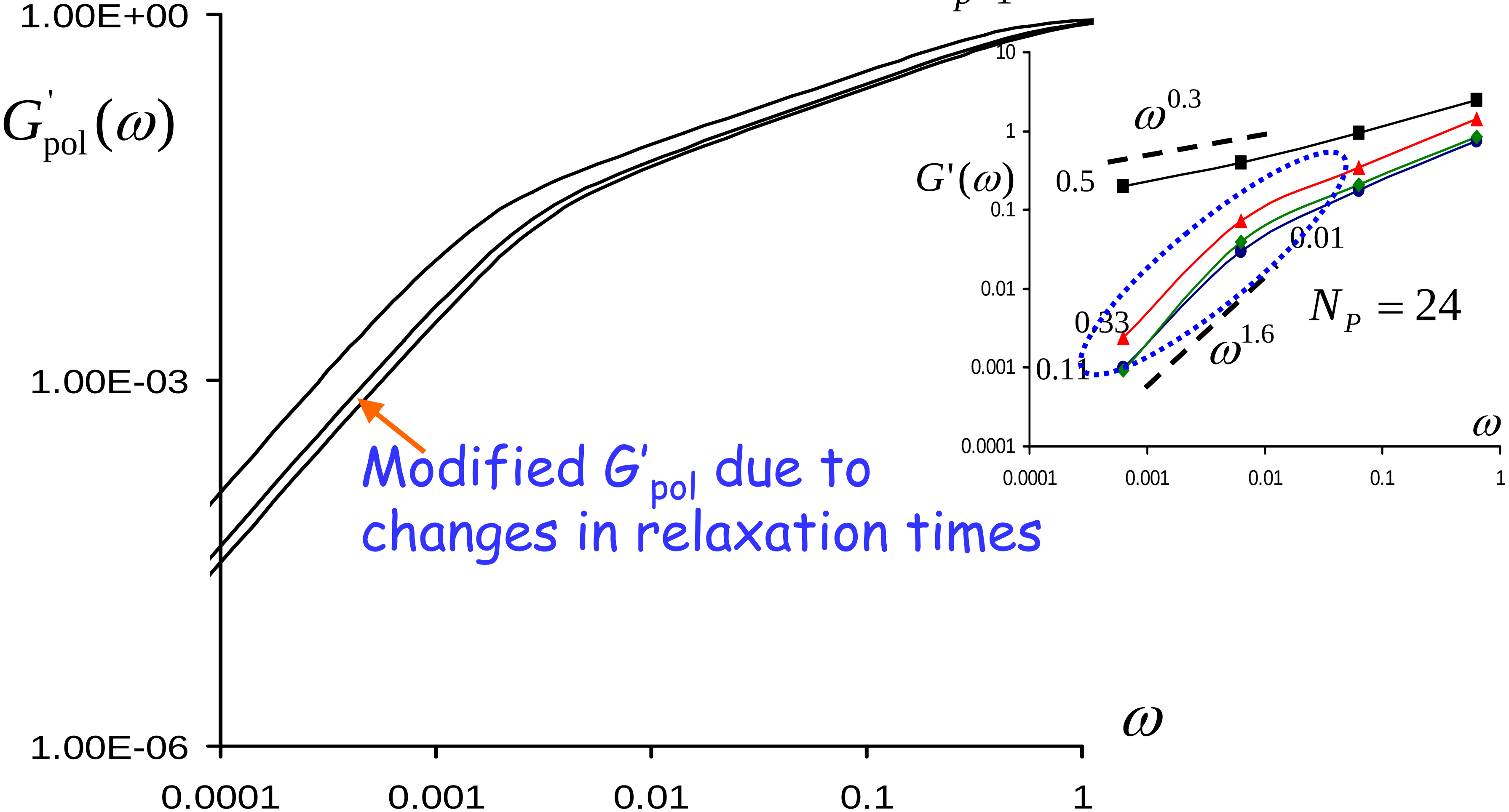

Effect of Particles on Polymer Viscoelasticity

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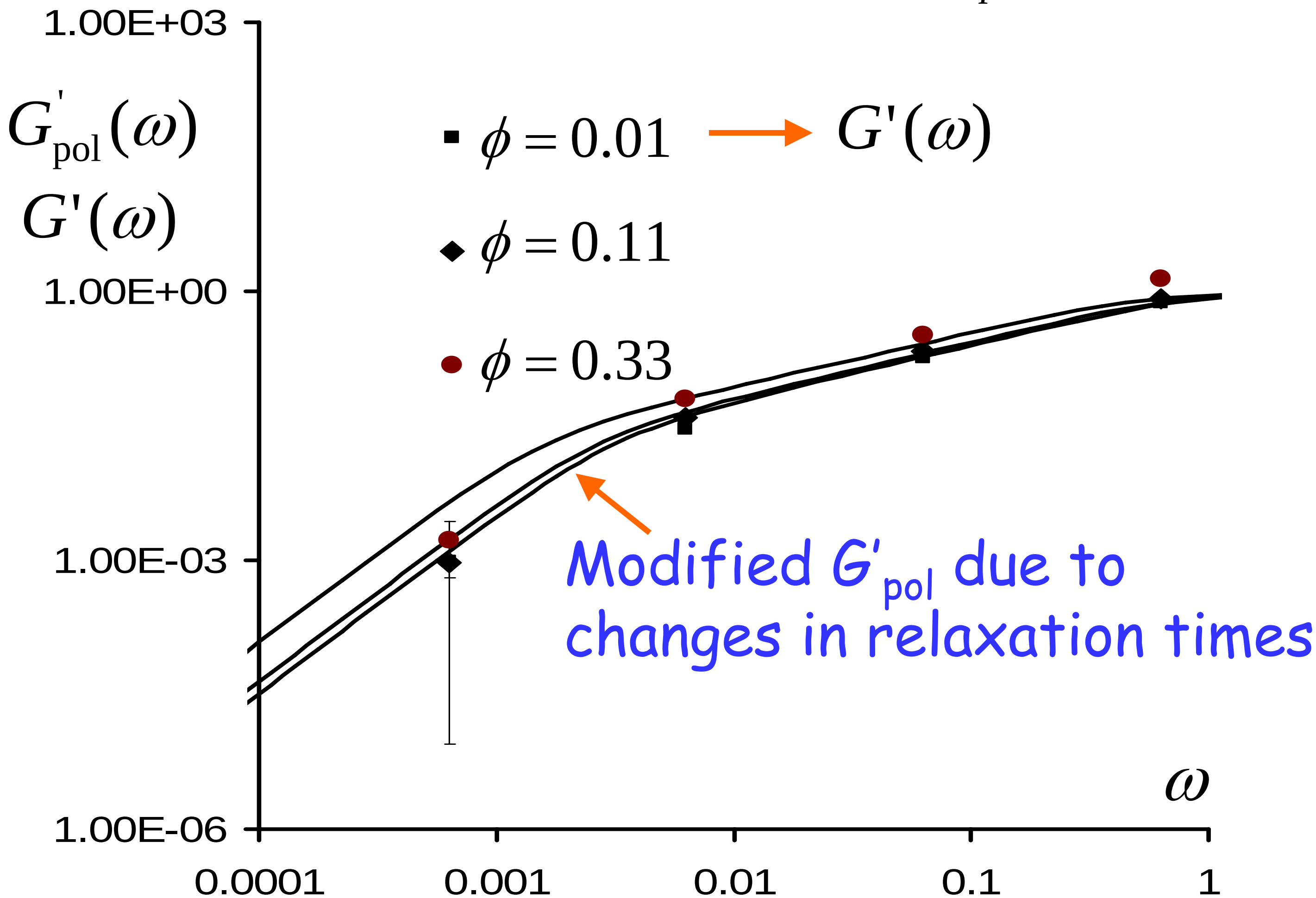


Physical Picture of Polymer Rheology at Low Loadings

• Particle-induced changes in polymer dynamics is responsible.

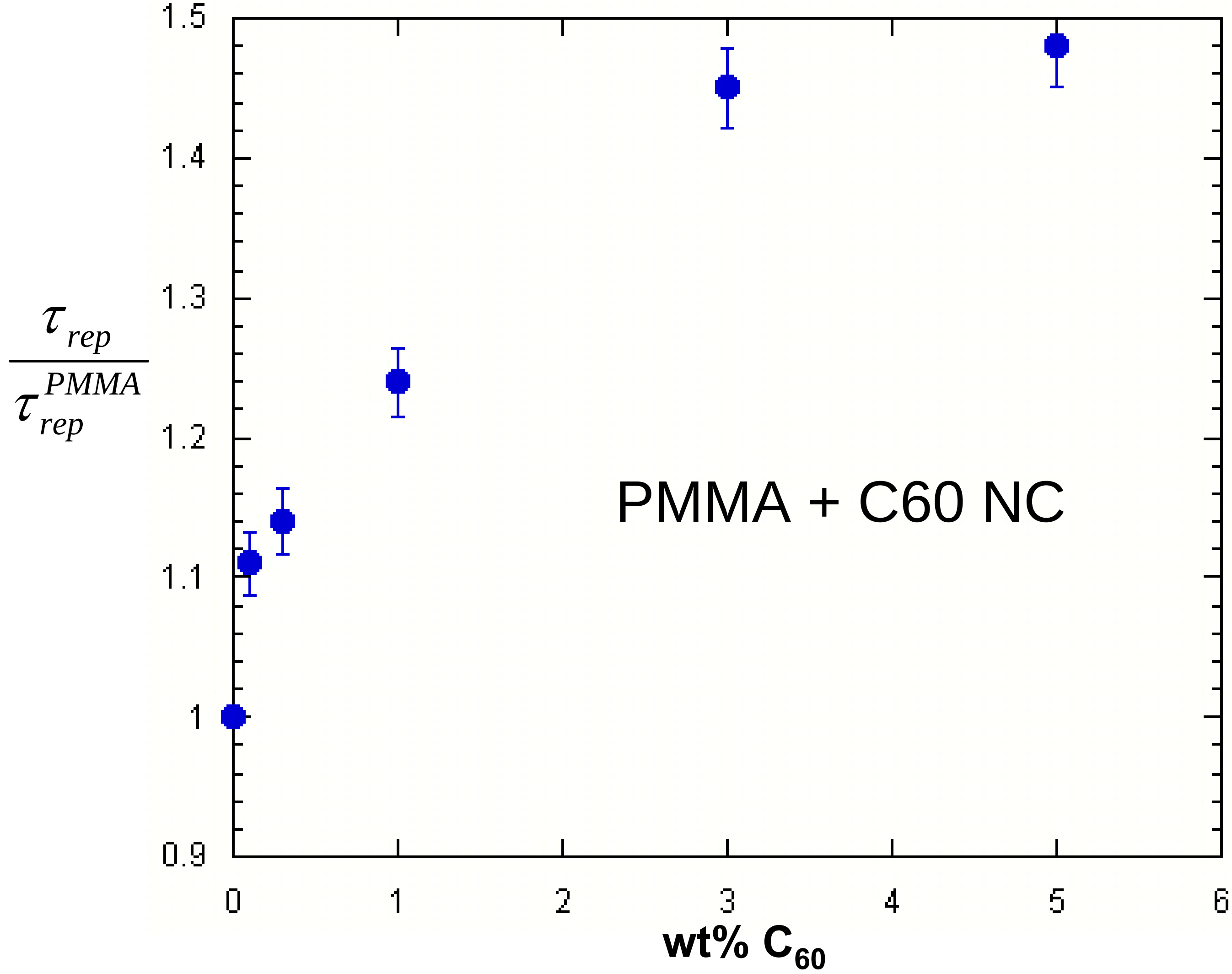
• For the weakly attractive particles, the above manifests as just a change in relaxation times.

• For strongly attractive particles, the above manifests as the modulus due to polymer-bridged networks.

Comparisons to Experiments

- (Kropka, Green and Ganesan, Macromolecules, In Press)

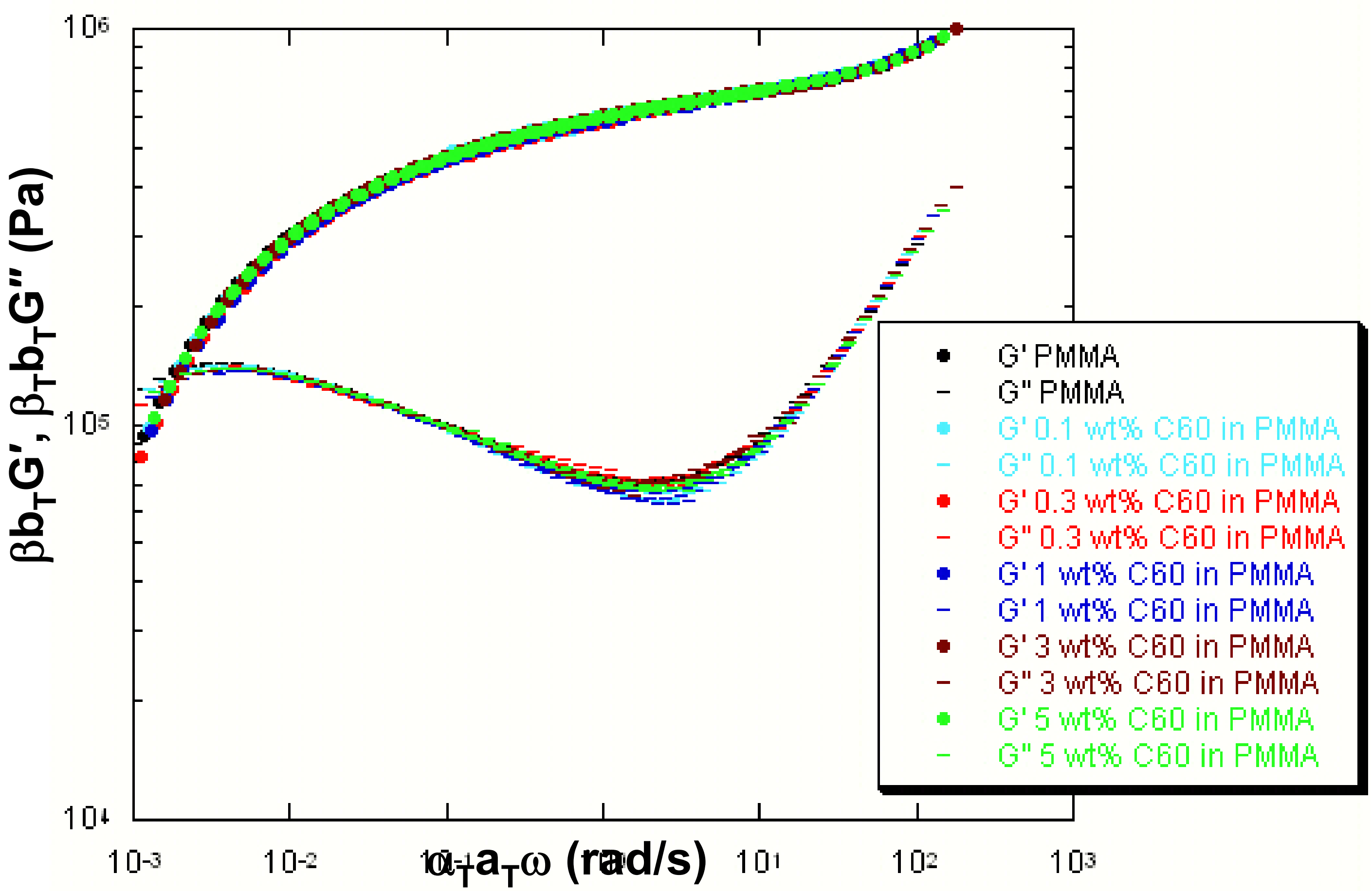
Comparison of the relaxation times in nanocomposites to the bare relaxation times.



Comparisons to Experiments

- (Kropka, Green and Ganesan, Macromolecules, in Press)

Superposition of mechanical modulii after renormalization of relaxation times.

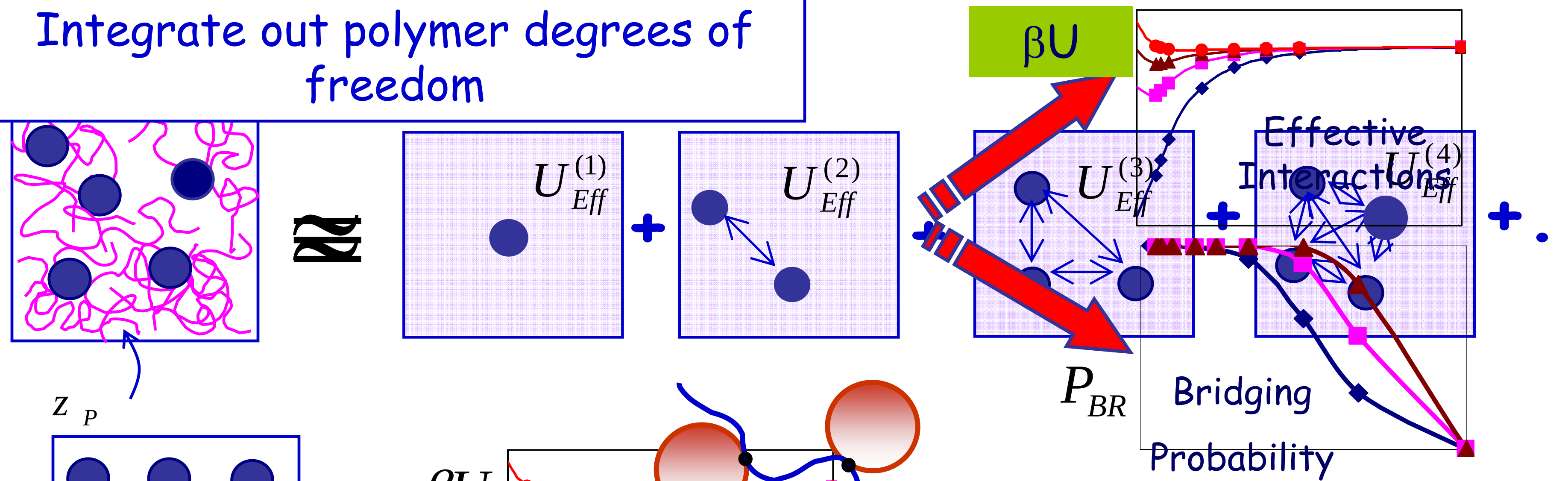


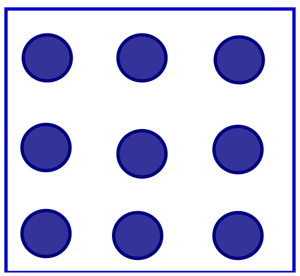
Rheology of PNCs: Issues and Questions

- How do nanoparticles modify the rheology of polymer matrices ?
- What are the mechanisms underlying the above effects ?
- At low particle loadings, polymer-bridging of particles is the responsible mechanism.
- What are the parameters governing the mechanisms ?
- What are the elastic and structural properties of the gels ?
- Why do nanoparticles lead to prevelant gelation ?
- How does the concentration of particles and polymer affect the gelation, stability characteristics of the mixture ?

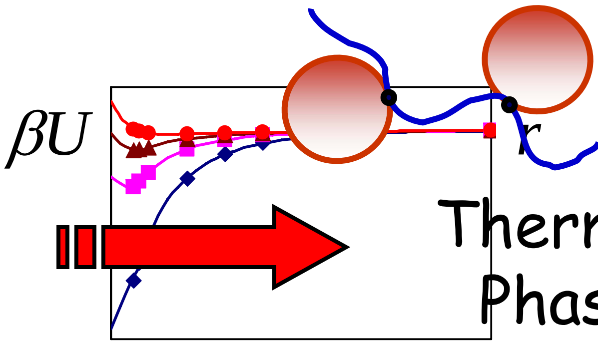
Outline of Approach

Integrate out polymer degrees of freedom



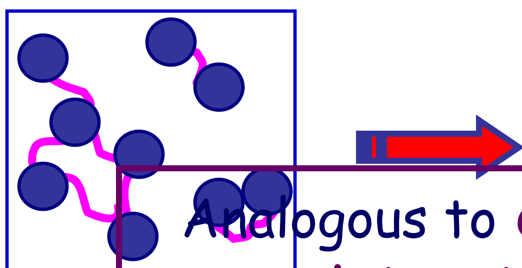


Monte Carlo
And Equilibration



Thermodynamics,
Phase Behavior

MS, VP, VG:
JCP 2005; Langmuir '06;
Macromolecules '06.



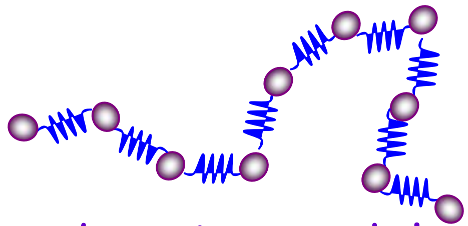
Gelation,
Elastic Modulus

Cluster Counting

Analogous to density functional theories used to obtain interatomic potentials in quantum chemistry

Integrating Out the Polymer By Mean-Field Theory

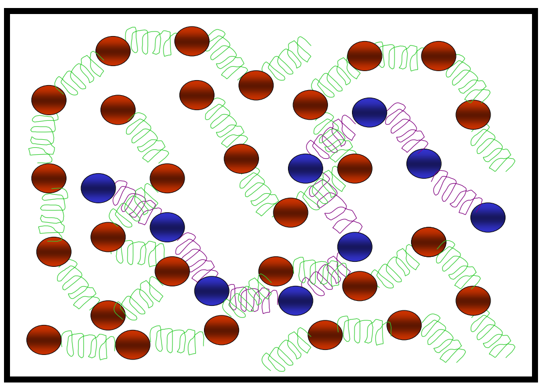
N segment chain

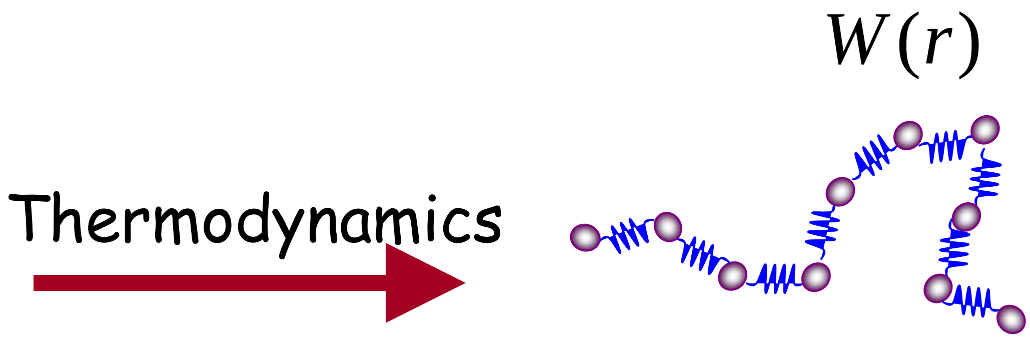


Bead-spring model of polymer

- Self avoiding random walk
- Charge effects

Idea behind mean-field theory*





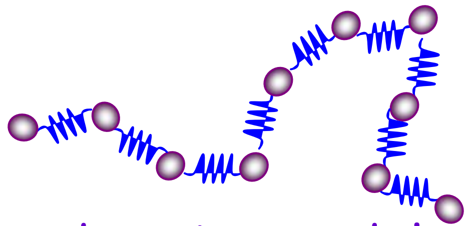
• Single chain in a potential field W(r).

• W(r) determined self-consistently to match statistical properties of polymers, say, the volume fraction.

*: Helfand (1975)

Integrating Out the Polymer By Mean-Field Theory

N segment chain



Bead-spring model of polymer

- Self avoiding random walk
- Charge effects

Mean Field Approach

Presence of other chains

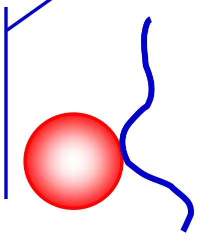
Self consistent potential field w(r)

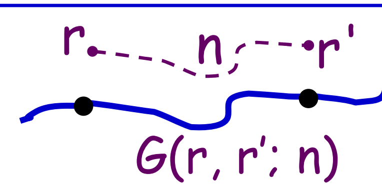
Configurations of a chain subjected to w(r)

$$\frac{\partial G(r,r';n)}{\partial s} = \nabla^2 G(r,r';n) - iw(r)G(r,r';n) \quad G(r,r';0) = \delta(r-r')$$

BCs :

Polymer - particle interactions



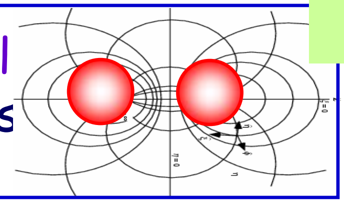


Field-Theory Model For Polymers

Density distributions for polymer → Polymer mediated effective interactions

Numerical solution

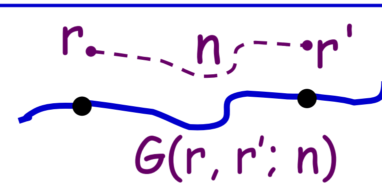
Bispherical coordinates

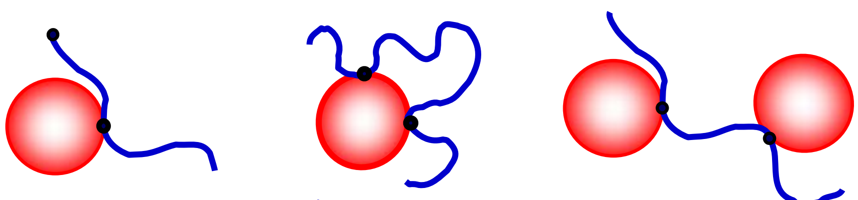


Curvature of particles accounted exactly!!!

Configurations of a chain subjected to w(r)

$$\frac{\partial G(r,r';n)}{\partial s} = \nabla^2 G(r,r';n) - iw(r)G(r,r';n) \quad G(r,r';0) = \delta(r-r')$$





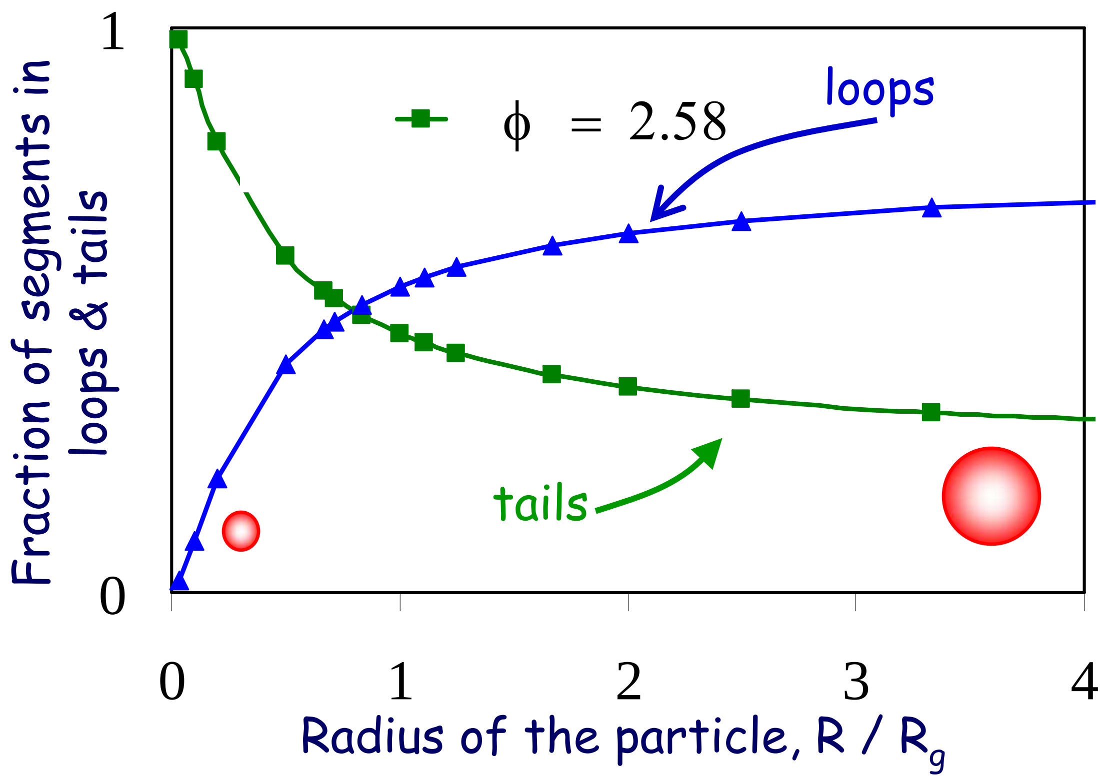
Tail

Loop

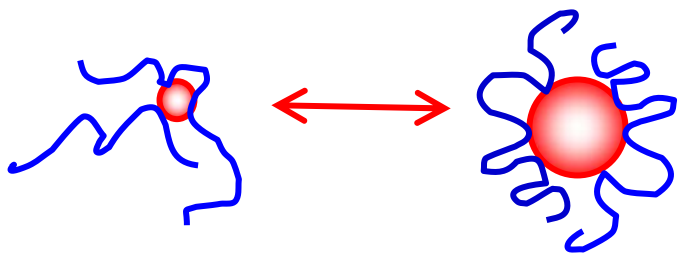
Bridge

Number and probability distribution

Adsorbed Layer: Particle Size Effects



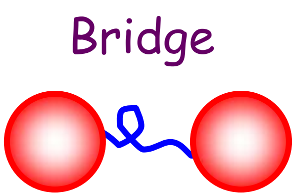
Tails dominate !

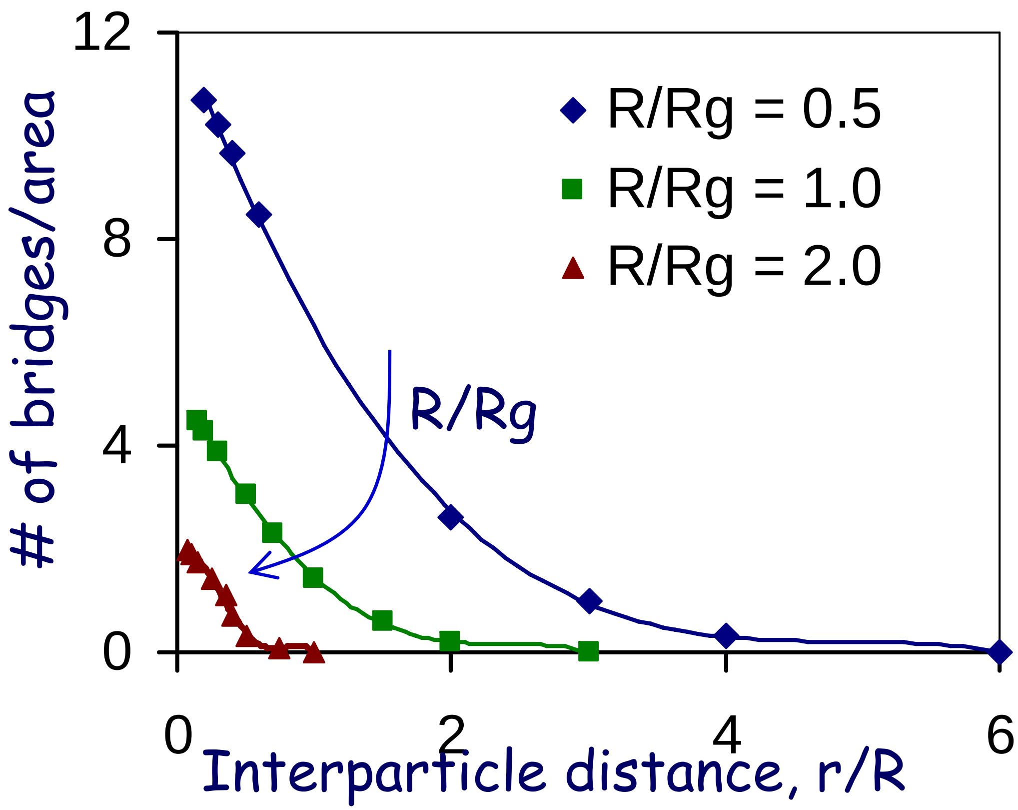


Loops dominate !

Smaller particles - tails dominate

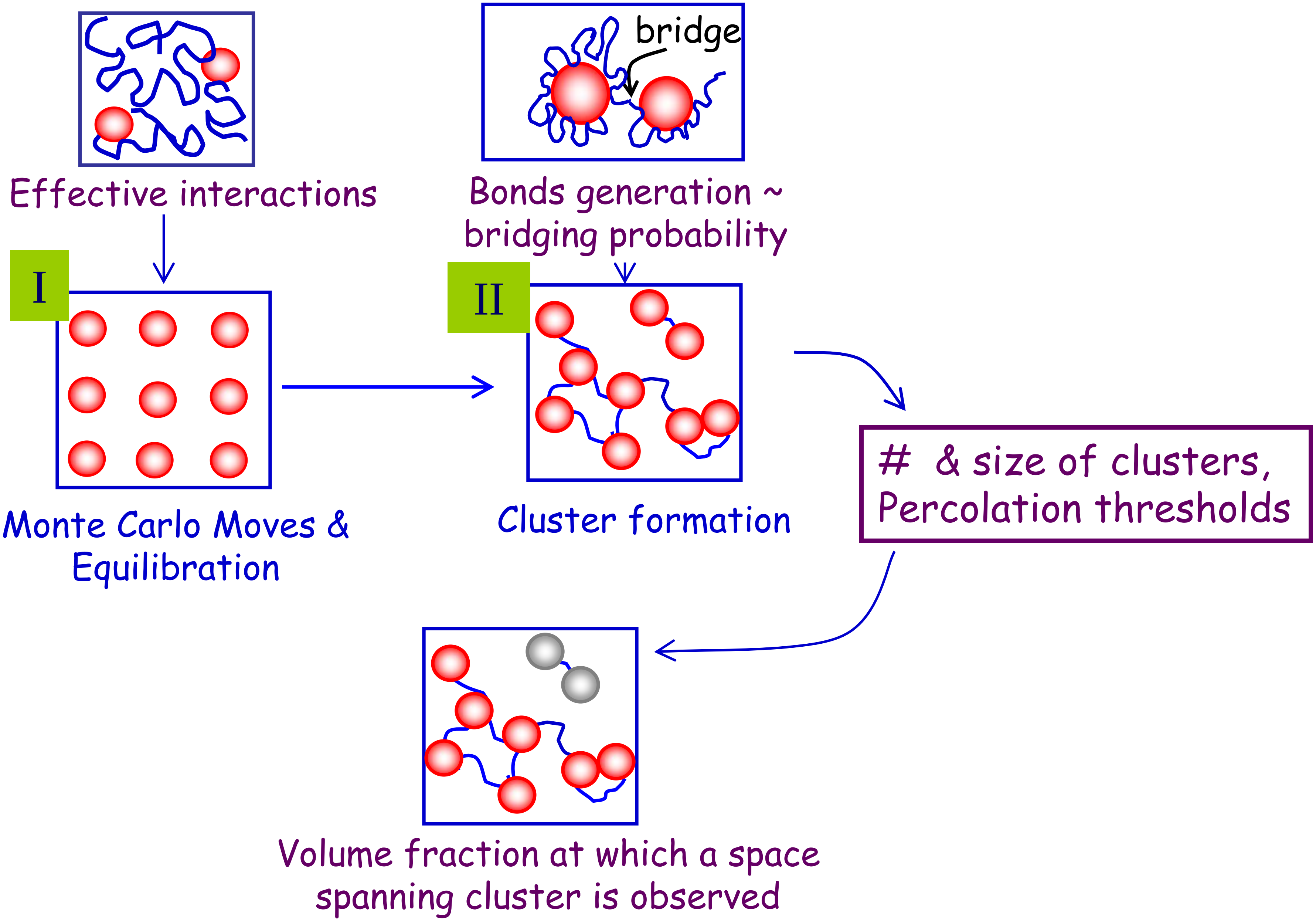
Bridging: Particle Size Effects





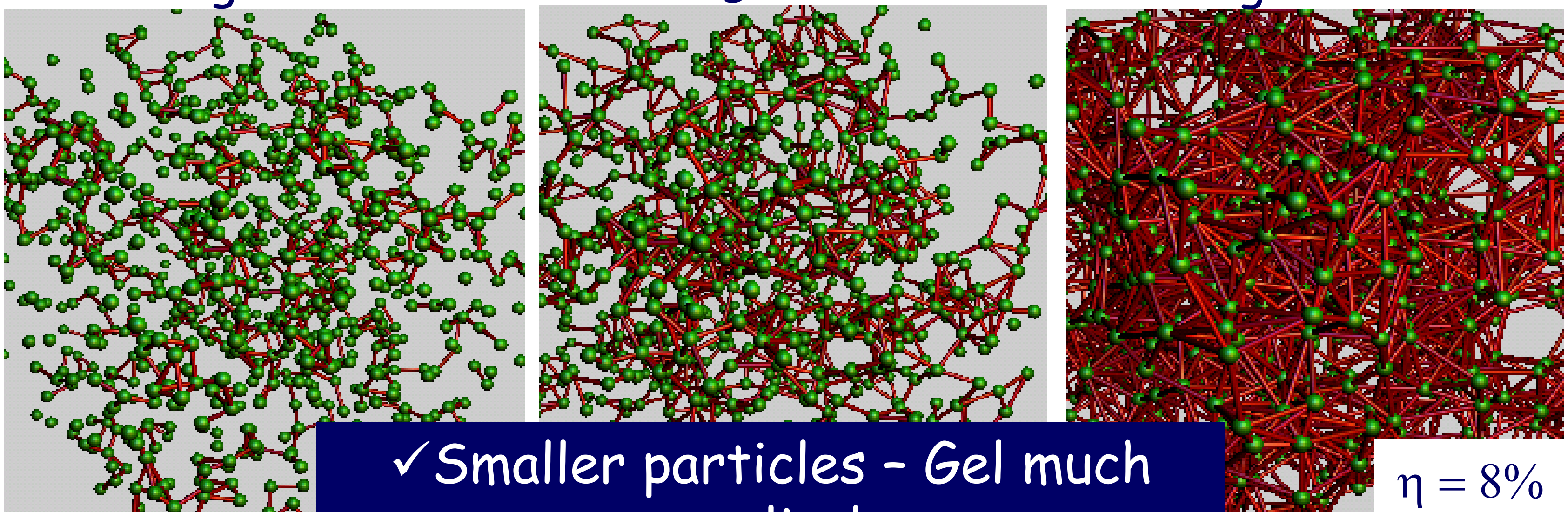
Smaller particles – More number of bridges

Cluster Statistics and Gelation



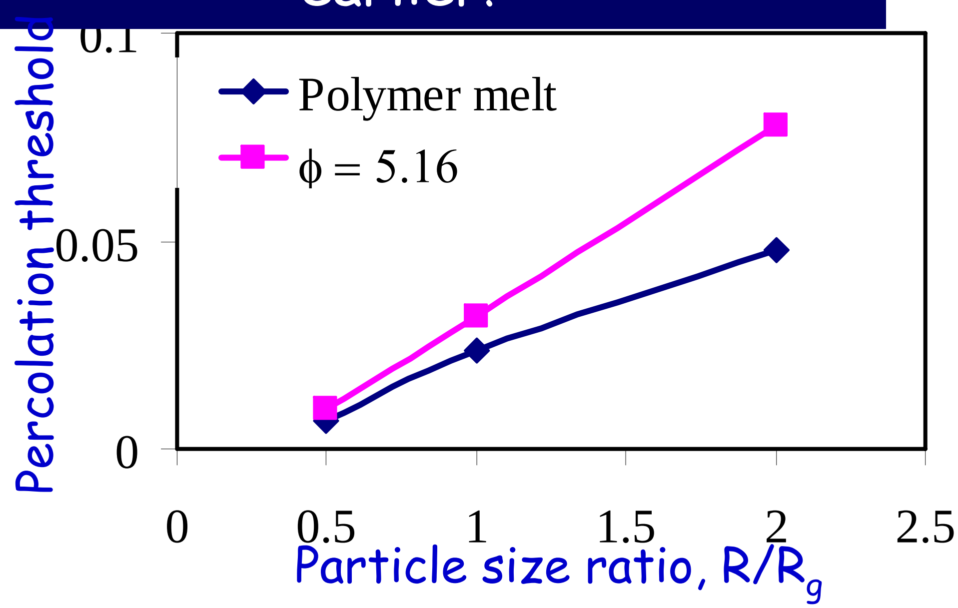
Cluster Statistics and Gelation

R/Rg = 2.0 R/Rg = 1.0 R/Rg = 0.5



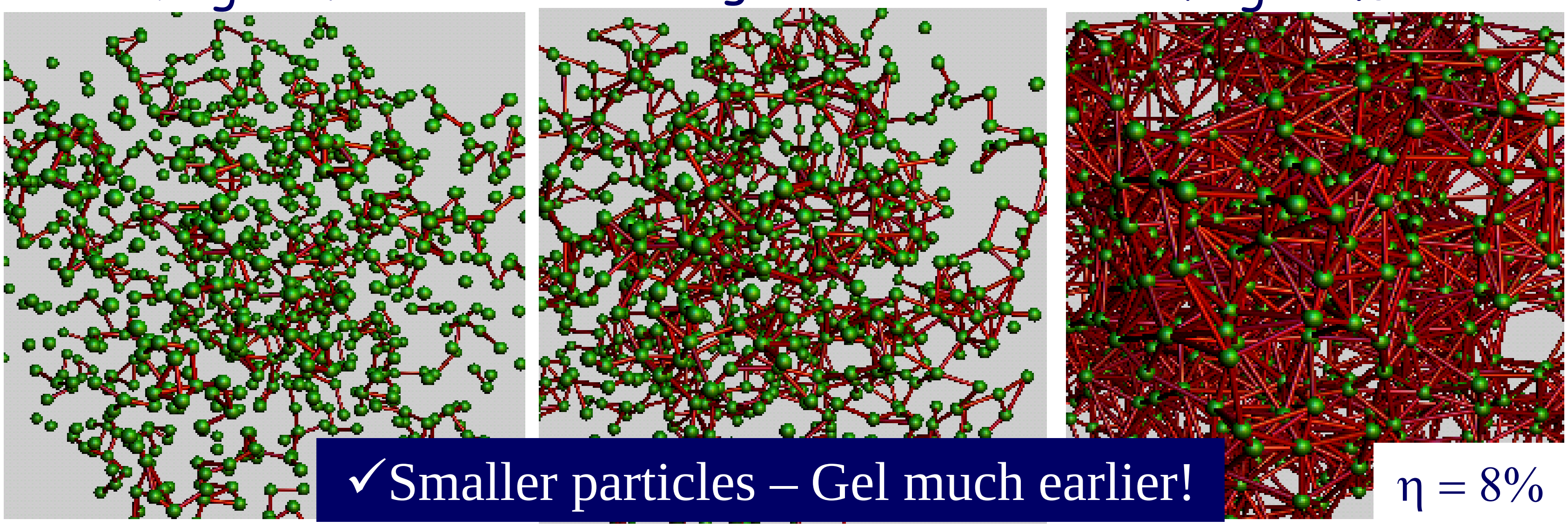
η = 8%

✓Smaller particles – Gel much earlier!



Determining Elastic Properties

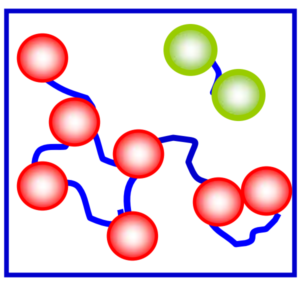
R/Rg = 2.0 R/Rg = 1.0 R/Rg = 0.5



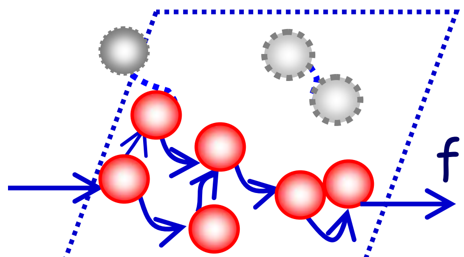
✓Smaller particles – Gel much earlier!

$\eta = 8\%$

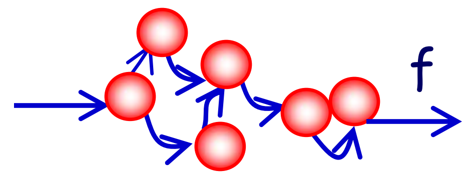
Post-gel systems



Identification of backbone



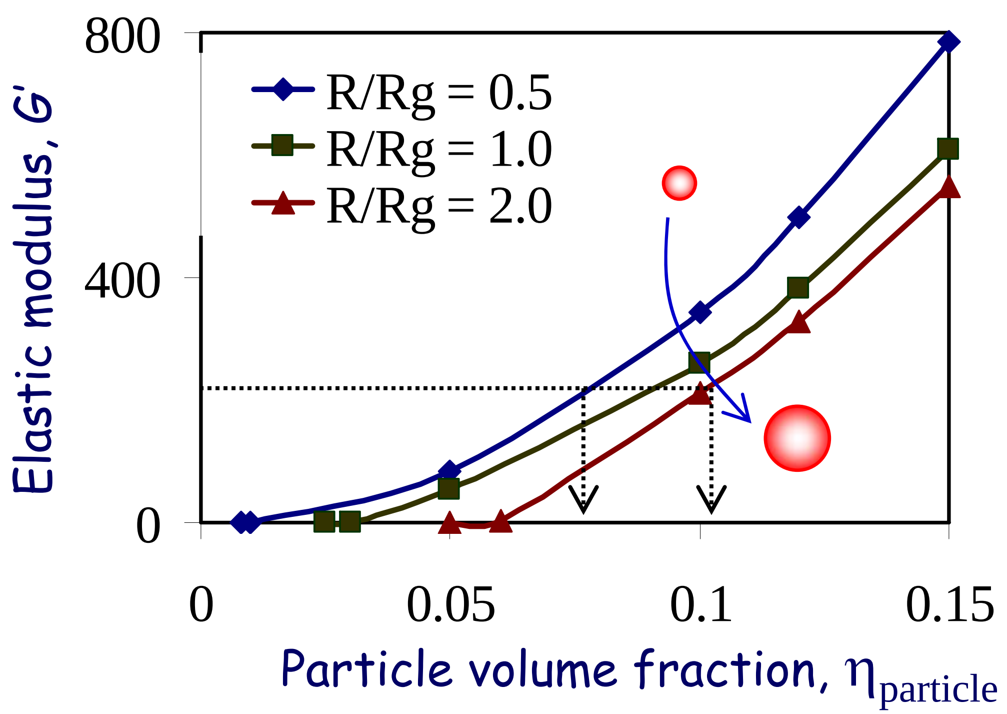
Graph theory



Elastic properties

Simple Network Theories: Elastic Modulii = Number of Bridges in backbone

Elastic Modulii of Gels



✓Smaller particles -> stronger reinforcement.

✓Smaller quantities of nanoparticles are required.

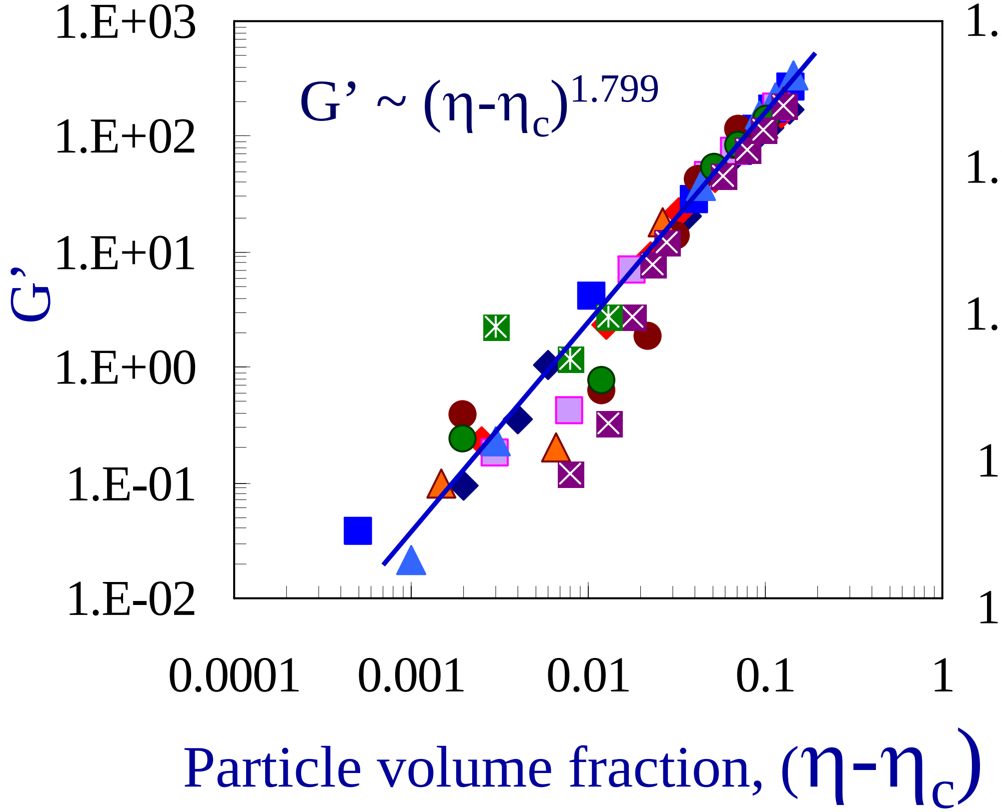
✓ Bridging induced clustering of particles responsible for reinforcement.

*Surve, Prymitsyn, Ganesan, Phys. Rev. Lett.

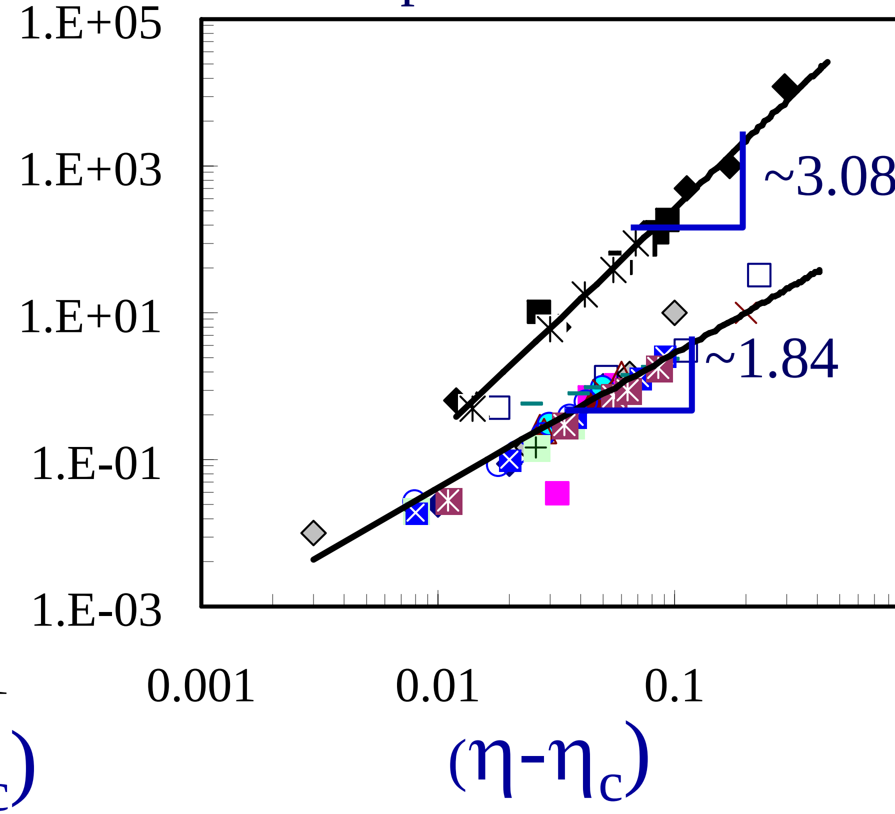
Much Stronger Enhancements of Moduli in Smaller Particles

Scaling of Elastic Modulii of Gels

Simulation results*



Experimental data



*Surve, Prymitsyn, Ganesan, Phys. Rev. Lett.

Universal scaling of elastic modulus

Conclusions – Part II

- ✓Gelation
  - ✓For smaller particles, gelation occurs at very low volume fractions
  - ✓Small particles -> dense networks
  - ✓Small particles -> Much stronger enhancements in modulii