

# Shear induced ordering in branched living polymer solutions

P. B. Sunil Kumar

Department of Physics, IIT Madras.



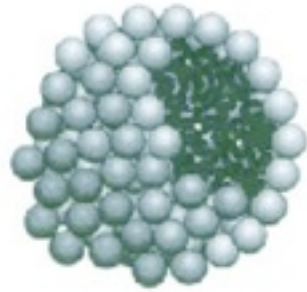
With Snigdha Thakur, Prathyusha K. R. , Abhijit P. Deshpande, Mohamed Laradji,

# Amphiphiles and aggregates

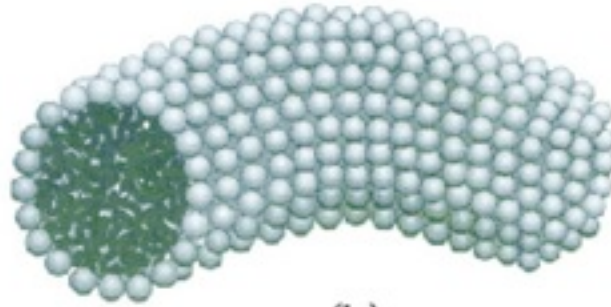


Hydrophilic

Hydrophobic



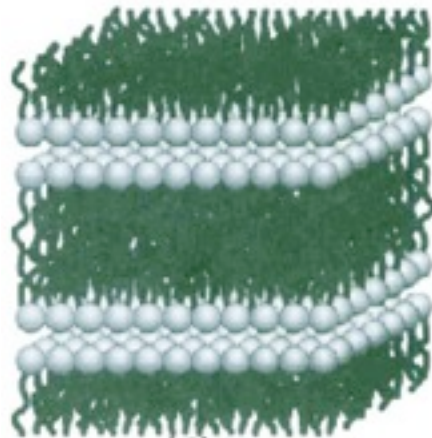
(a)



(b)



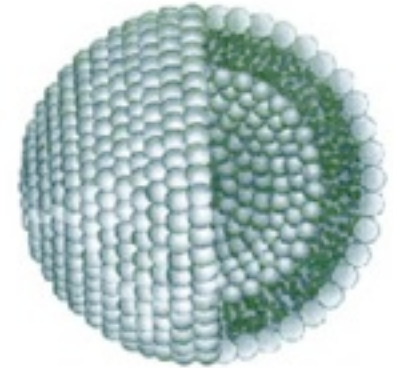
(c)



(d)



(e)



(f)

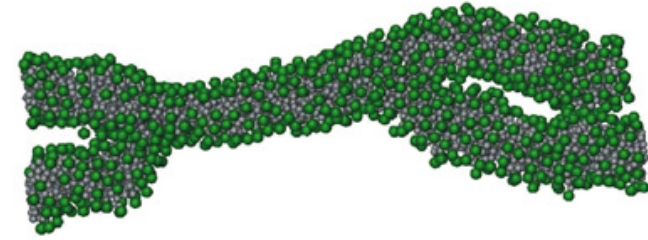
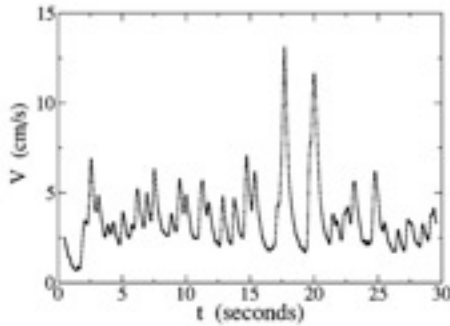
(a) Spherical Micelle, (b) Cylindrical Micelle, (c) Reverse Micelle, (d) Bilayer,  
(e) Hexagonal phase, (f) Vesicles

Cylindrical micelles also called living polymers

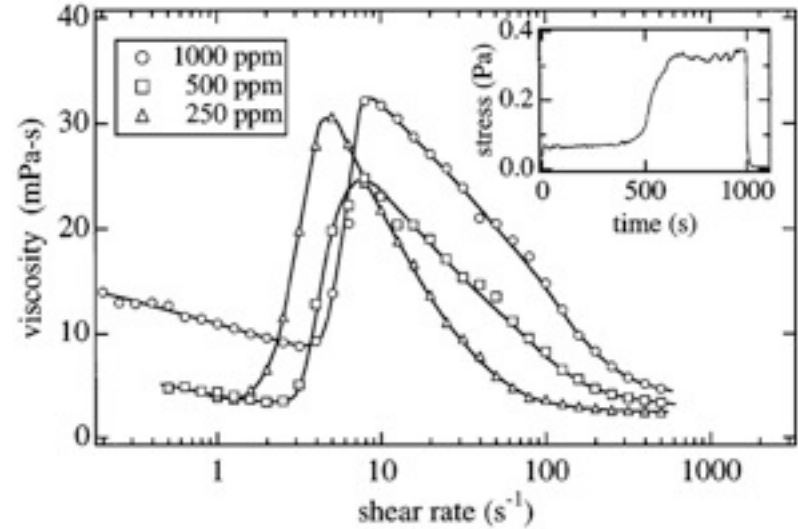
Can undergo scission/recombination under thermal fluctuations <sup>2</sup>

# Micellar solutions are examples of living polymers

## Oscillating solid sphere



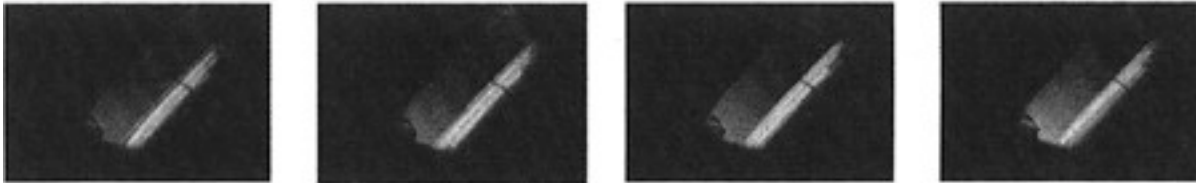
## Shear induced gelation



*Jayaraman et al. PRE, 67, 65301 (2003)*

*Liu et al. PRL, 77, 2121 (1996)*

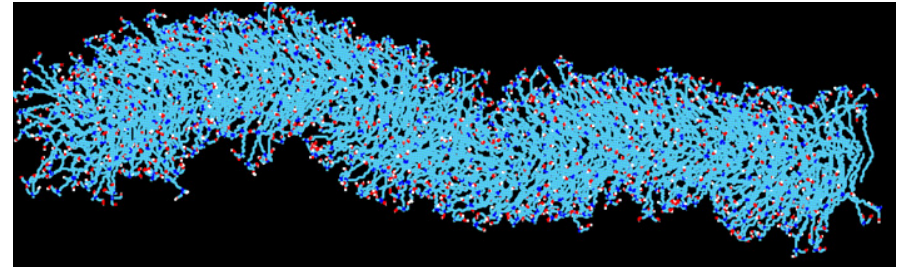
## Shear banding



*Lerouge et al.  
PRL, 81, 5457 (1998)*

**Rheocaos** : R. Bandyopadhyay, G. Basappa, and A. K. Sood, Phys. Rev. Lett. **84**, 2022 (2000).

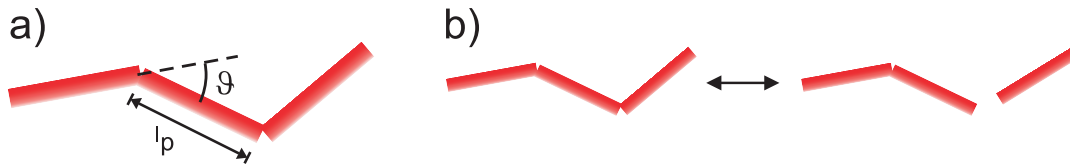
Padding and Boek (2004): Atomistic MD simulations elucidate than for EHAC surfactants to compute the mechanical properties of atomistic micelles such as persistence length, elastic modulus and scission energy



- [8] Padding J T and Boek E S 2004 *Europhys. Lett.* **66** 756  
 [9] Padding J T and Boek E S 2004 *Phys. Rev. E* **70** 031502

MD simulations of micelles consisting of coarse-grained (CG) mode surfactants to optimize the CG model with respect to the structure factor  $S(q)$  of the atomistic micelle at large values of the wavevector  $q$ . The CG model is used to extrapolate the structure factor for small  $q$  in order to obtain reliable values for the micelle bending rigidity and persistence length .

Boek E S, den Otter W K, Briels W J and Iakovlev D 2004 *Phil. Trans. R. Soc. A* **362** 1625  
 den Otter W K, Shkulipa S A and Briels W J 2003 *J. Chem. Phys.* **119** 2363

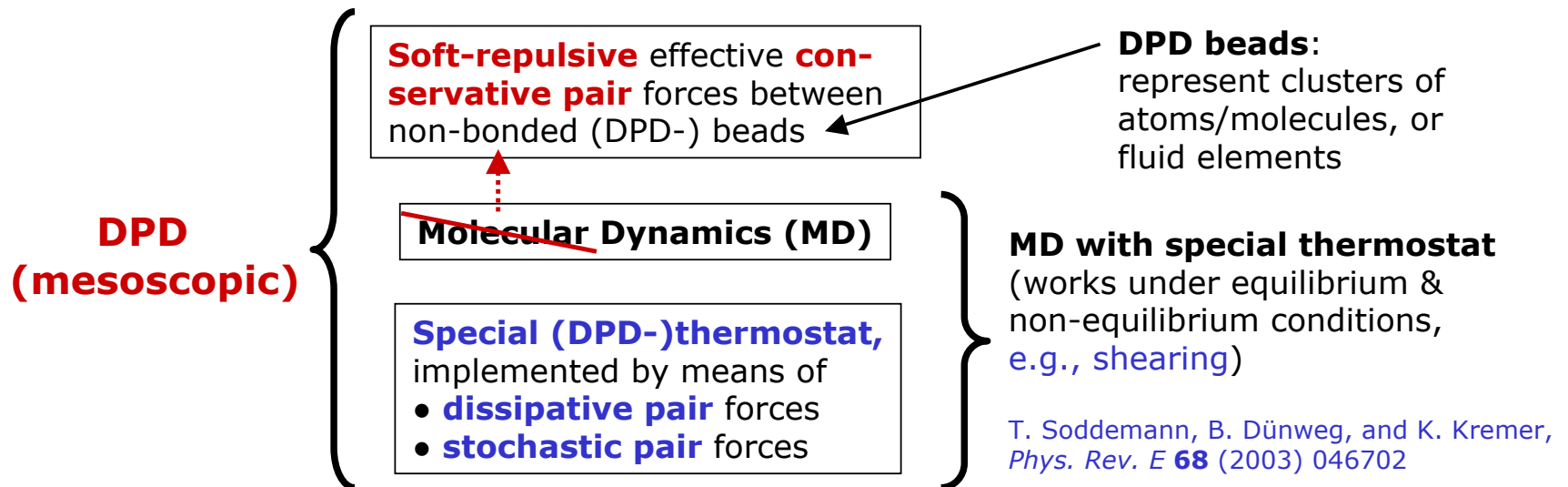


Padding, Boek and Briels ((2005): a mesoscopic model of wormlike micelles, represented by chains which can break and recombine and can be subjected to shear flow. For this model, where the smallest length-scale is the persistence length, the elastic modulus , scission energy and persistence length are taken as input parameter from the atomistic and CG MD.

# Dissipative Particle Dynamics (DPD) is a particle based “meso-fluid” model

- P.J. Hoogerbrugge and J.M.V.A. Koelman, *Europhys. Lett.* **19** (1992) 155
- P. Español and P. Warren, *Europhys. Lett.* **30** (1995) 191

From a technical point of view ...



“Hydrodynamic interactions” (flow effects) are fully taken into account!



## DPD- Basic model

N "dpd" particles interacting via conservative, dissipative and random pair wise interactions

$$F_{ij}^C = a_{ij}\omega_{ij}(r_{ij})\hat{r}_{ij},$$

$$\omega(r) = \begin{cases} 1 - r/r_c & \text{for } r \leq r_c, \\ 0 & \text{for } r > r_c. \end{cases}$$

$$F_{ij}^D = \gamma\omega_{ij}^D(r_{ij})(\hat{r}_{ij} \cdot \vec{v}_{ij})\hat{r}_{ij}$$

$$\langle \theta_{ij}(t) \rangle = 0,$$

$$F_{ij}^R = \sigma(\Delta t)^{-1/2}\omega_{ij}^R(r_{ij})\theta_{ij}\hat{r}_{ij}$$

$$\langle \theta_{ij}(t)\theta_{kl}(t') \rangle = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta(t - t').$$

$$\omega^D = (\omega^R)^2 = (1 - r/r_c)^{0.25} \quad \text{for } r < r_c$$

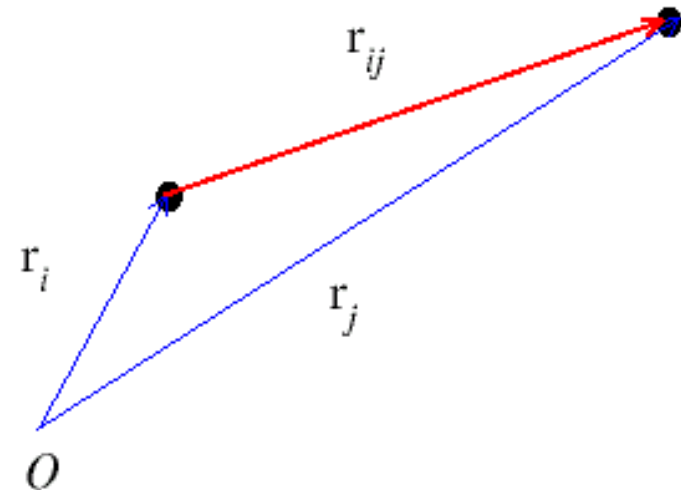
Dissipative & random forces related through fluctuation-dissipation theorem

$$\gamma = \sigma^2 / 2k_B T.$$

**Pair-wise random and dissipative forces conserve momentum**

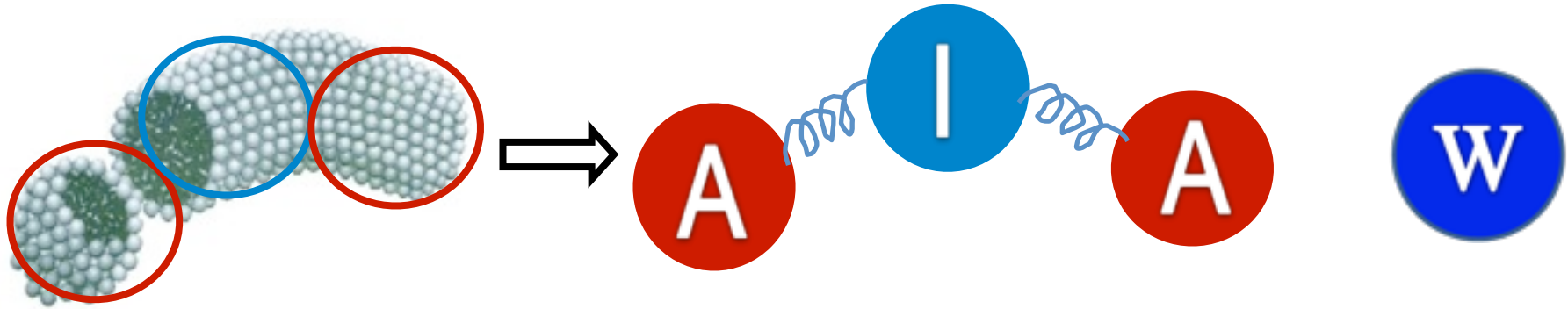
**Resulting in correct description of hydrodynamics**

**Soft interactions allow for longer time steps, and therefore much longer times can be probed via DPD as opposed to MD**



- P. J. Hoogerbrugge and J. M. V. A. Koelman, *Europhys. Lett.* **19**, 155 (1992)

# DPD model for living polymers ( LP )



$$F_{ij}^C = \alpha_{ij} (\omega_1^C(r_{ij}) + \omega_2^C(r_{ij})) \hat{r}_{ij} \quad \alpha_{ij} = a_{ij}$$

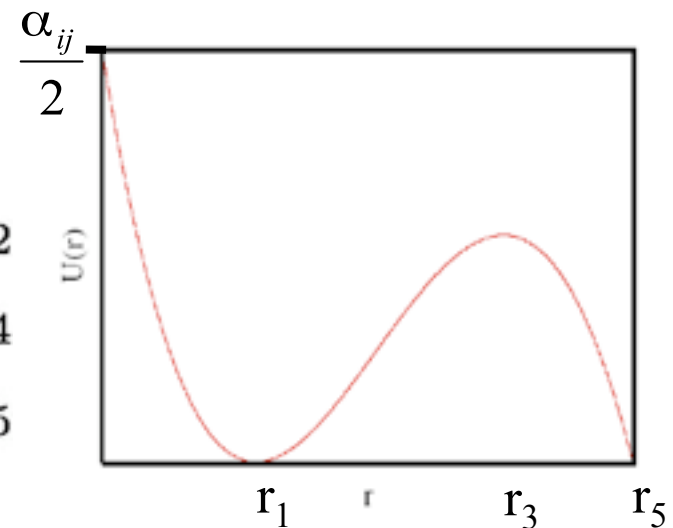
For,  
 W - W, W - I  
 W - A, I - I, I - A

$$\omega_1^C(r_{ij}) = \left(1 - \frac{r_{ij}}{r_c}\right) \quad \text{for } r_{ij} < r_c$$

$$\omega_2^C(r_{ij}) = 0$$

For, A-A

$$\omega_2^C(r) = \begin{cases} (r_1 - r) & r < r_1 \\ a(r_1 - r) & r_1 \leq r < r_2 \\ a(r - r_3) & r_2 \leq r < r_4 \\ a(r_5 - r) & r_4 \leq r < r_5 \\ 0 & r \geq r_5, \end{cases}$$

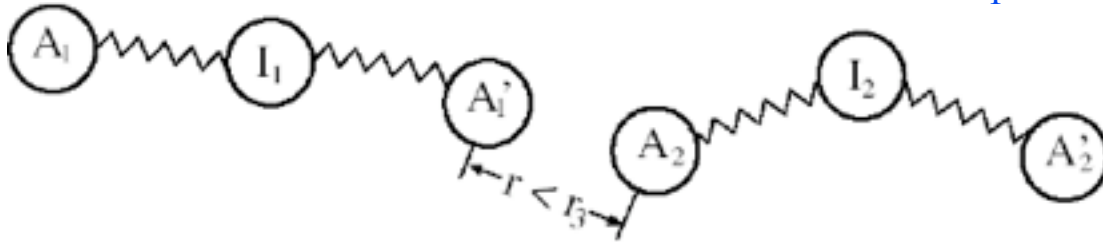


# A trimer based model for living polymers

## The three-body bending potential

$$U_{3body} = \frac{k_3}{2} (1 - r_{jk}/r_3)^2 (1 - \hat{r}_{ij} \cdot \hat{r}_{jk})$$

$$I_1 - A'_1 - A_2 \quad \& \quad A'_1 - A_2 - I_2$$



Three body potentials  $U_{ijk} = k_3(1 - \hat{r}_{ij} \cdot \hat{r}_{jk})$  for  $A_1I_1A'_1$  and  $A_2I_2A'_2$

$$\mathbf{f}_i = \sum_{ij} \mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R + \mathbf{F}_{ij}^S + \mathbf{F}_{3body} \quad \text{For LP}$$

$$\mathbf{f}_i = \sum_{ij} \mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R \quad \text{For solvent}$$

- Simulation box size  $L = 40$  , Periodic Boundary Condition
- density  $\rho = 3$  , number of particles 192000
- Resting length A-I = 1.0 , A-A = 2.0
- Spring constant  $k = 200$
- Time step = 0.01  $\tau$  , with  $\tau$  of the order of  $10^{-6}$  sec
- We use LAMMPS ( modified)



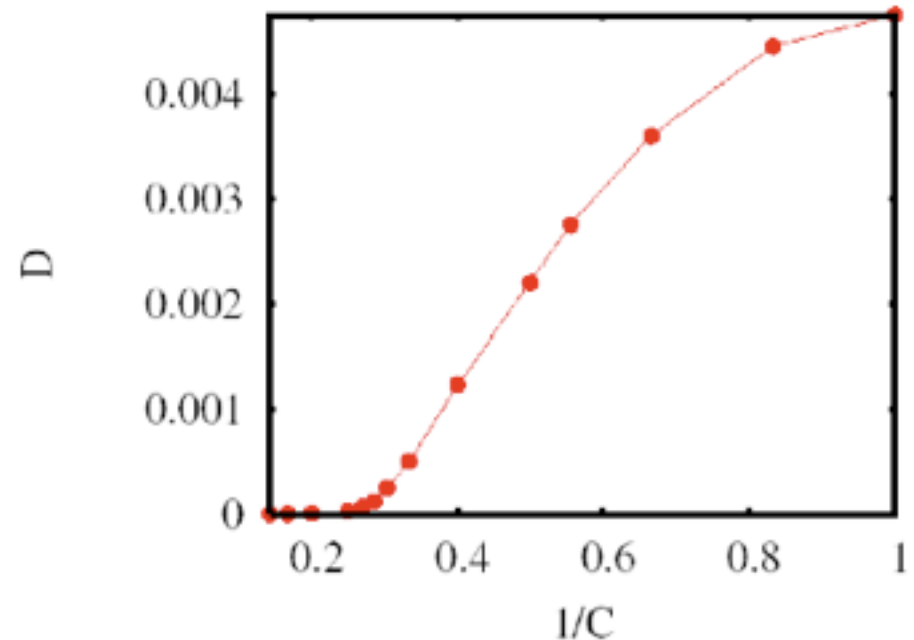
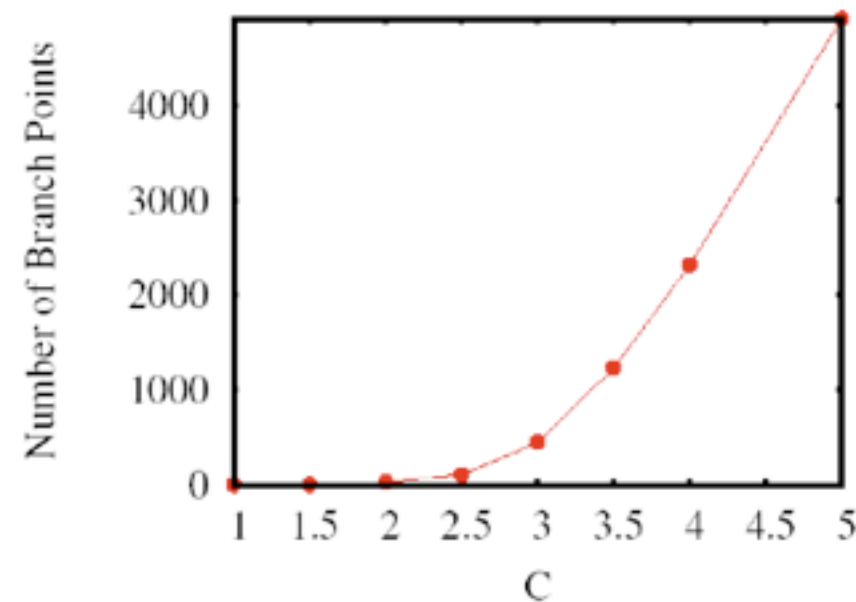
# Fluid-gel transition

C -- % ratio of number of monomers to the total number of particles

Phase behavior was characterized by diffusivity of trimers

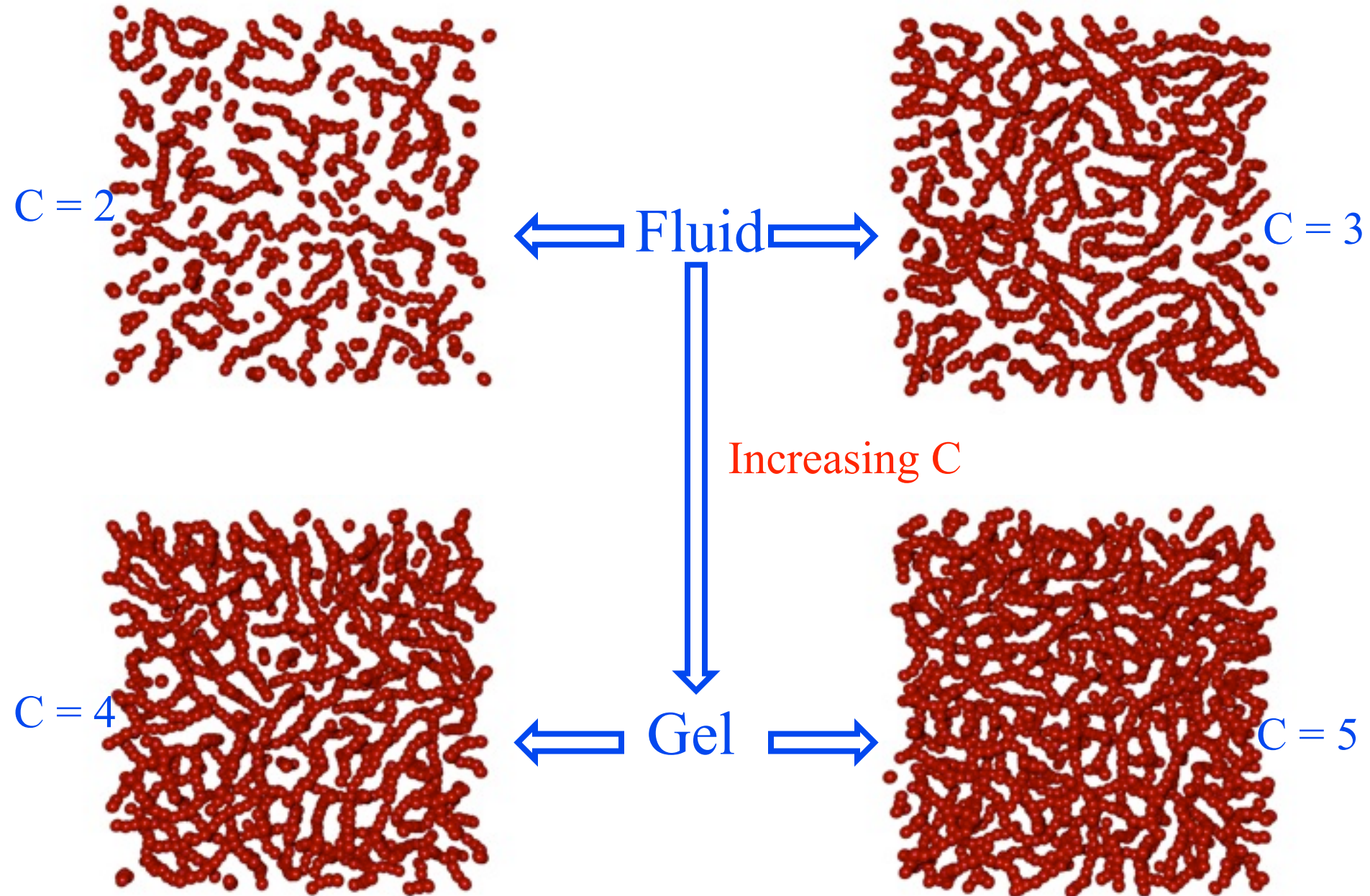
- Fluid phase at low C
- Gel phase at higher C
- Transition point  $C = C_p = 3.5$

$$D = \frac{1}{6Nt} \left[ \sum_{i=1}^N (X_i^{cm}(t_0 + t) - X_i^{cm}(t_0))^2 \right]$$



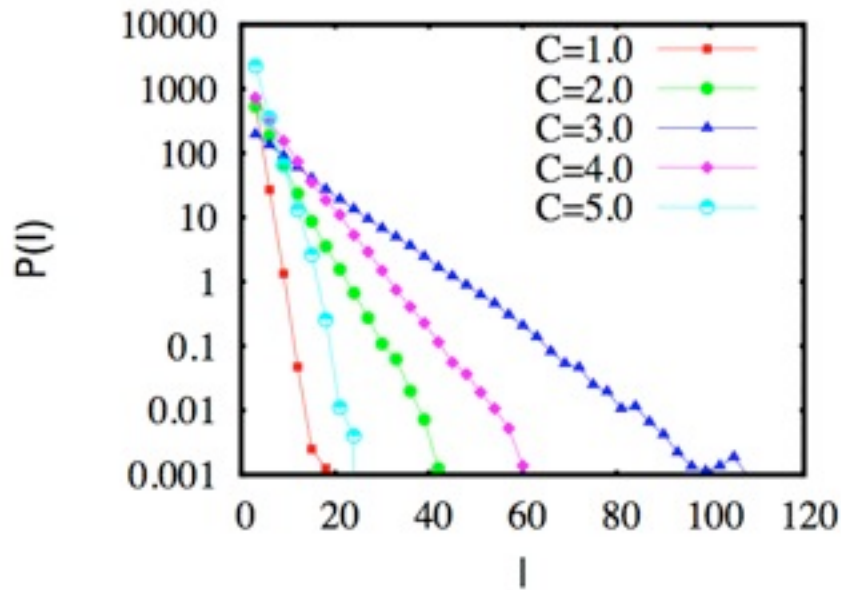
• Branched point ---- coordination number of particle is  $> 2$

# Organization of polymers



## Segment length distribution

$$P(l, T) = \frac{\phi}{\bar{l}^2} \exp(l/\bar{l})$$

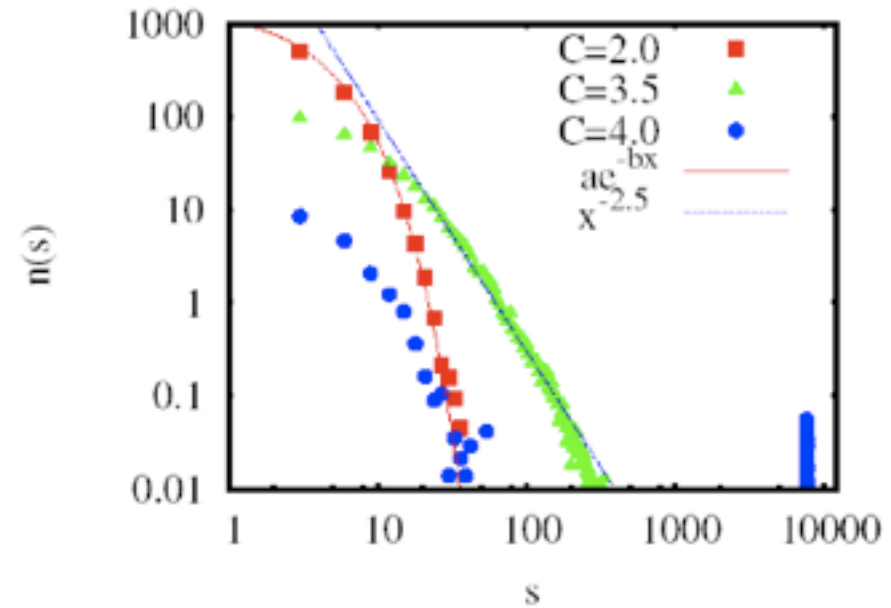


$\bar{l}$  Average polymer length  
 $\Phi$  Monomer concentration

Branching reduces the average segment length

## Cluster size distribution

branching of polymers lead to random percolation

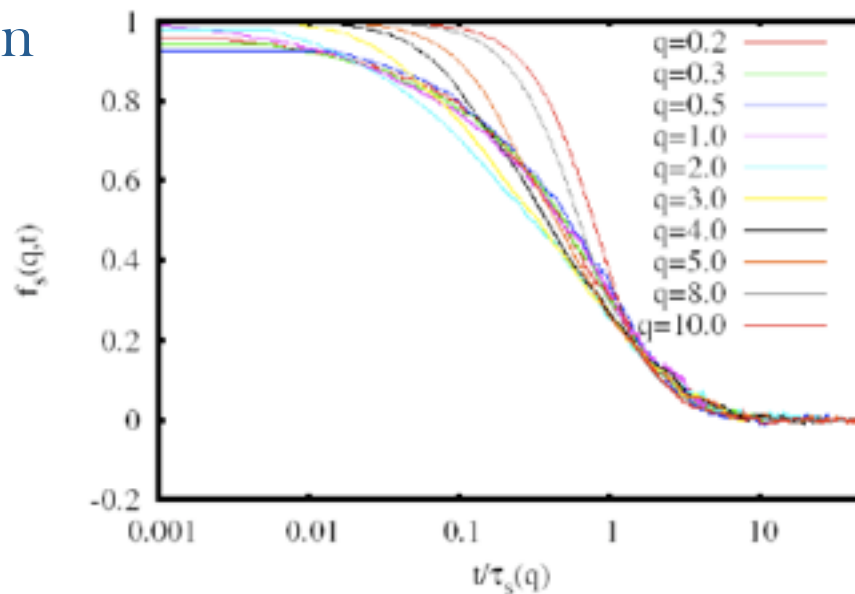


- Exponential distribution at low  $C < C_p$
- Power law distribution at  $C = C_p$ : random percolation
- Gel phase contains spanning clusters and small segments

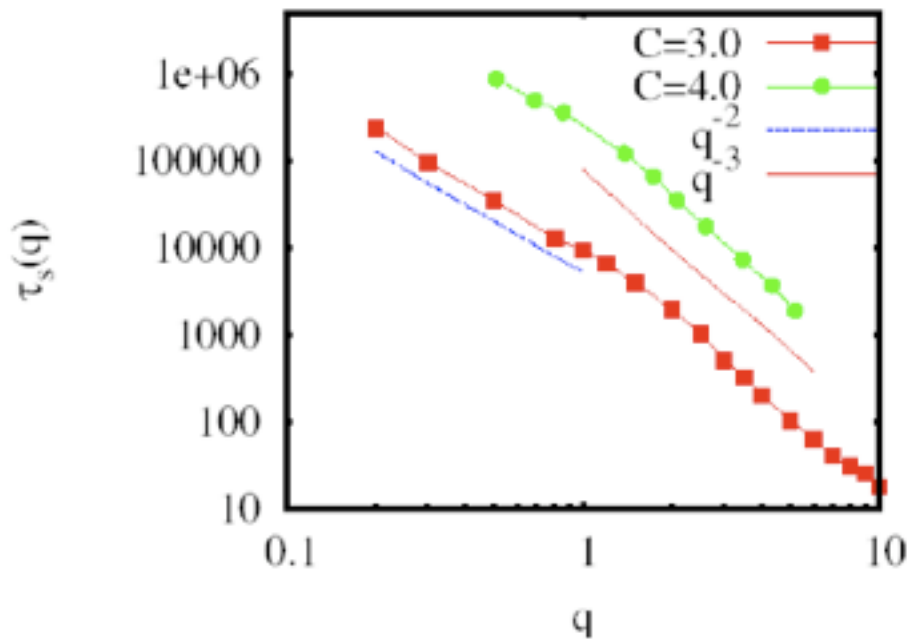
# Self-intermediate scattering function

$$F_s(\vec{q}, t) = \frac{1}{N} \sum_{i=1}^N \exp(i\vec{q} \cdot (\vec{r}_i(t) - \vec{r}_i(0)))$$

N: total number of monomers



## Relaxation time



$$\tau_s(\vec{q}, T) = \int F_s(\vec{q}, t) dt$$

Zimm dynamics at large  $q$ :  $\tau_s \sim q^{-3}$

Diffusive at low  $q$ :

$$\tau_s \sim q^{-2}$$

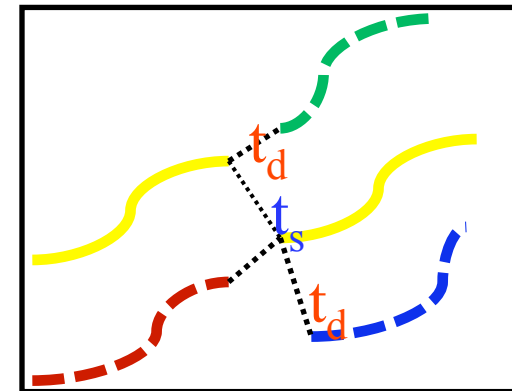
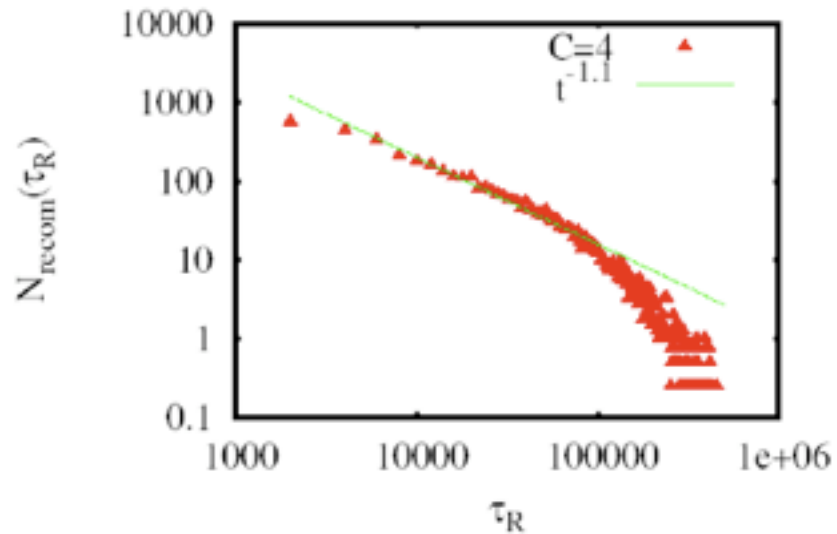
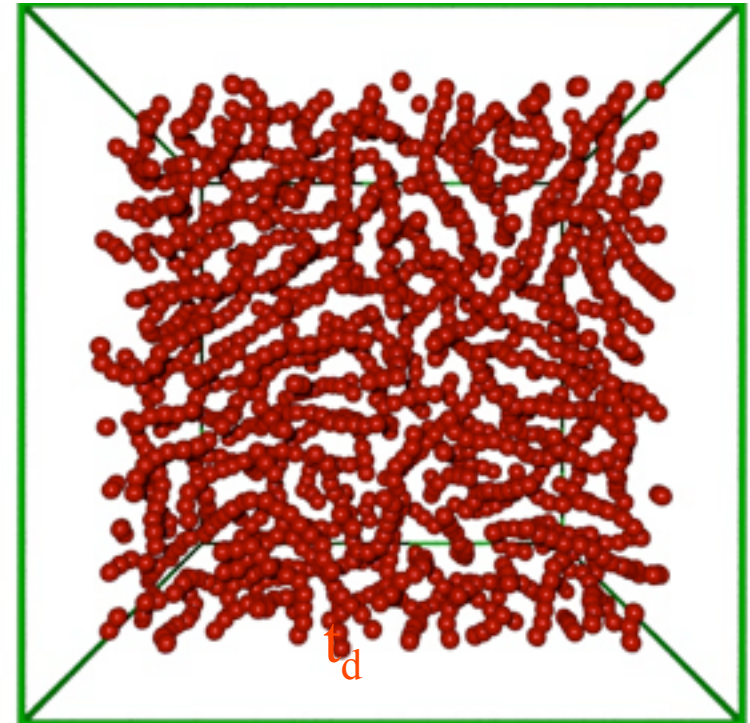
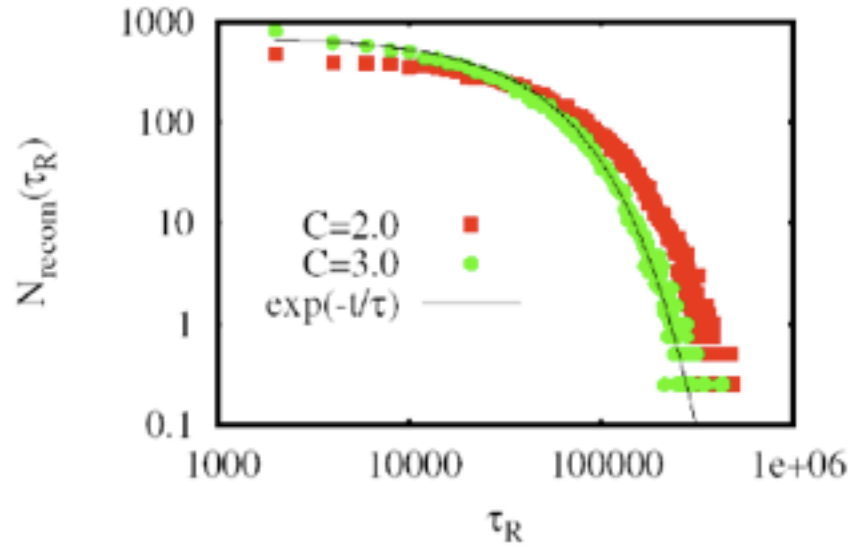
S. Thakur et al Soft Matter **6**, 489, 2010



First recombination time  $\tau_R = \text{scission time } (t_2) - \text{recombination time } (t_1)$

Two classes of recombination kinetic: Mean field (MF) and Diffusion controlled (DC)

• Ben O'Shaughnessy and Jane Yu, PRL, 74, 4329 (1995)





# stress relaxation

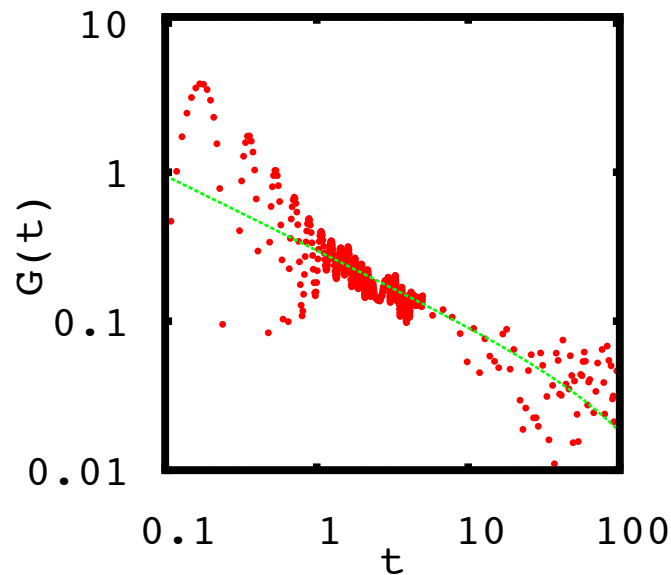
$$G(t) = \frac{V}{K_B T} \langle \sigma_{\alpha\beta}(t) \sigma_{\alpha\beta}(0) \rangle$$

$$\sigma_{\alpha\beta} = -\frac{1}{V} \left( \sum_{i=1}^N m_i v_{i\alpha} v_{i\beta} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N r_{ij\alpha} F_{ij\beta} \right)$$

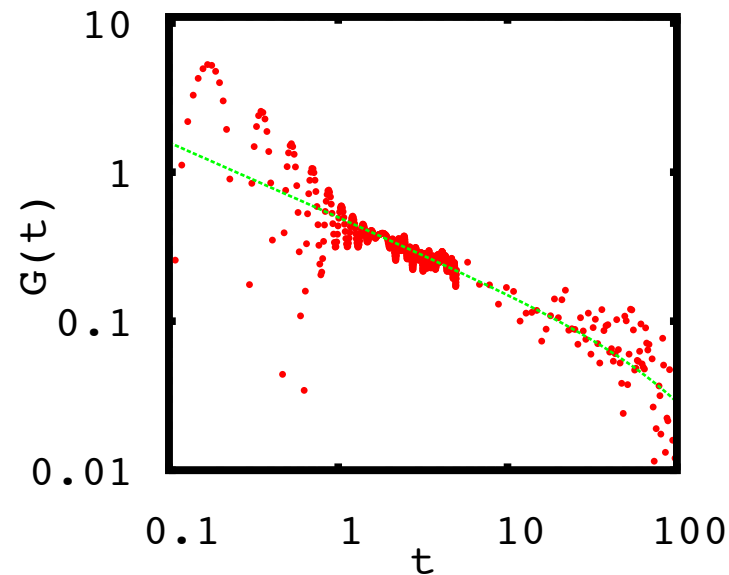
- We find a residual stress is due to the spanning clusters with stretched bonds
- Early time oscillation is the result of bond potential within a trimer

- $G(t)$  decays as:  $G(t) = A \sqrt{\frac{\tau_0}{t}} \exp(-t/\tau)$

• *G. Faivre and J. L. Gardissat, Macromolecule, 19, 1988 (1986)*

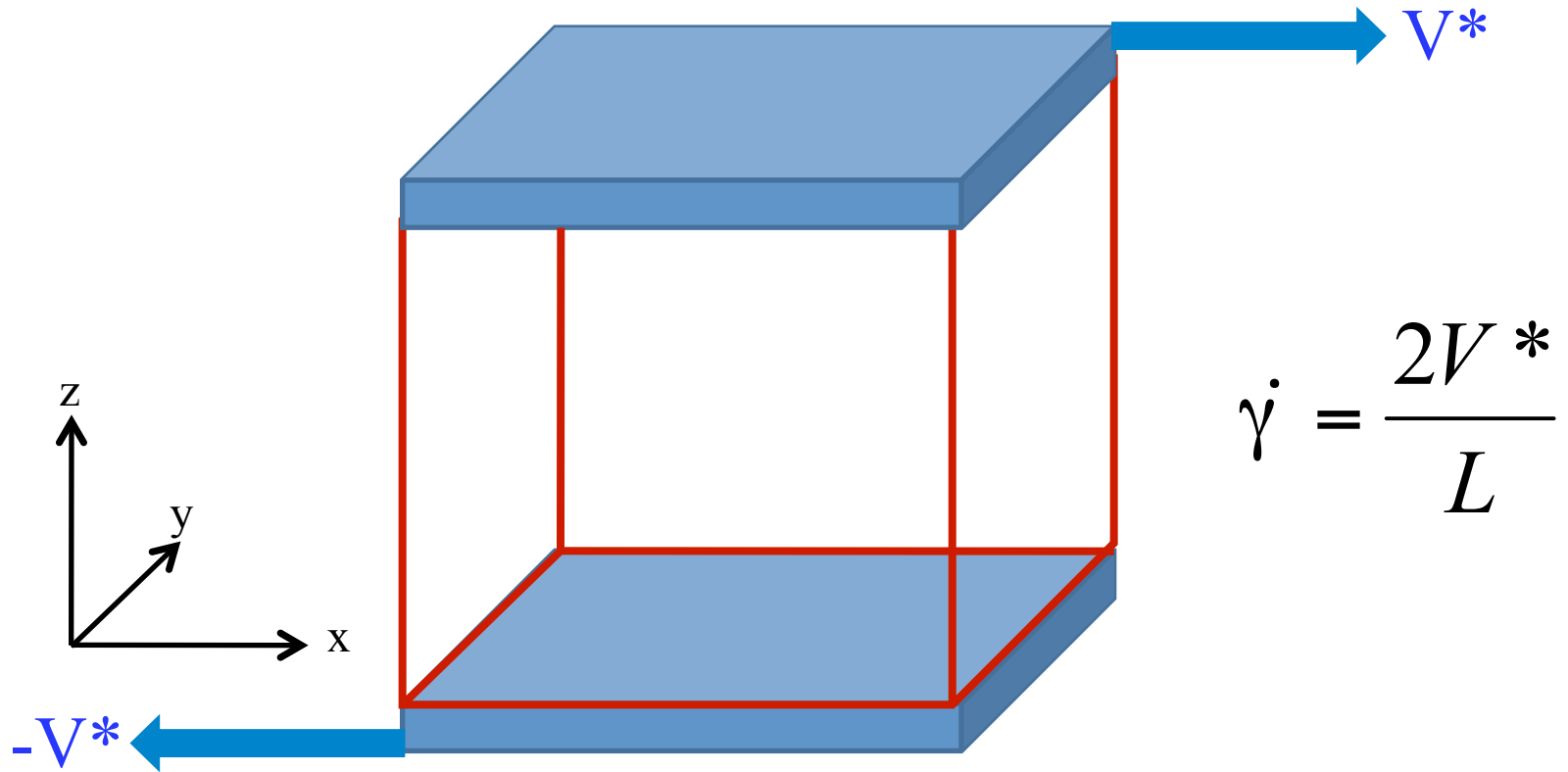


$C=3.0$



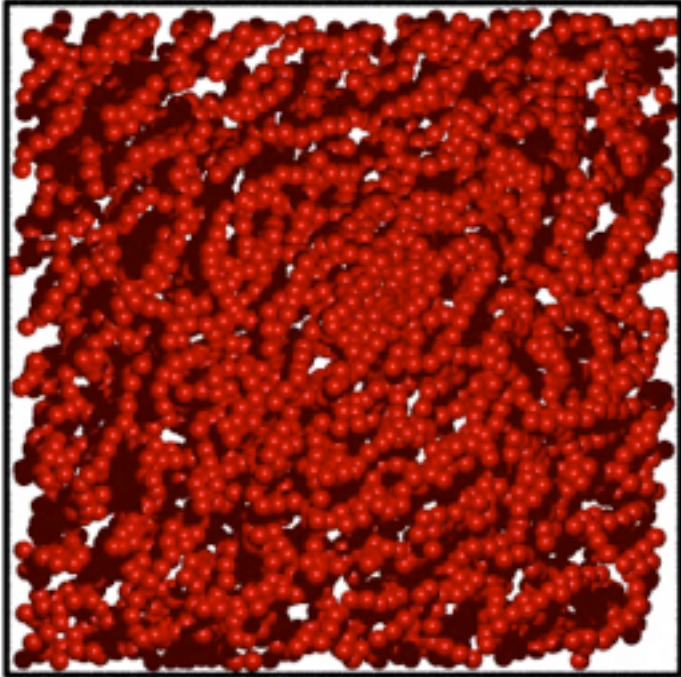
$C=4.0$

# Shear



- Density of wall =  $20^*$  Density of fluids
- Periodic boundary in x & y directions
- Results were verified using Lees-Edward method to rule out wall effect

## Shear induced Lamellar phase



Initiated by migration of polymers towards the higher velocity regions

First layer forms near the shear boundaries

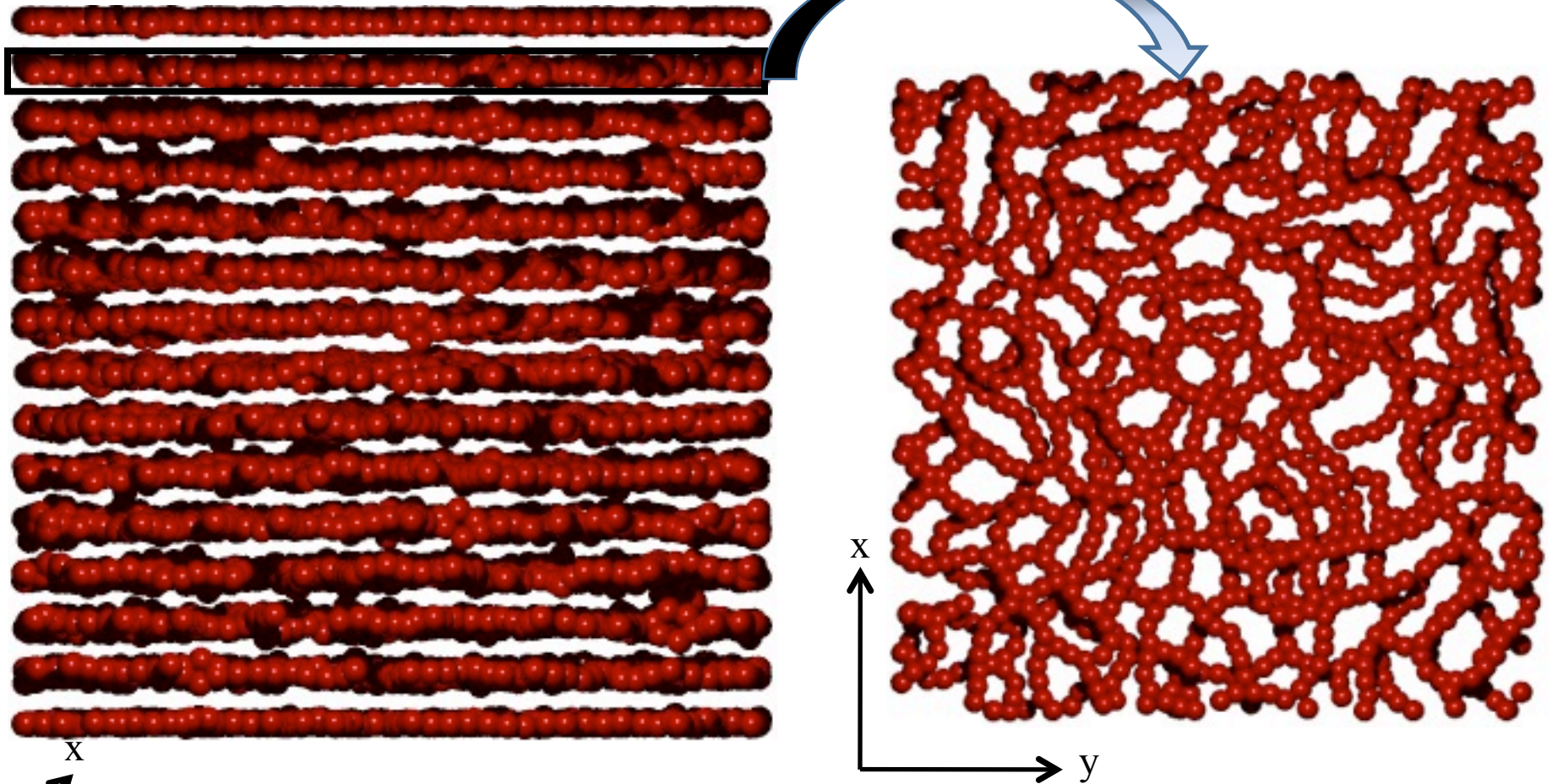
All the polymers within a range of  $r_5$  is pulled towards the boundary

Next layer forms exactly at a distance  $r_5$  from the first

# Shear induced structures

- $\dot{\gamma} = 1.0$

- $r_1, r_2, r_3, r_4, r_5 = 1.0, 1.5, 2.0, 2.5, 3.0$

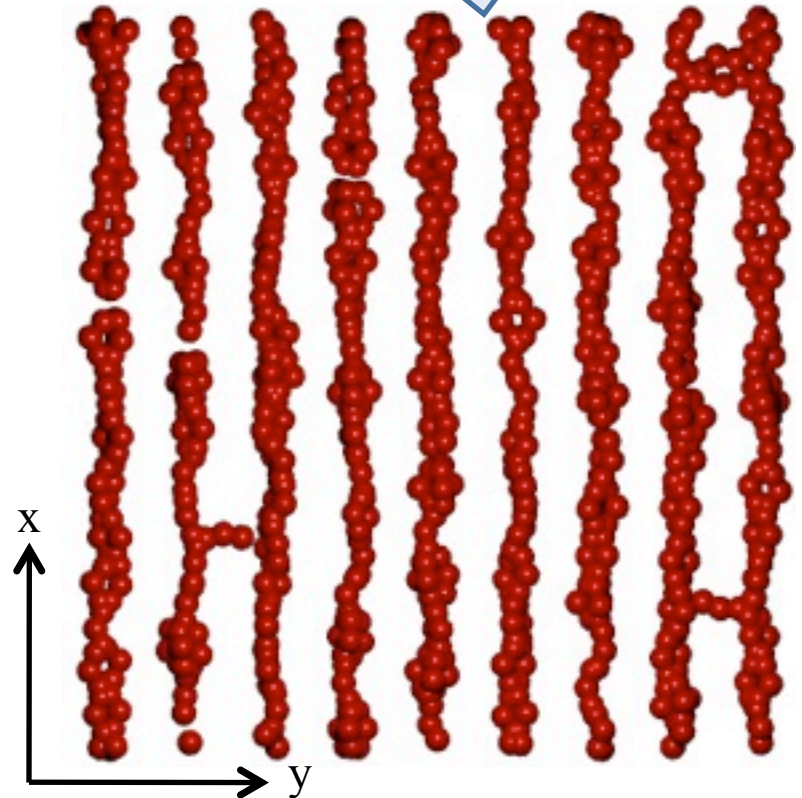
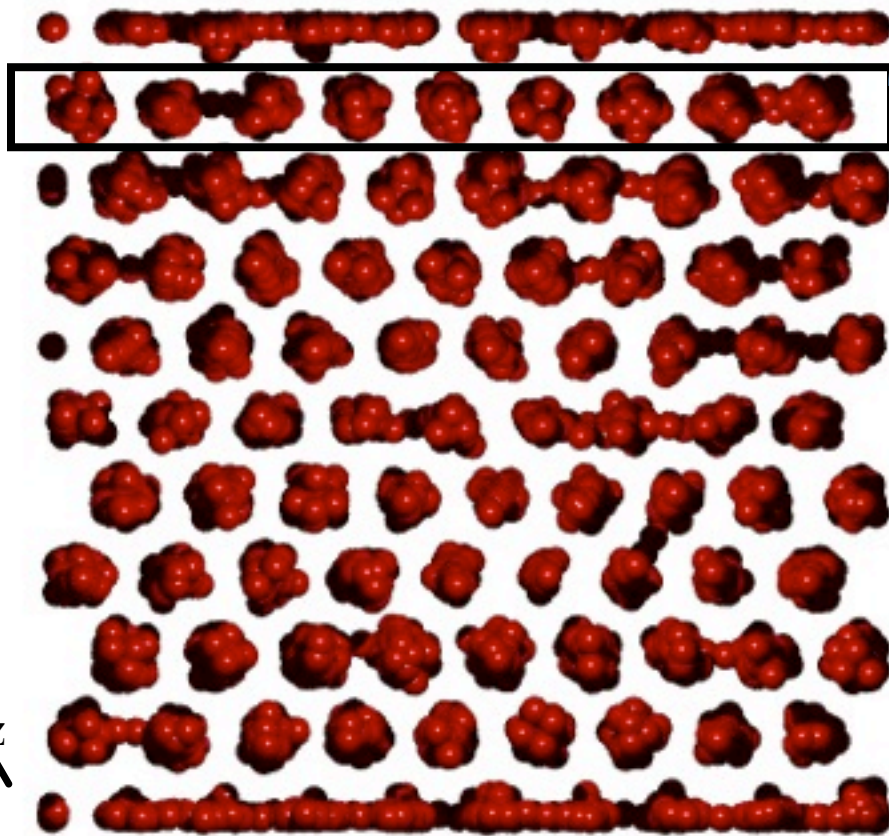


- Lamellar phase in the system with  $C = 5$



# Shear induced structures

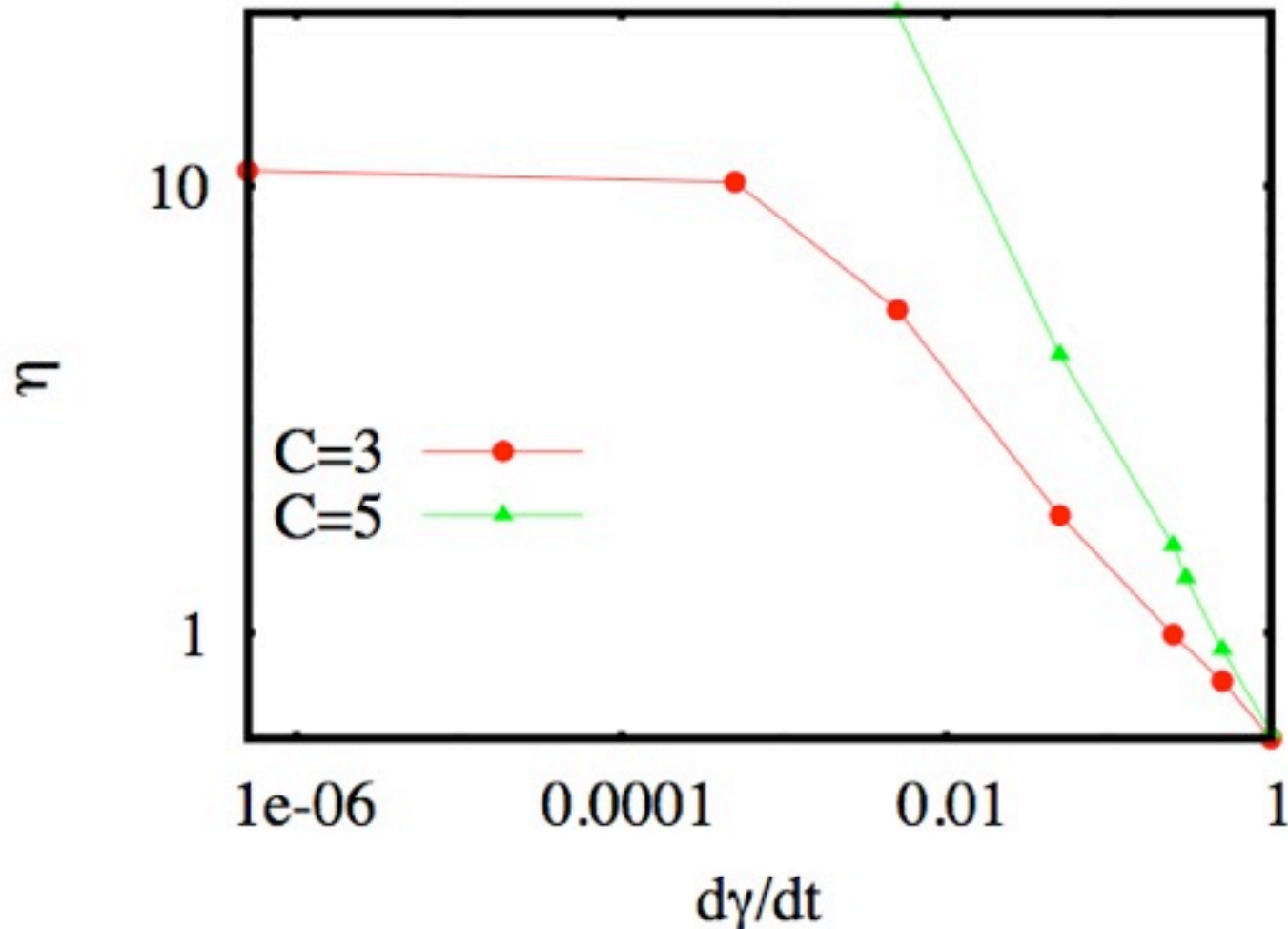
- $\dot{\gamma} = 1.0$
- $r_1, r_2, r_3, r_4, r_5 = 1.0, 2.0, 3.0, 3.5, 4.0$



- Columnar phase in the system with  $C = 5$
- Layer spacing is decided by  $r_5$



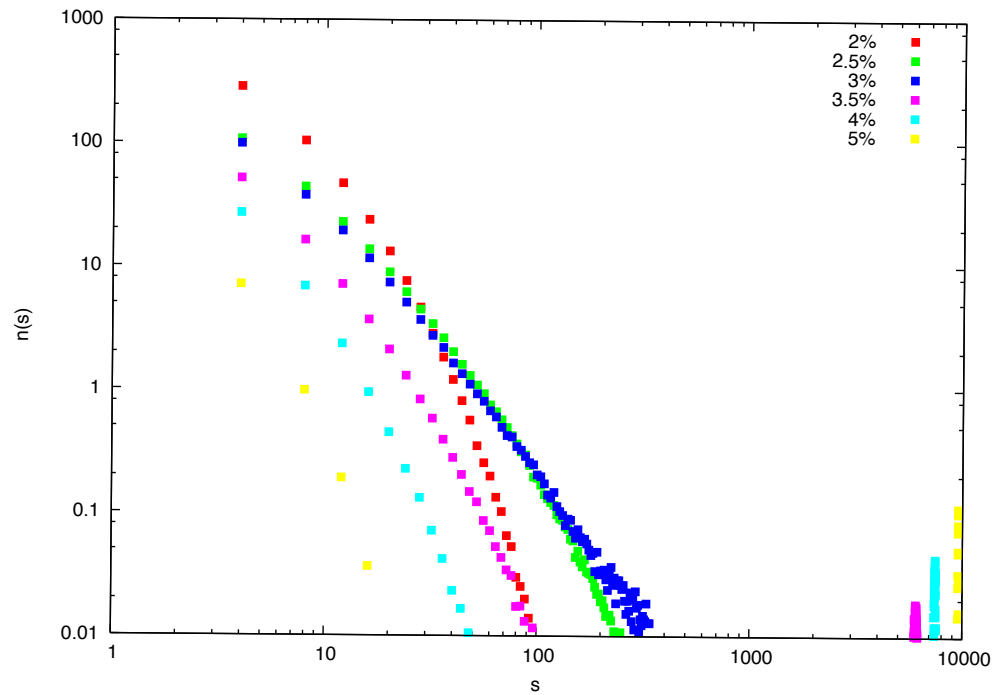
# Stress and viscosity



- Alignment of polymers leads to decrease in viscosity

Cluster size distribution for a tetramer building block.

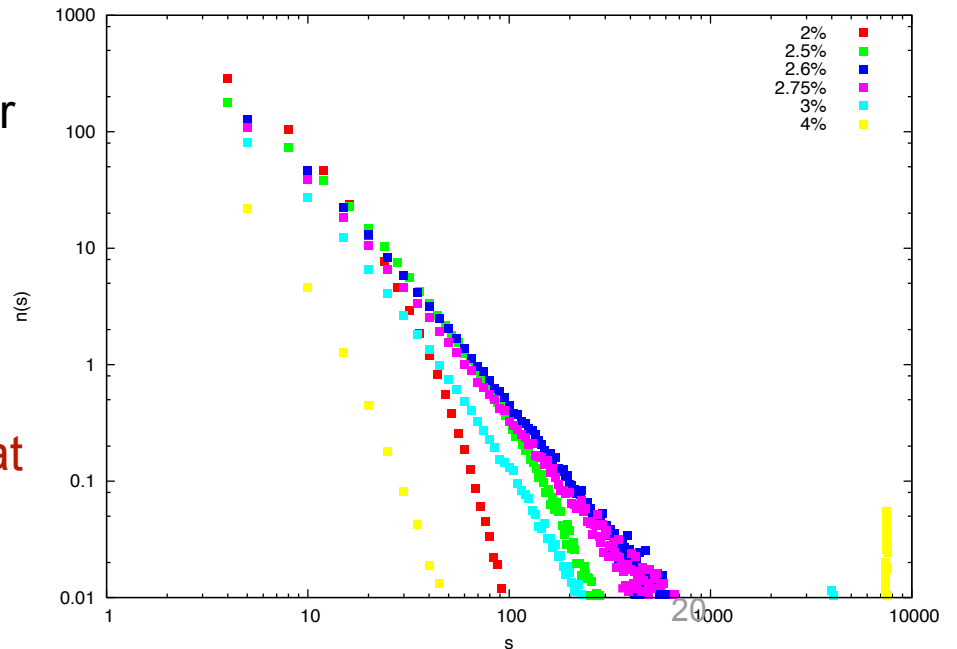
Percolation at 3% concentration



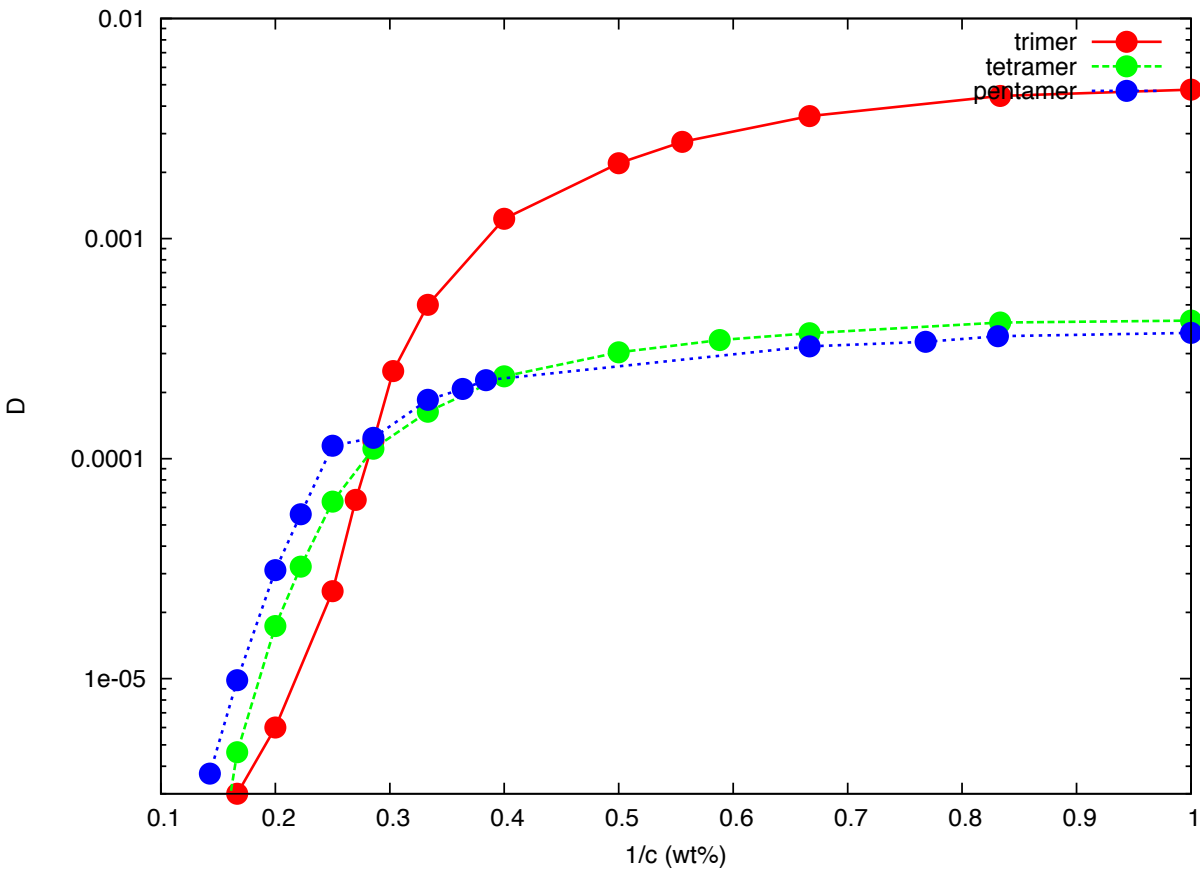
Cluster size distribution for a pentamer building block.

Percolation at 2.75% concentration

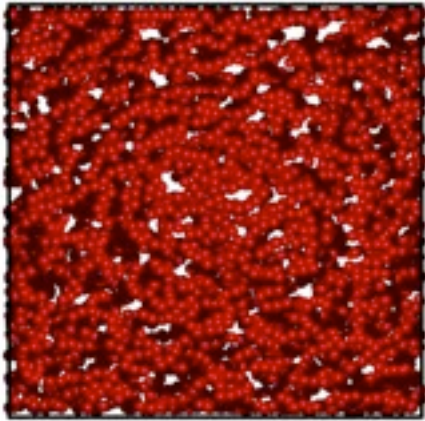
For larger segments the percolation is at a lower concentration



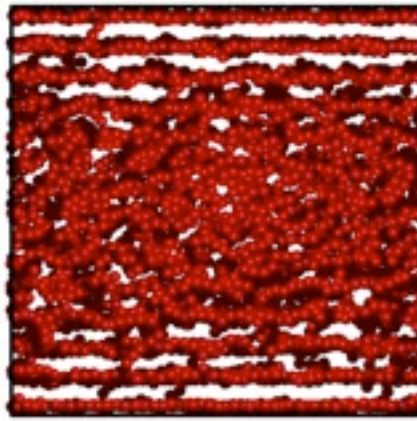
# Diffusion coefficient as a function of concentration for different building blocks



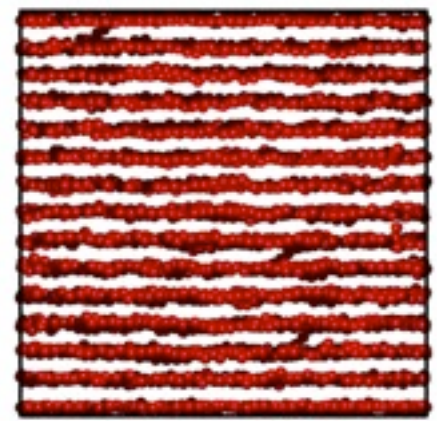
## Trimer



$$a_1 = a_2 = 0.1$$

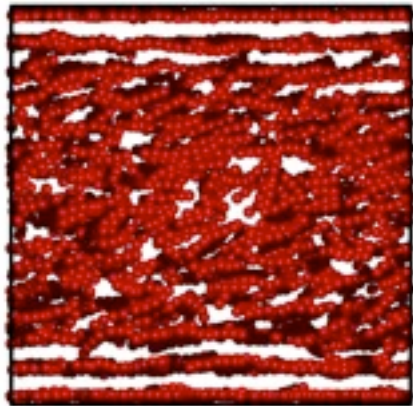


$$a_1 = a_2 = 0.5$$



$$a_1 = a_2 = 1.0$$

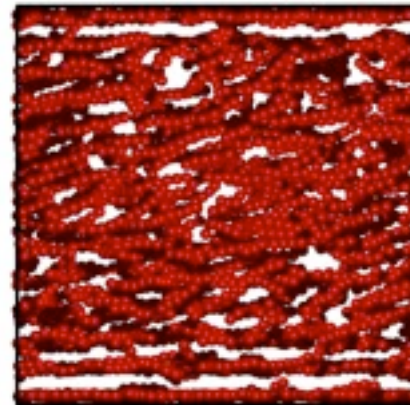
## Tetramer



$$a_1 = a_2 = 1.0$$

$$\dot{\gamma} = 1$$

## Pentamer



$$a_1 = a_2 = 1.0$$

Sc of DPD fluid is around 1, while that for a real fluid is about 1000 !!

## Higher Sc fluid ?

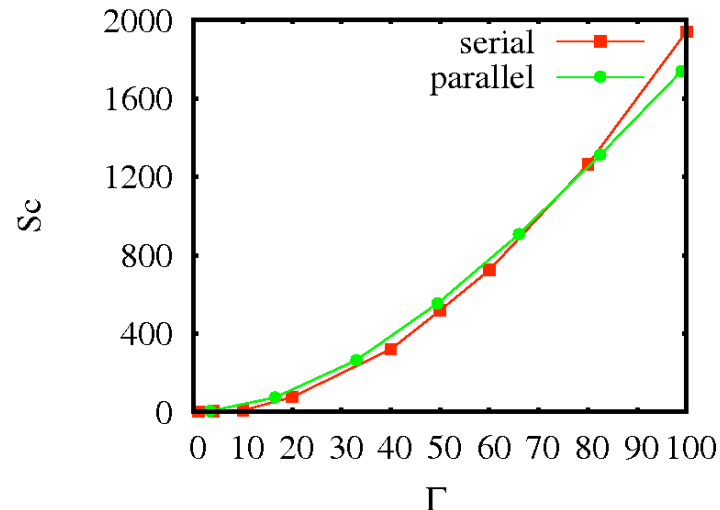
### Lowe's approach (Lowe-Andersen thermostat) \*

(thermalize by drawing relative velocities for particle pairs from a Maxwell distribution; allows in principle to adjust the kinematic viscosity so that the **correct Schmitt number** [ $Sc \sim 10^3$  for a liquid] is obtained)

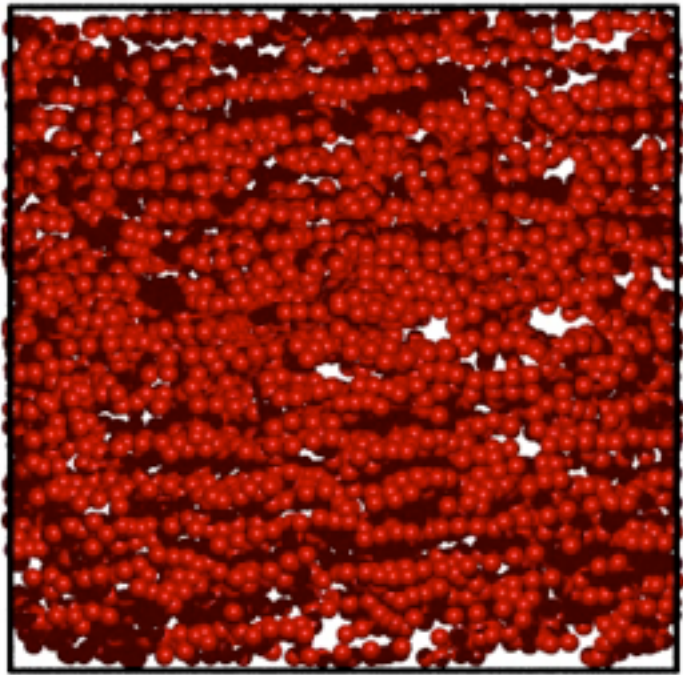
- 
- (1)  $\vec{v}_i \leftarrow \vec{v}_i + \frac{1}{2} \frac{1}{m} \vec{F}_i^C \Delta t$
  - (2)  $\vec{r}_i \leftarrow \vec{r}_i + \vec{v}_i \Delta t$
  - (3) Calculate  $\vec{F}_i^C \{\vec{r}_j\}$
  - (4)  $\vec{v}_i \leftarrow \vec{v}_i + \frac{1}{2} \frac{1}{m} \vec{F}_i^C \Delta t$
  - (5) For all pairs of particles for which  $r_{ij} < r_c$ 
    - (i) Generate  $\vec{v}_{ij}^o \cdot \vec{e}_{ij}$  from a distributor  $\xi_{ij}^{(g)} \sqrt{2k_B T^*/m}$
    - (ii)  $2\vec{\Delta}_{ij} = \vec{e}_{ij} (\vec{v}_{ij}^o - \vec{v}_{ij}) \cdot \vec{e}_{ij}$
    - (iii)  $\vec{v}_i \leftarrow \vec{v}_i + \vec{\Delta}_{ij}$
    - (iv)  $\vec{v}_j \leftarrow \vec{v}_j - \vec{\Delta}_{ij}$   
with probability  $\Gamma \Delta t$
  - (6) Calculate physical quantities
- 



\* C. P. Lowe, *Europhys. Lett.* **47** (1999) 145



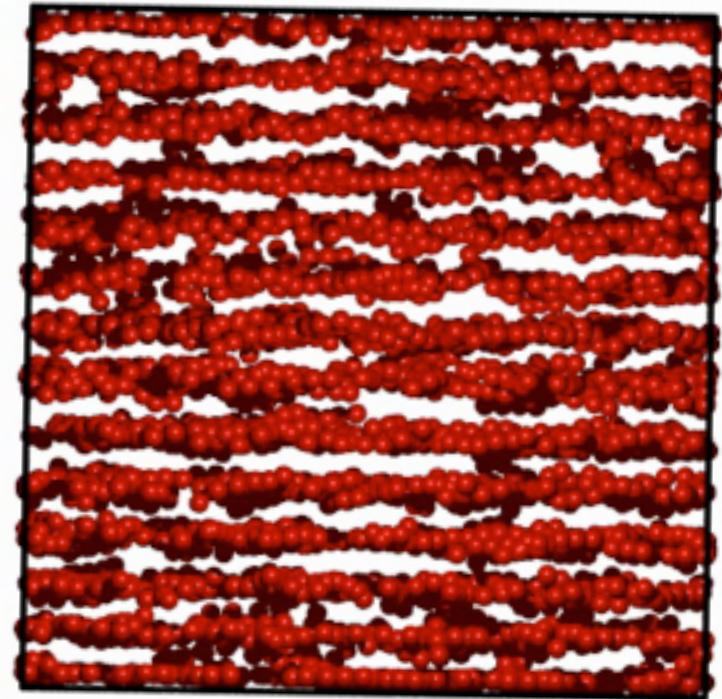




Early stage

$$Sc=7, \dot{\gamma}=1$$

steady state



# Conclusions

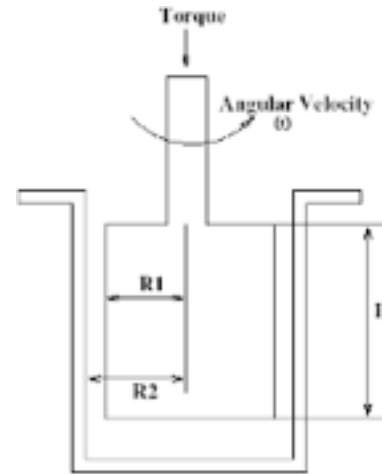
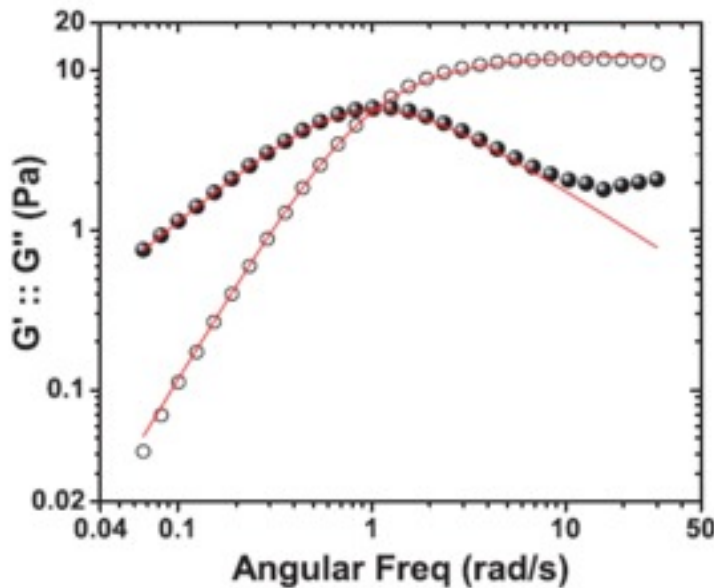
- A coarse grained model was developed for studying the dynamics of living polymer solutions
- The model based on Dissipative Particle Dynamics predicts a fluid to gel transition as the concentration of polymer is increased
- The self intermediate scattering function indicates Zimm like dynamics at large wave vectors and diffusive dynamics at large length scales
- The scission and recombination kinetics demonstrates the presence of mean field like behavior in the fluid phase and a diffusion controlled behavior in the gel phase
- Zero shear relaxation modulus confirms the crucial role of scission and recombination in relaxation
- We show the emergence of lamellar and columnar phase when the solution is subjected to simple shear
- The gelation point shifts to lower concentration and the size of the basic building block ( molecular weight) is increased , however the diffusion coefficient increases (above the gelation point ) .
- Higher viscous coupling was required, to obtain the layering transition, when the size of the basic unit was increased from trimer to tetramer and pentamer.

# Rheological measurement of surfactant solutions

Equimolar solution: CTAB (Hexadecyl-trimethyl-ammoniumbromide)  
NaSal (Sodium salicylate)

Rheometer: Concentric cylindrical geometry

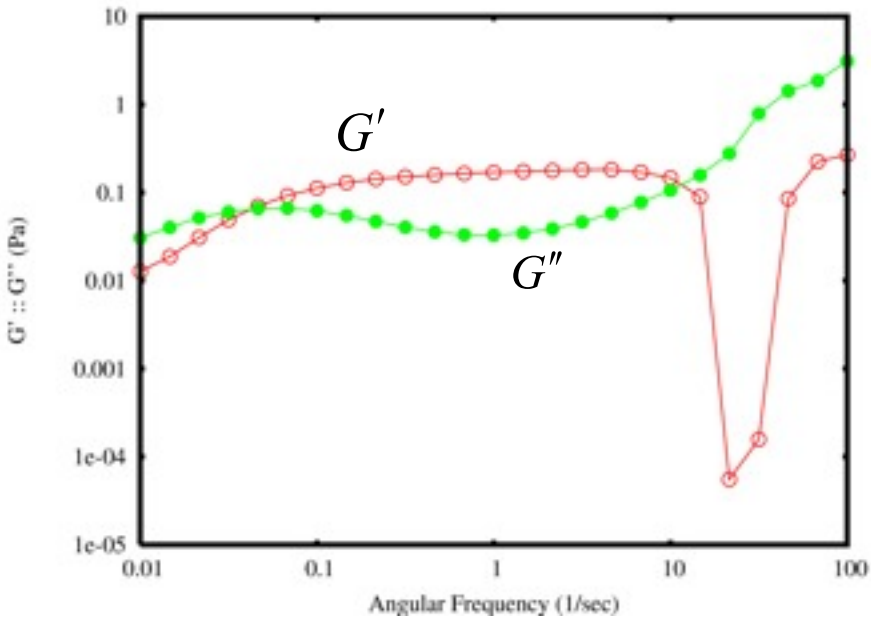
At low frequency



$G'$  (hollow circle) and  $G''$  (solid circle) for CTAT + NaCl Solution

*Jayaraman and Belmonte, PRE, 67, 065301 (2003)*

Something happens at high frequencies ..

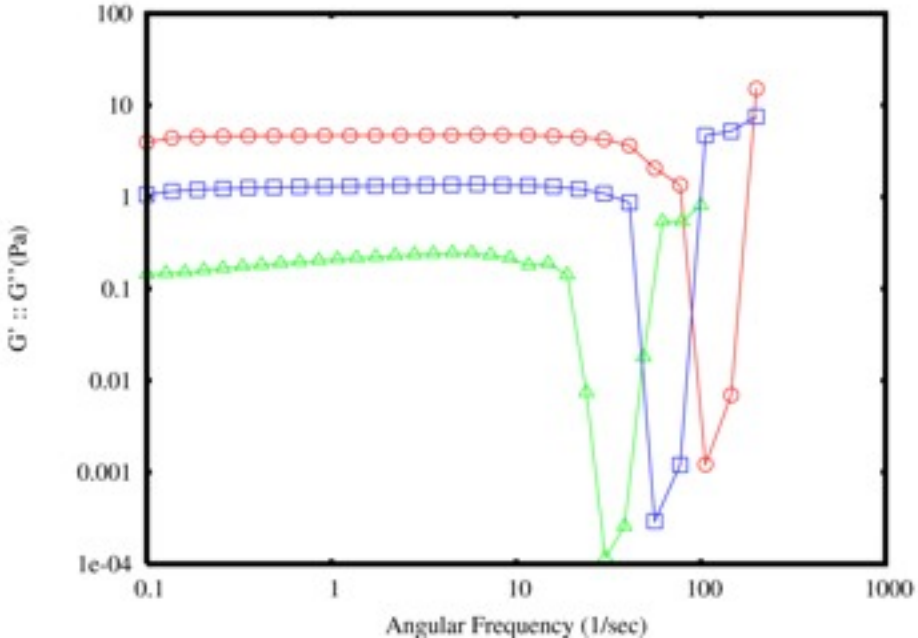


9 mM equimolar CTAB + NaSal solution

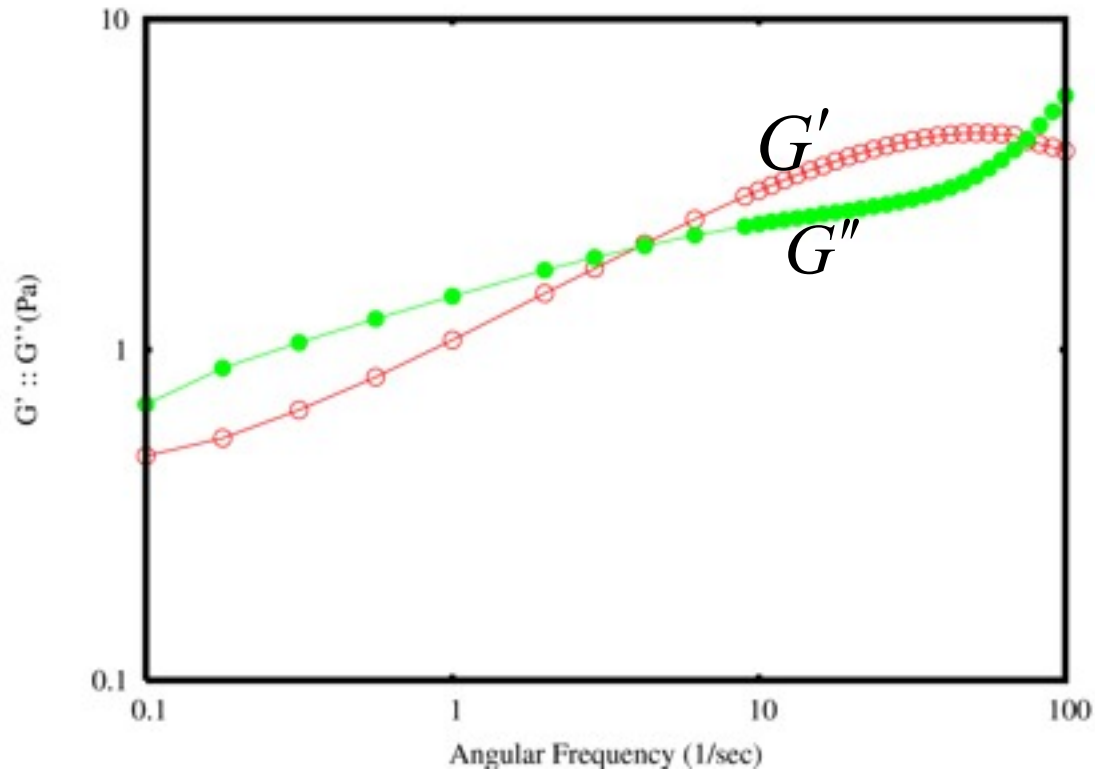
- Second crossing of  $G'$  and  $G''$
- Elastic modulus  $G'$  shows a sudden fall of many orders

Effect of surfactant concentration ---->

Discontinuity shifts to higher frequency on increasing the concentration



# Polymer solution



100 ppm polyacrylamide

Polymer solution does not show any Discontinuity in  $G'$

Sudden fall of elastic modulus in micellar solution is due to some structural changes in the fluid