Dynamics of polyelectrolytes and living polymers in shear flow
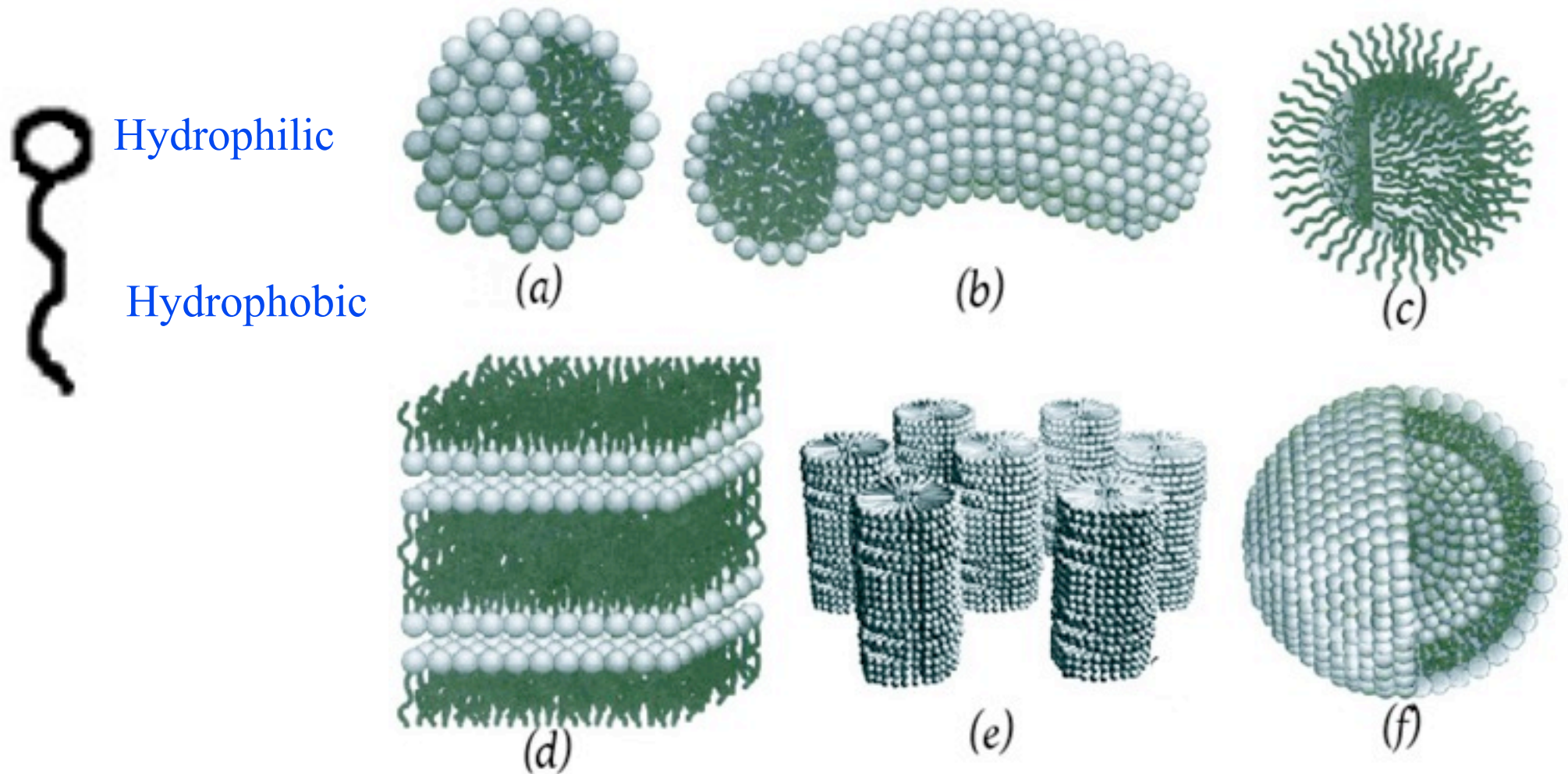
P. B. Sunil Kumar

Department of Physics, IIT Madras.

Tuesday 10 August 2010

Amphiphiles and aggregates

Hydrophilic
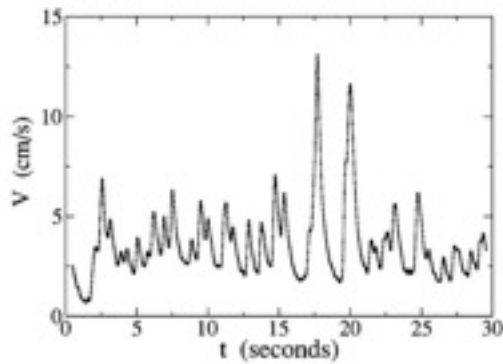
Hydrophobic

(a)

(b)

(c)

(d)

(e)

(f)

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

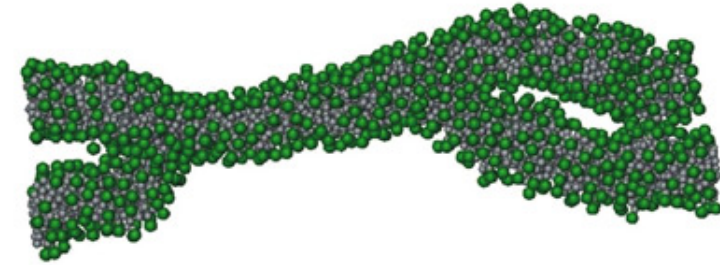Cylindrical micelles also called living polymers
Can undergo scission/recombination under thermal fluctuations
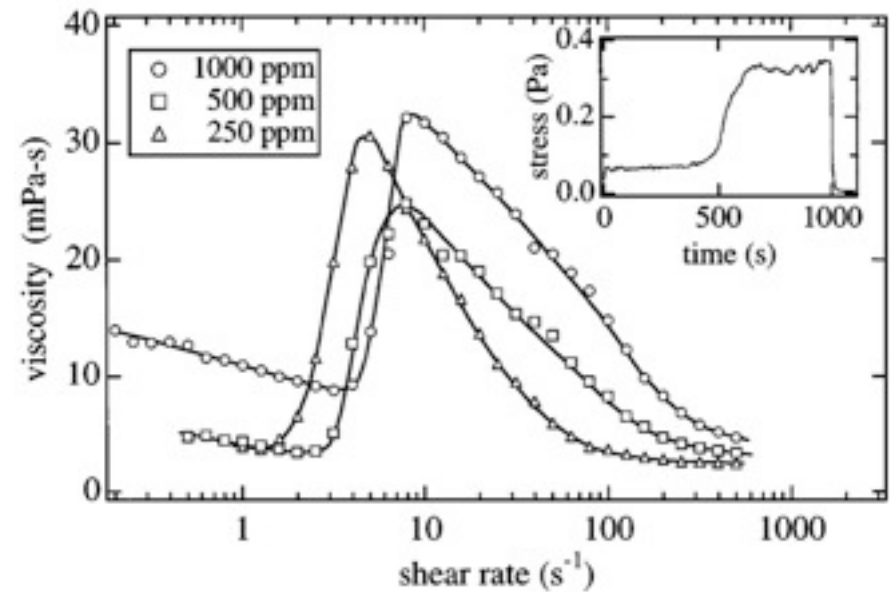
2

Micellar solutions are examples of living polymers

Oscillating solid sphere
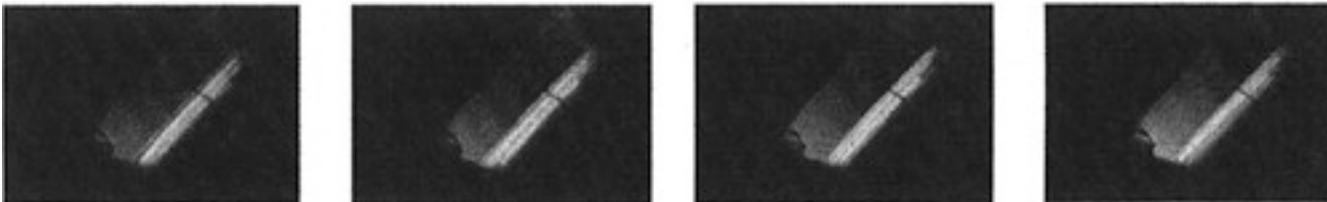

Jayaraman et al. PRE, 67, 65301 (2003)

Shear induced gelation

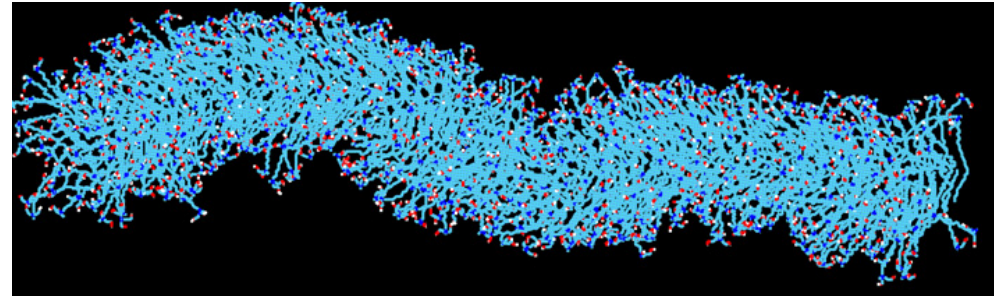*Liu et al. PRL, 77, 2121 (1996)*

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 erucate 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
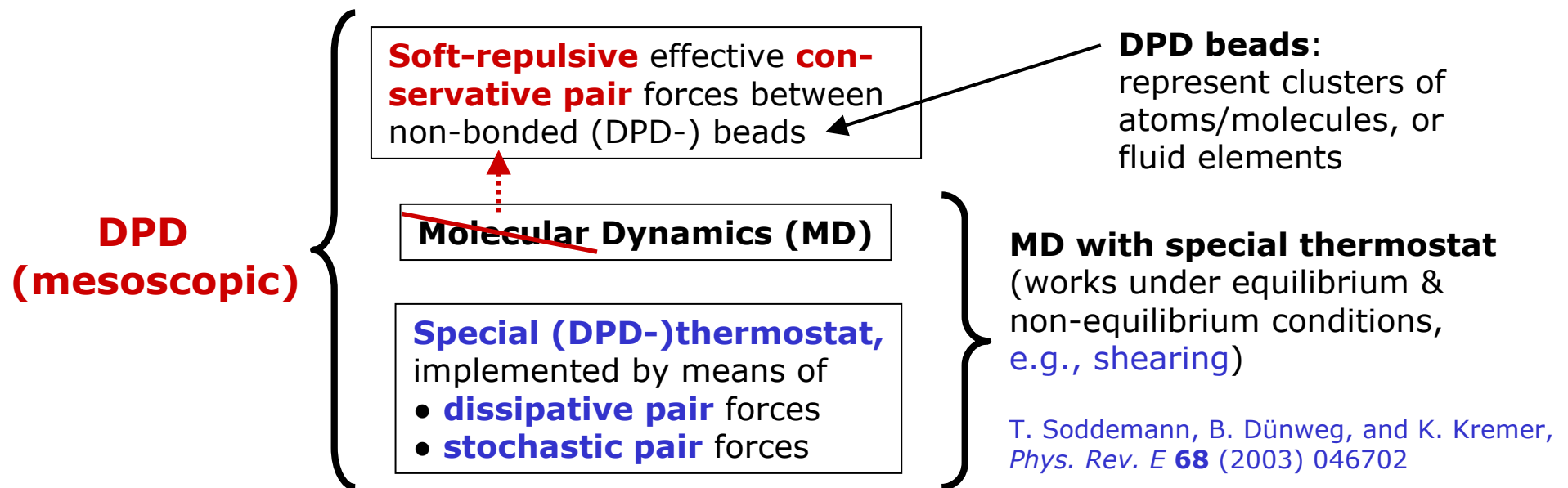
a)

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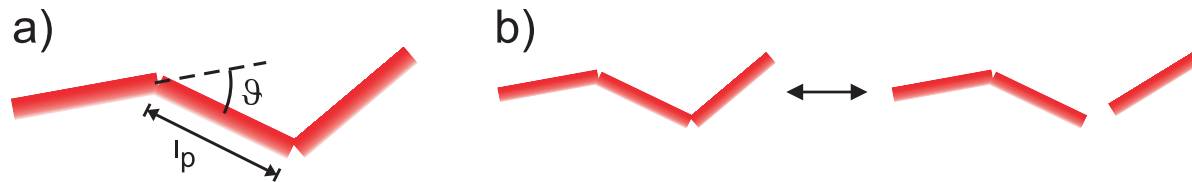
Padding, Boek and Briels ((2005): a mesoscopic model of wormlike micelles, represented by chains which can break and recombine and can be subjected to shear flow. For this model, where the smallest length-scale is the persistence length, the elastic modulus , scission energy and persistence length are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

4

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 ...

DPD (mesoscopic)

Soft-repulsive effective **conservative pair** forces between non-bonded (DPD-) beads

DPD beads: represent clusters of atoms/molecules, or fluid elements

~~Molecular Dynamics (MD)~~

MD with special thermostat (works under equilibrium & non-equilibrium conditions, e.g., shearing)

Special (DPD-)thermostat, implemented by means of
- **dissipative pair** forces
- **stochastic pair** forces

T. Soddemann, B. Dünweg, and K. Kremer, *Phys. Rev. E* **68** (2003) 046702

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

DPD- Basic model

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

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

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

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

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

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

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

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

Dissipative & random forces related through fluctuation-dissipation theorem

$$\gamma = \sigma^2/2k_{\rm B}T.$$

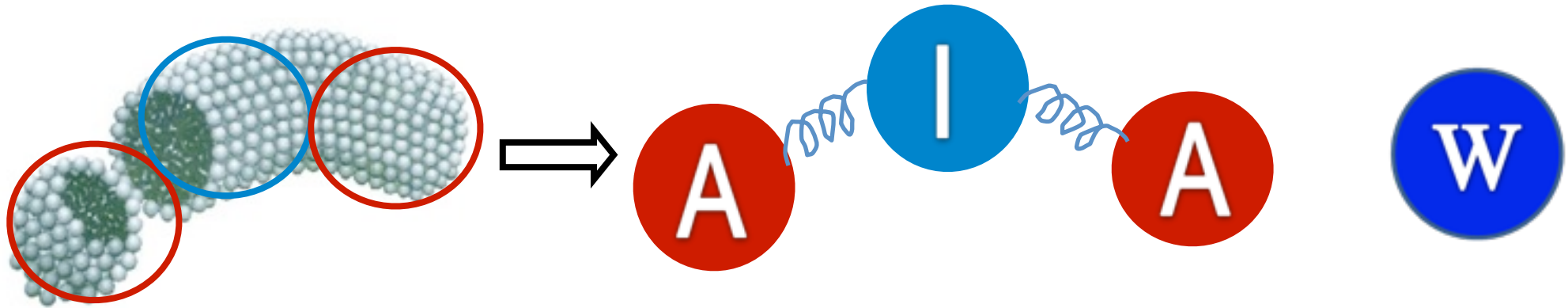**Pair-wise random and dissipative forces conserve momentum**
Resulting in correct description of hydrodynamics
Soft interactions allow for longer time steps, and therefore much longer times can be probed via DPD as opposed to MD

r_{ij}

r_i

r_j

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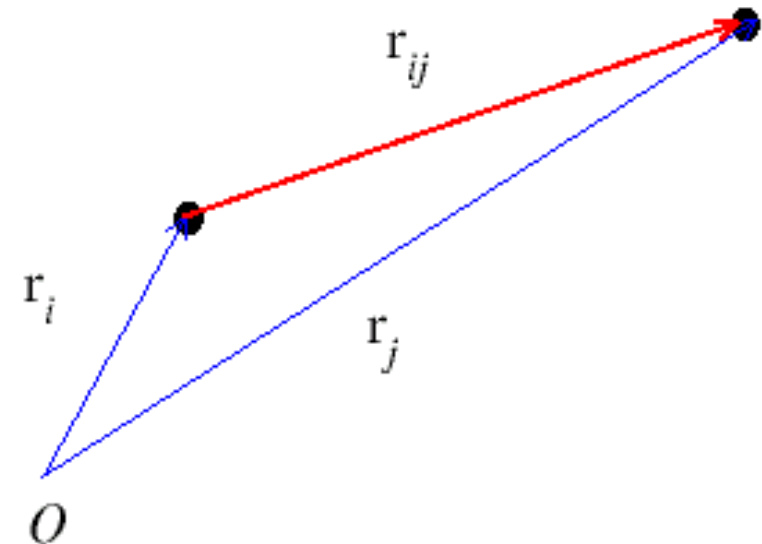
- *P. J. Hoogerbrugge and J. M. V. A. Koelman, Europhys. Lett.* **19***, 155 (1992)*

DPD model for living polymers (LP)

$$F_{ij}^C = \alpha_{ij} \left(\omega_1^C(r_{ij}) + \omega_2^C(r_{ij}) \right) \hat{r}_{ij} \qquad \alpha_{ij} = a_{ij}$$
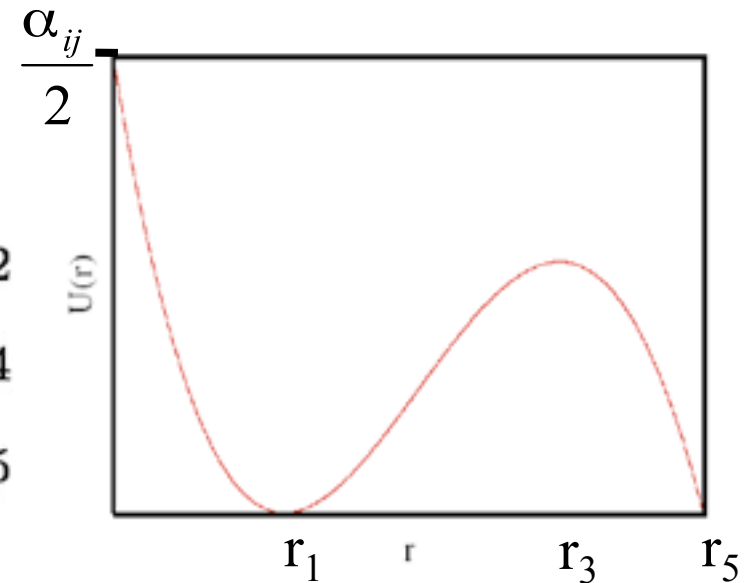
For,
W − W, W − I
W − A, I − I, I − A

$$\omega_1^C(r_{ij}) = \left(1 - \frac{r_{ij}}{r_c}\right) \quad \text{for } r_{ij} < r_c$$
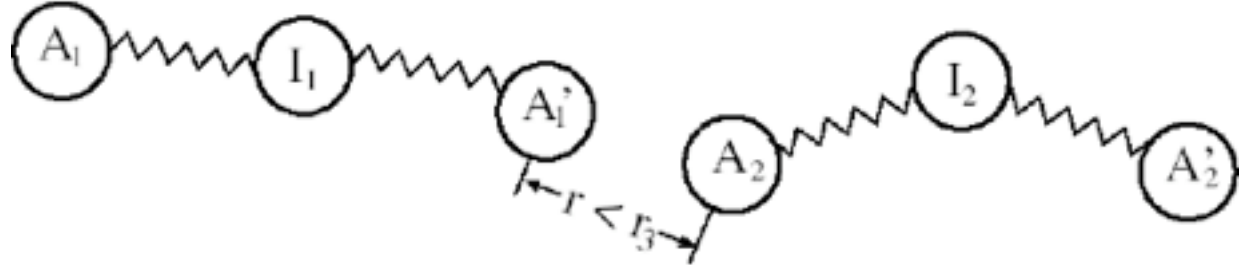
$$\omega_2^C(r_{ij}) = 0$$

For, A-A

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

Tuesday 10 August 2010

The three-body bending potential

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

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

Three body potentials $U_{ijk} = k_3(1 - \hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{r}}_{jk})$ for $A_1I_1A_1'$ and $A_2I_2A_2'$

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

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

- Simulation box size L = 40 , Periodic Boundary Condition
- density ρ = 3 , number of particles 192000
- Resting length A-I = 1.0 , A-A = 2.0
- Spring constant k = 200
- Time step = 0.01 τ, with τ of the order of 10^{-6} sec

Tuesday 10 August 2010

Fluid-gel transition

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

Phase behavior was characterized by diffusivity of trimers
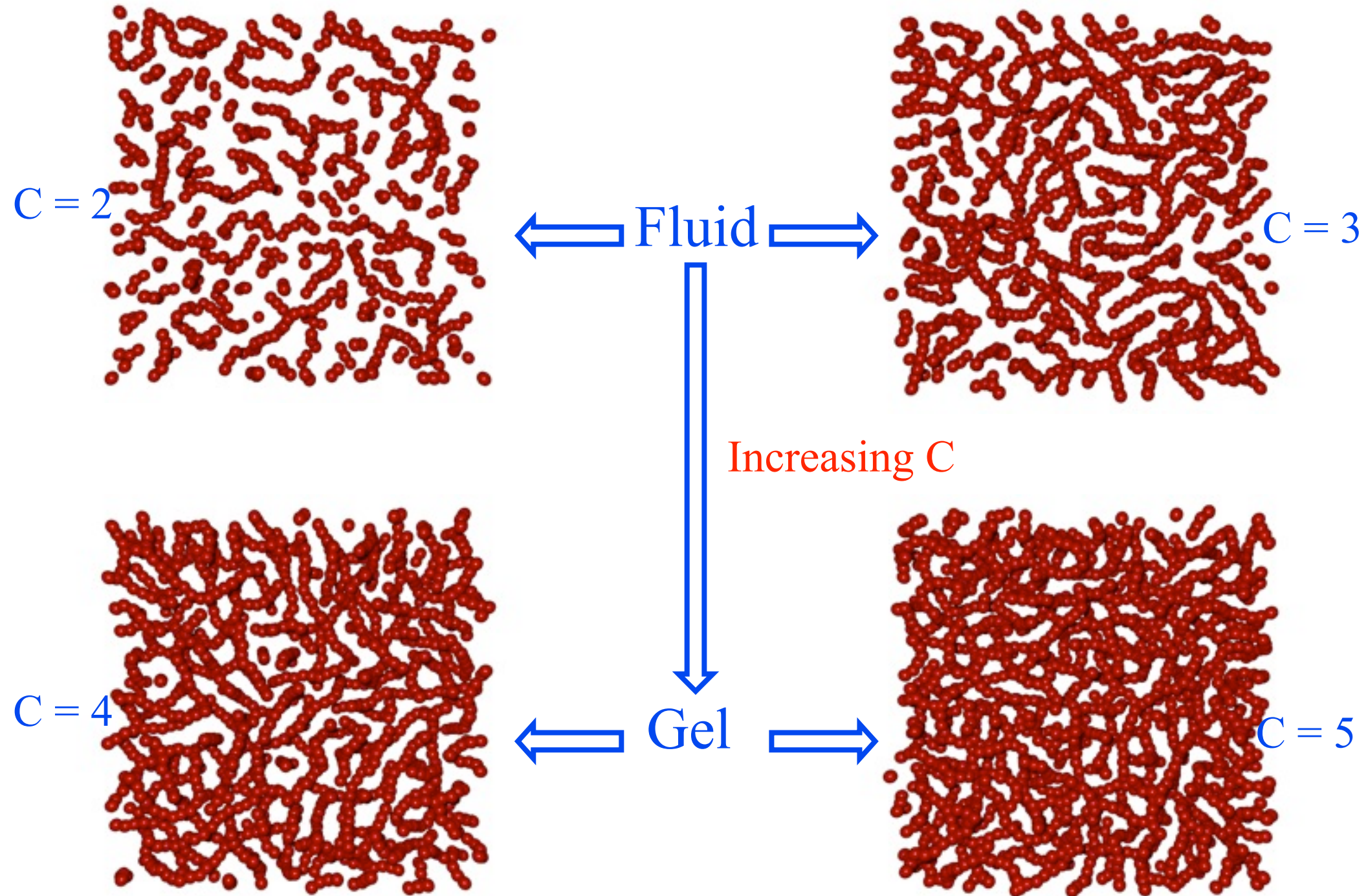
- Fluid phase at low C
- Gel phase at higher C
- Transition point C = Cp = 3.5

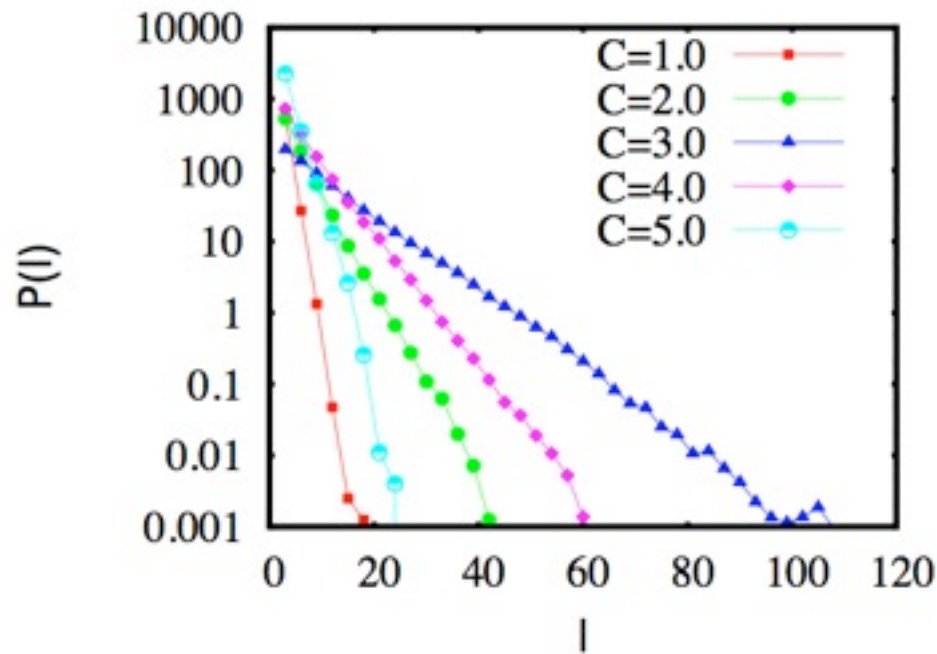$$D = \frac{1}{6Nt}\left[\sum_{i=1}^{N}(X_i^{cm}(t_0+t) - X_i^{cm}(t_0))^2\right]$$
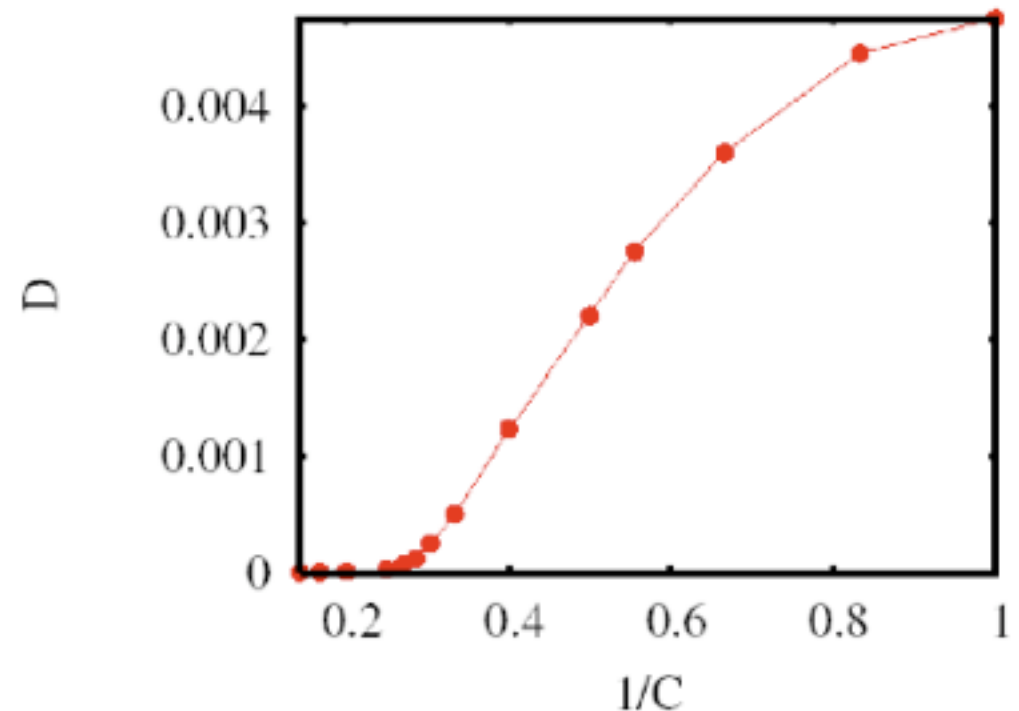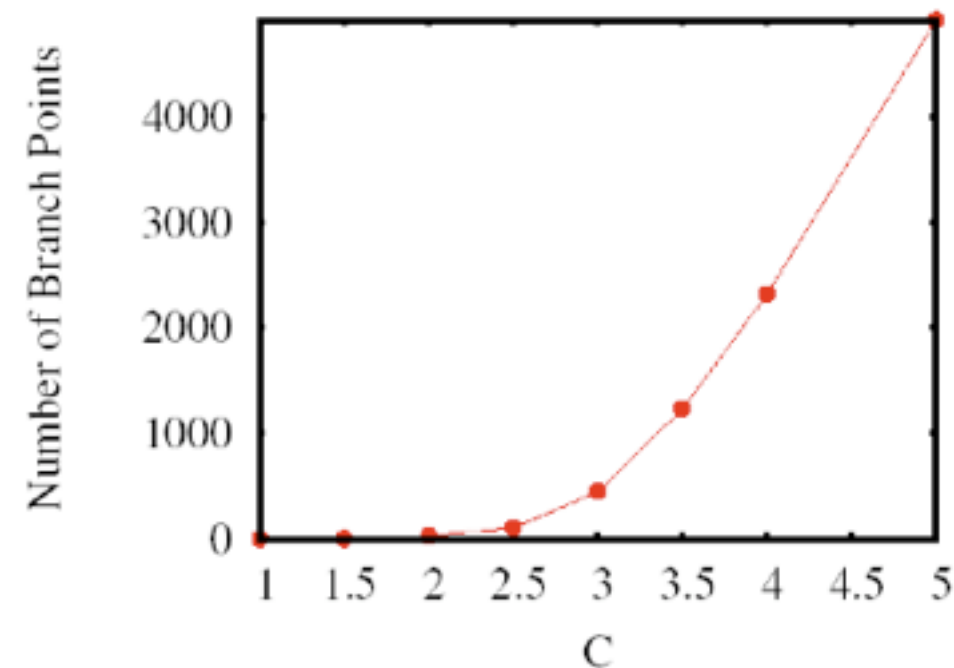
- Branched point   ----   coordination number of particle is > 2

Tuesday 10 August 2010

Organization of polymers

C = 2

Fluid

C = 3

Increasing C

C = 4

Gel

C = 5

Segment length distribution

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

Cluster size distribution

branching of polymers lead to random percolation
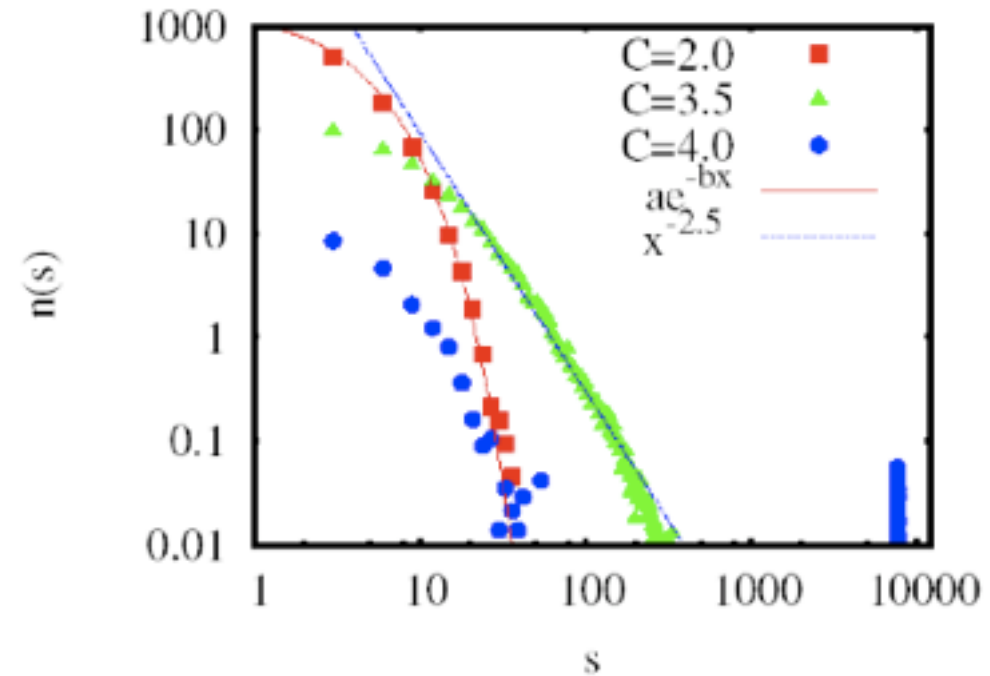
- Exponential distribution at low C < Cp

- Power law distribution at C = Cp: random percolation
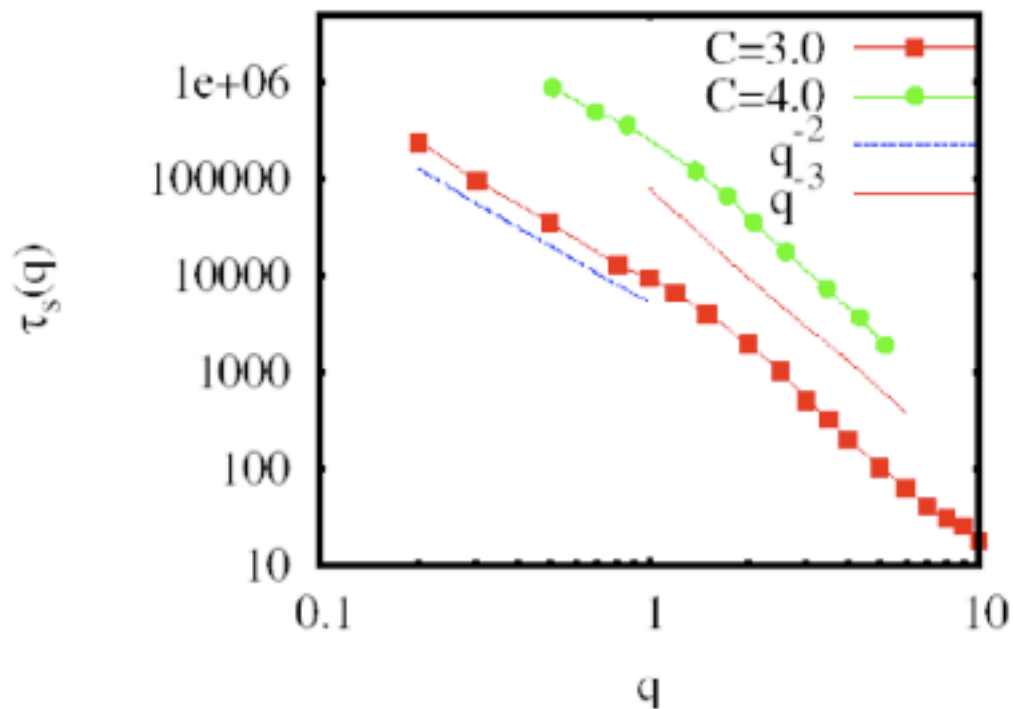
- Gel phase contains spanning clusters and small segments

T   Average polymer length

Φ   Monomer concentration

Branching reduces the average segment length

- *M. E. Cates and S. J. Candau, J. Phys 2, 6869 (1990)*

Tuesday 10 August 2010

Self-intermediate scattering function

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

N: total number of monomers
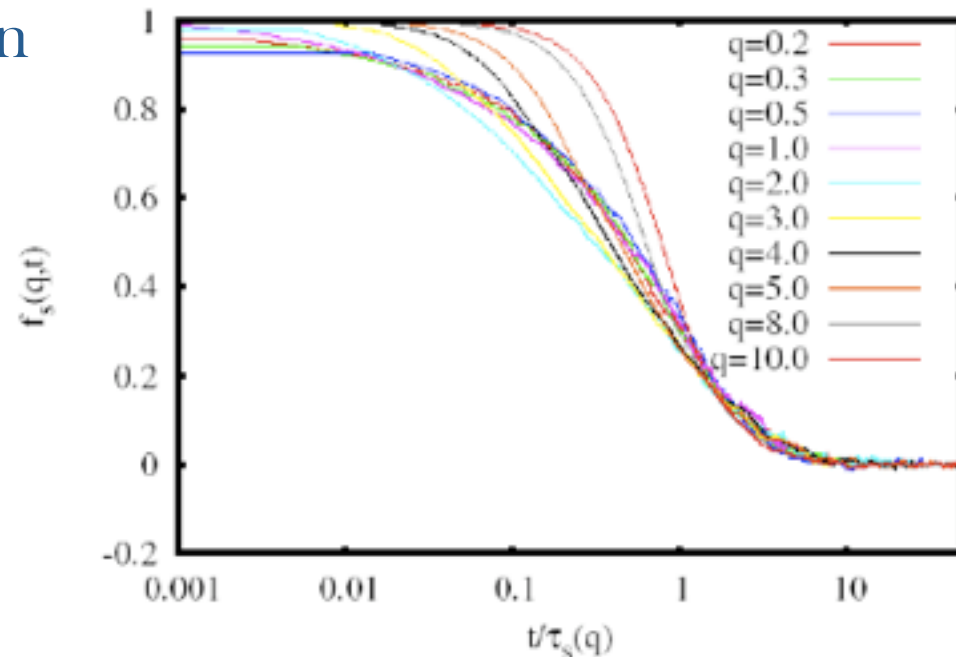
Relaxation time

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

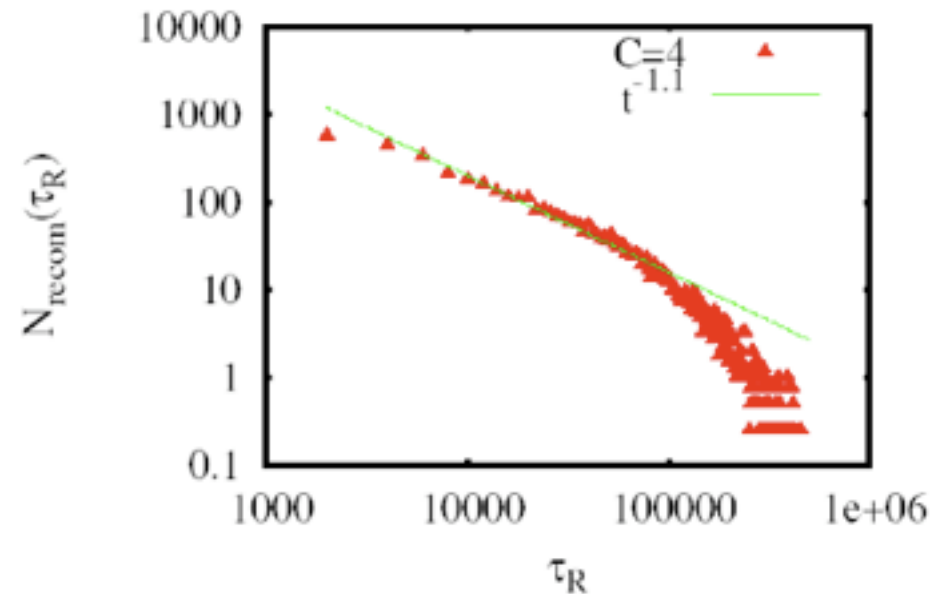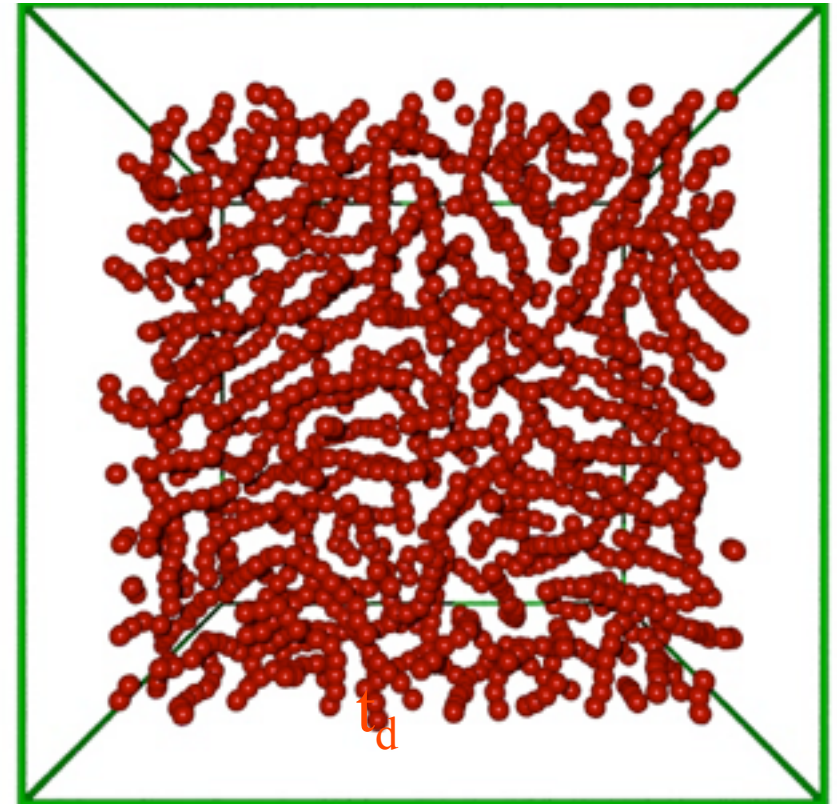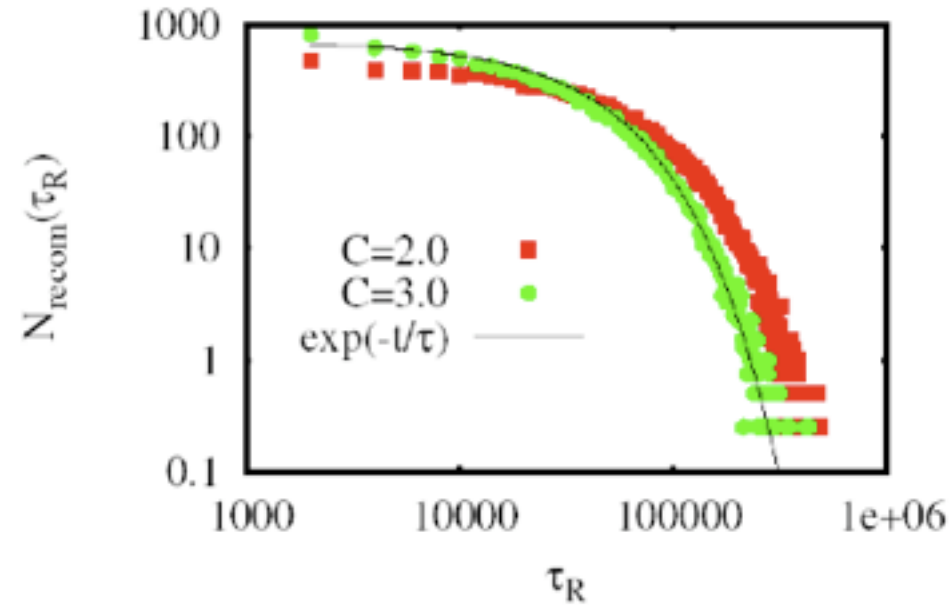Zimm dynamics at large q: $\tau_s \sim q^{-3}$

Diffusive at low q: $\tau_s \sim q^{-2}$

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

14

Tuesday 10 August 2010

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

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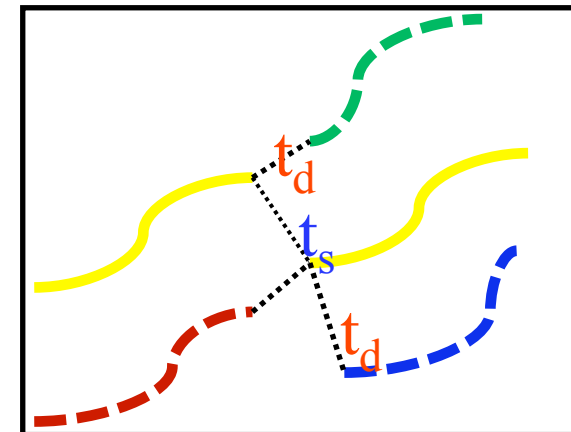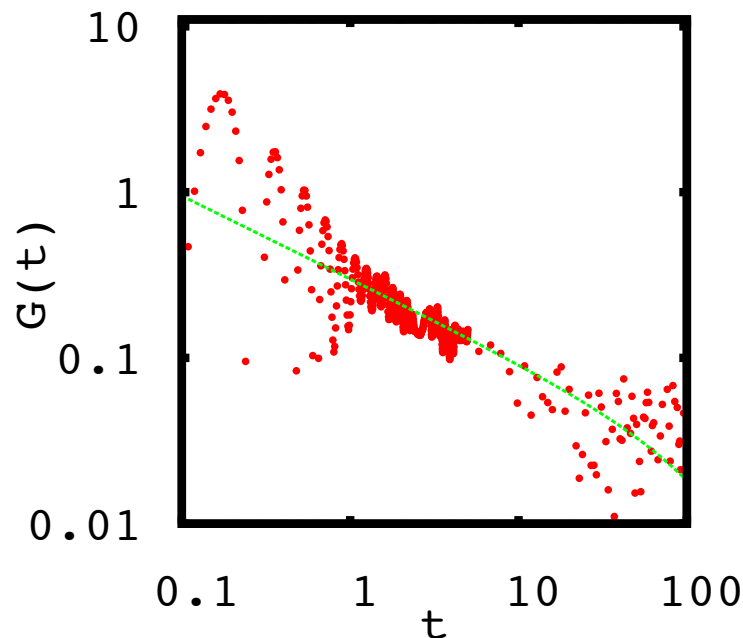
stress relaxation

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

$$\sigma_{\alpha\beta} = -\frac{1}{V}\left(\sum_{i=1}^{N} m_i v_{i\alpha}v_{i\beta} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} r_{ij\alpha}F_{ij\beta}\right)$$
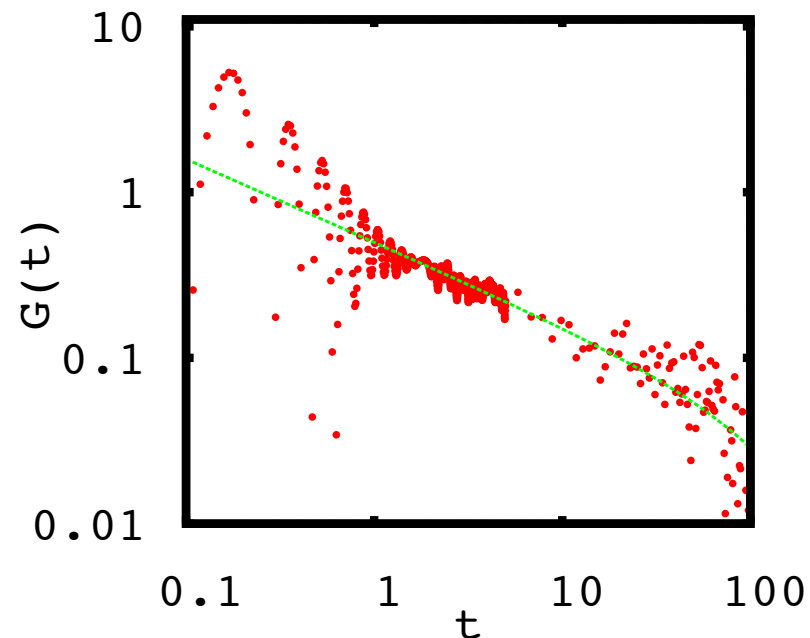
- We find a residual stress is due to the spanning clusters with stretched bonds
- Early time oscillation is the result of bond potential within a trimer

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

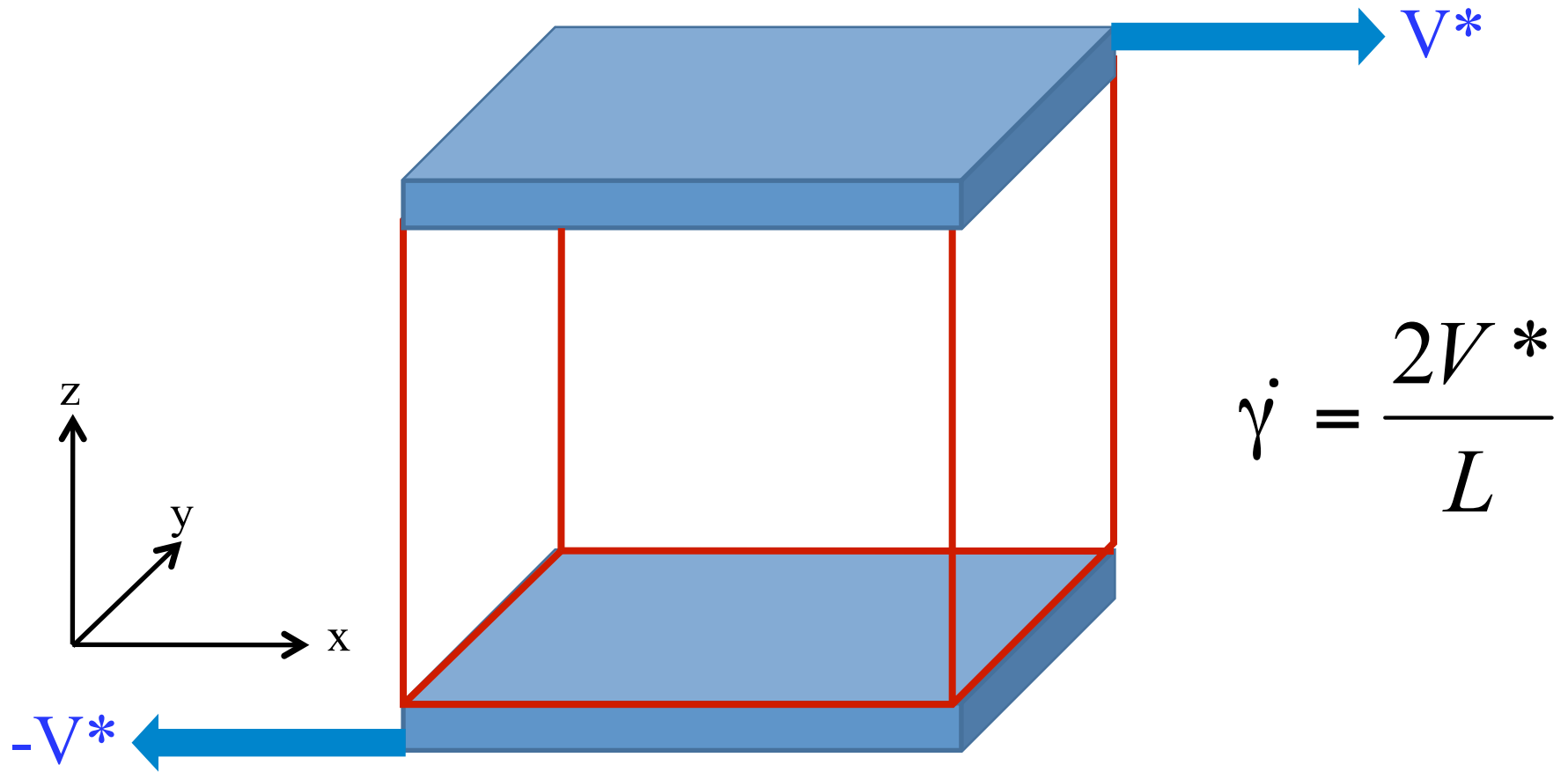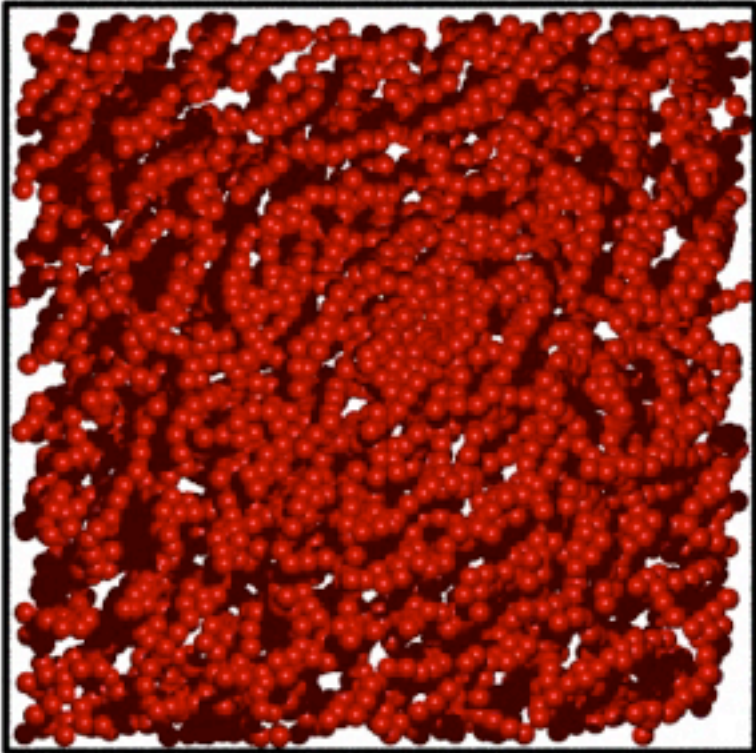• *G. Faivre and J. L. Gardissat, Macromolecule, 19, 1988 (1986)*

C=3.0

C=4.0

16

Shear

$$\dot{\gamma} = \frac{2V*}{L}$$

- 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
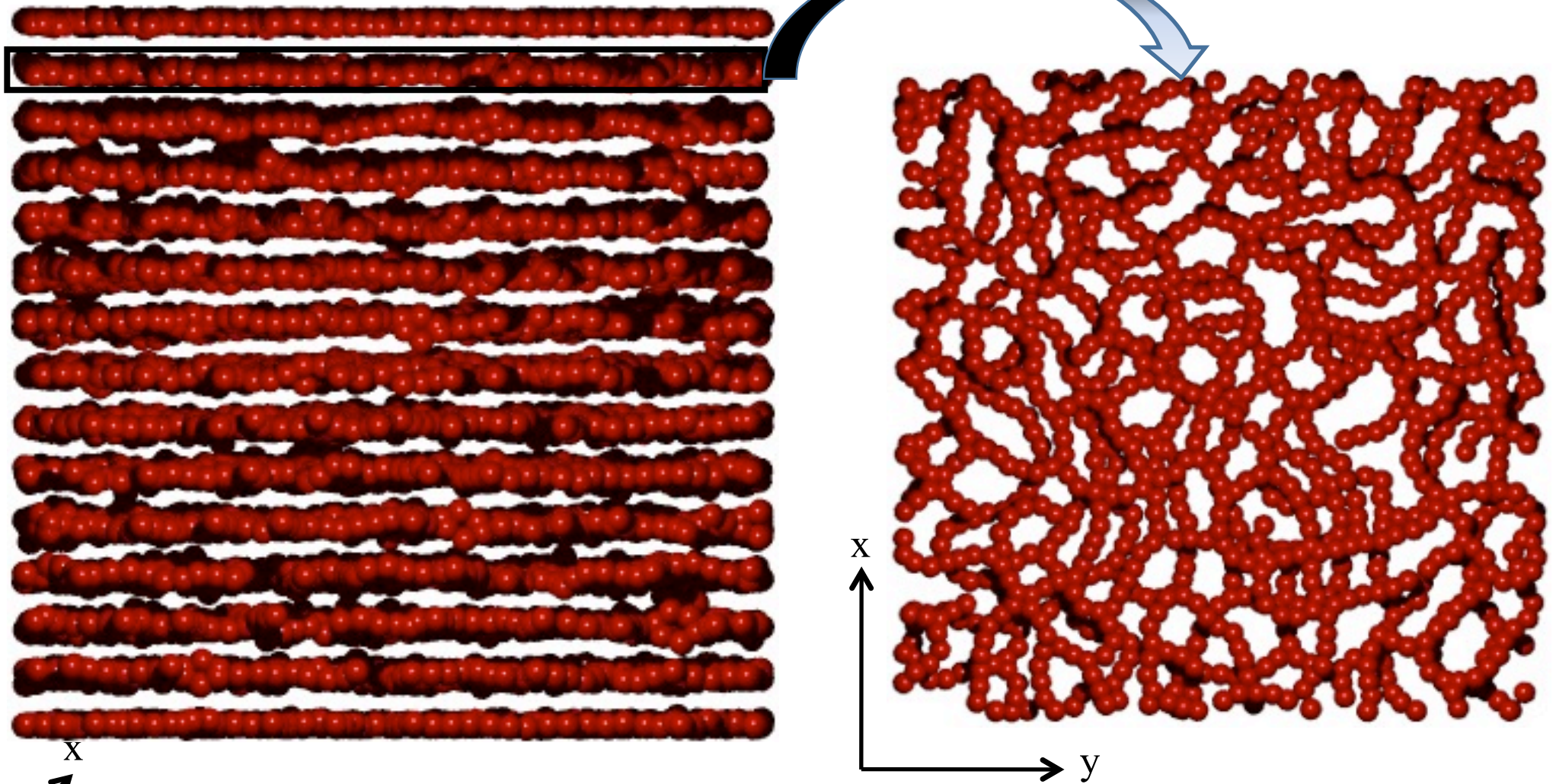

First layer forms near the shear boundaries

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

Tuesday 10 August 2010

Shear induced structures

- $\dot{\gamma} = 1.0$

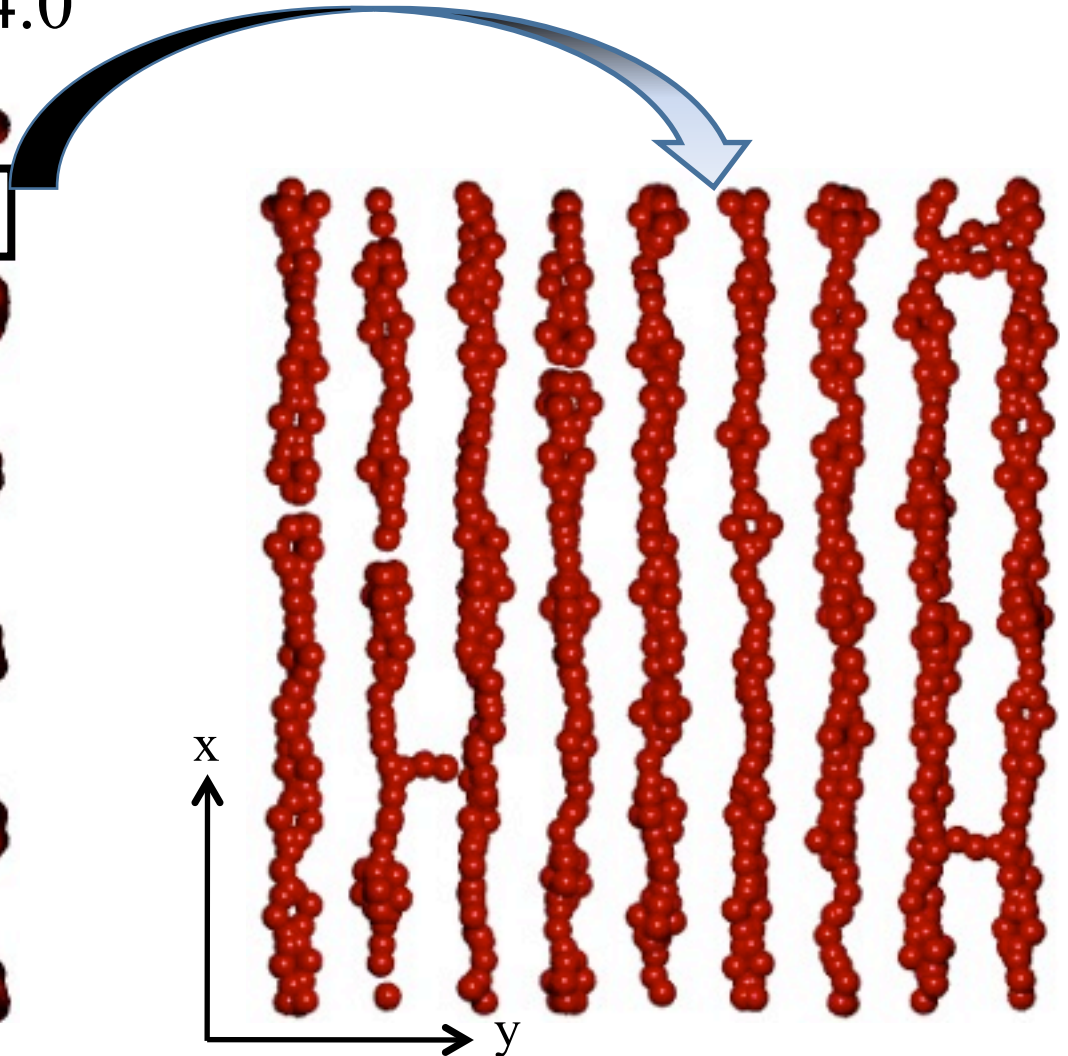- $r_1, r_2, r_3, r_4, r_5 = 1.0, 1.5, 2.0, 2.5, 3.0$
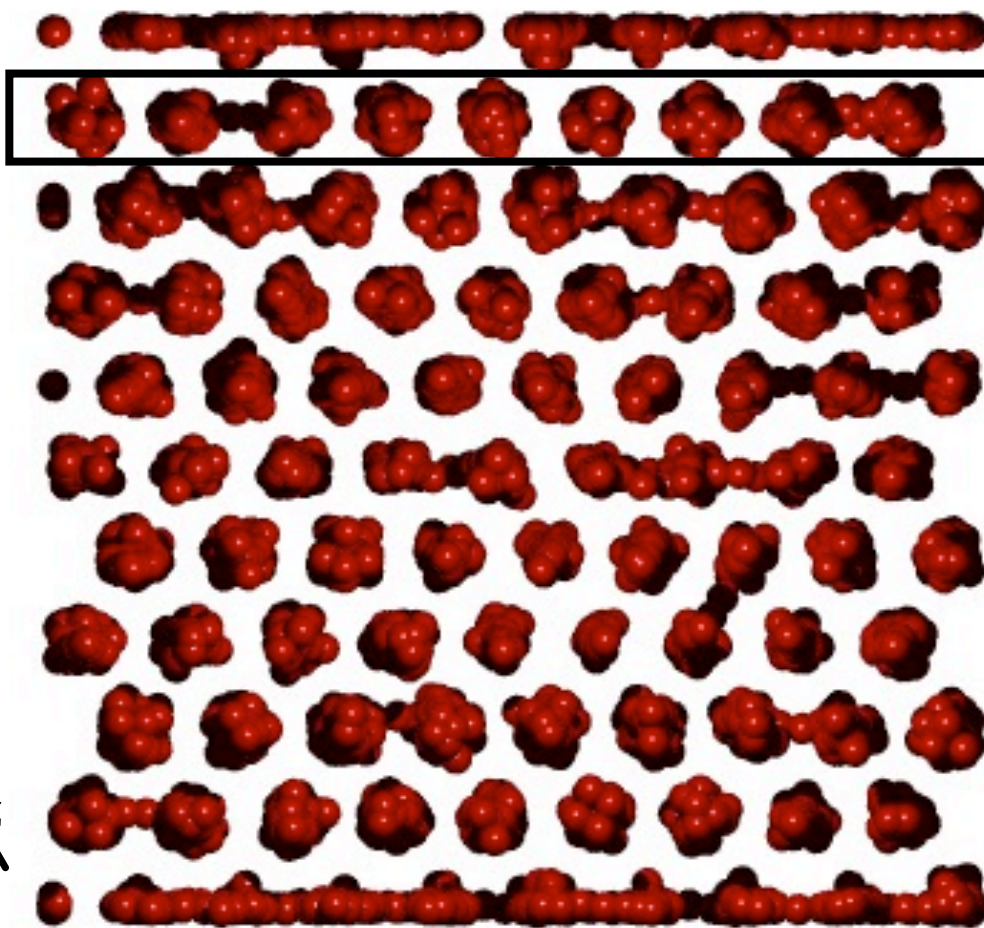

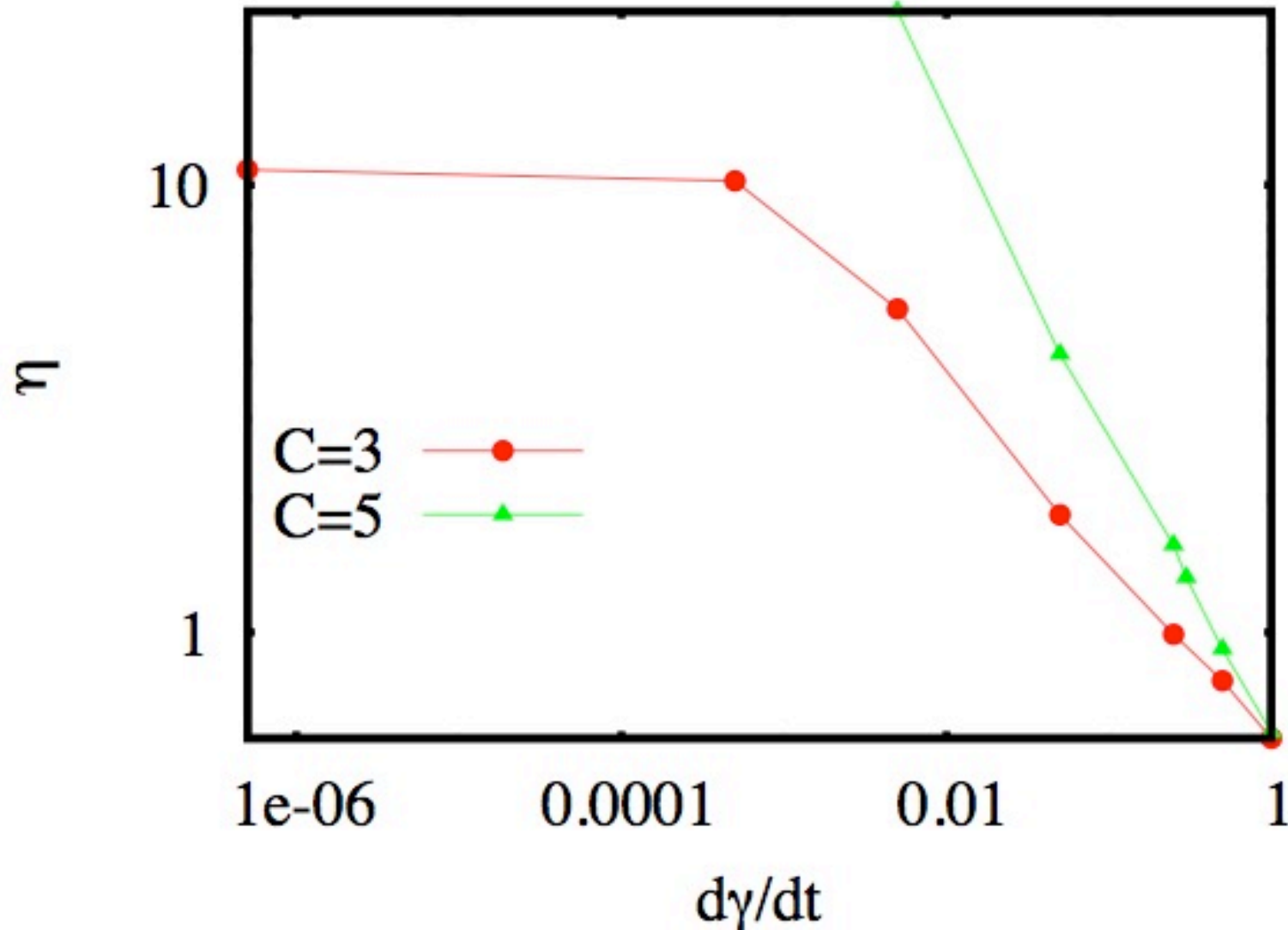- Lamellar phase in the system with C = 5

Shear induced structures

- $\dot{\gamma} = 1.0$

- $r_1, r_2, r_3, r_4, r_5 = 1.0, 2.0, 3.0, 3.5, 4.0$
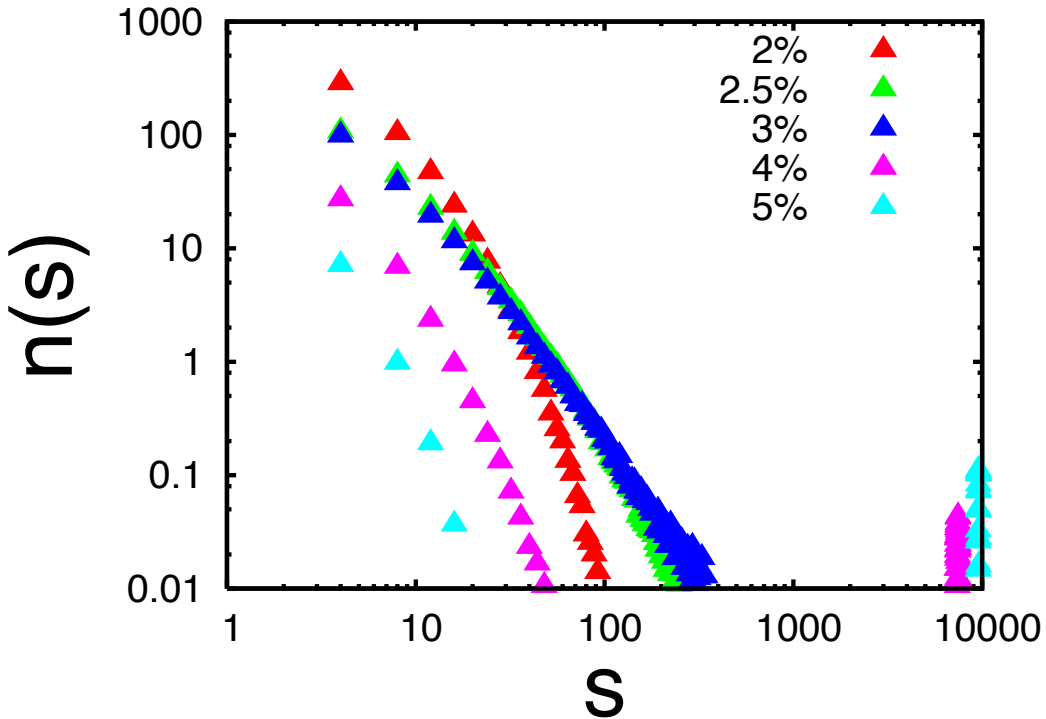

- Columnar phase in the system with C = 5
- Layer spacing is decided by r_5

Stress and viscosity

- Alignment of polymers leads to decrease in viscosity
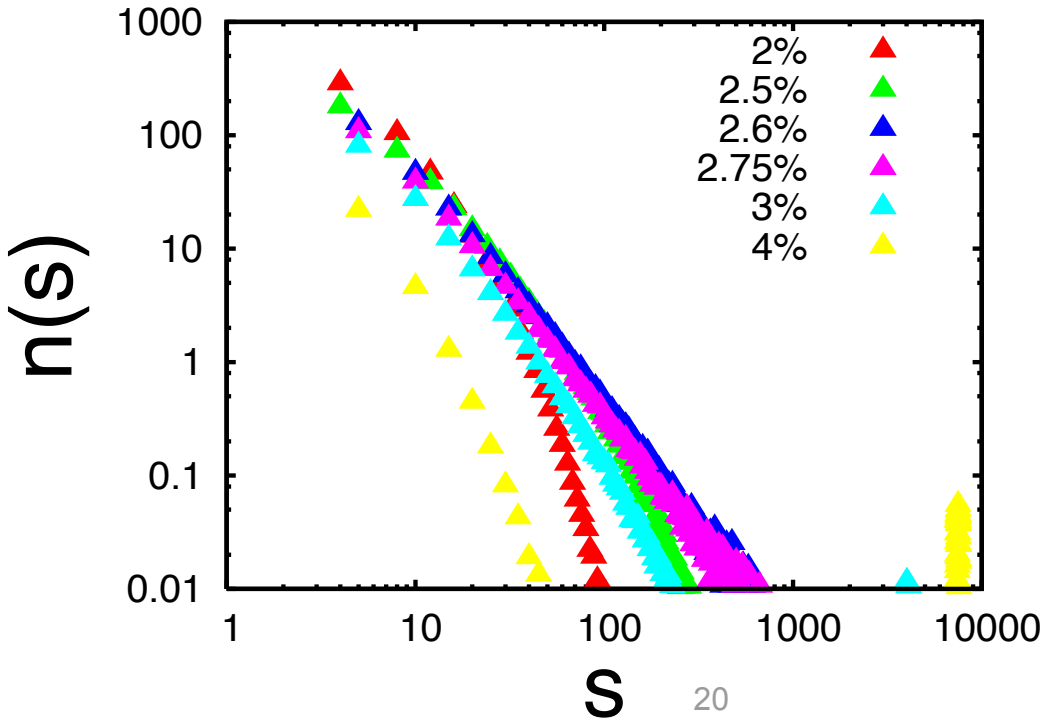
Tuesday 10 August 2010

Cluster size distribution for a tetramer building block.

Percolation at 3% concentration

Cluster size distribution for a pentamer building block.

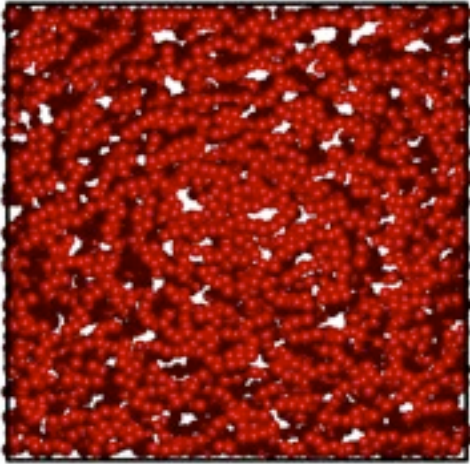Percolation at 2.75% concentration

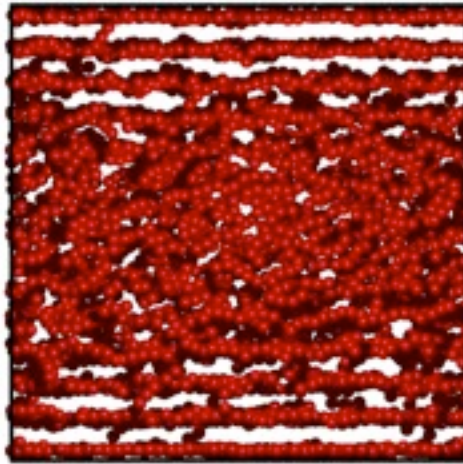For larger segments the percolation is at a lower concentration

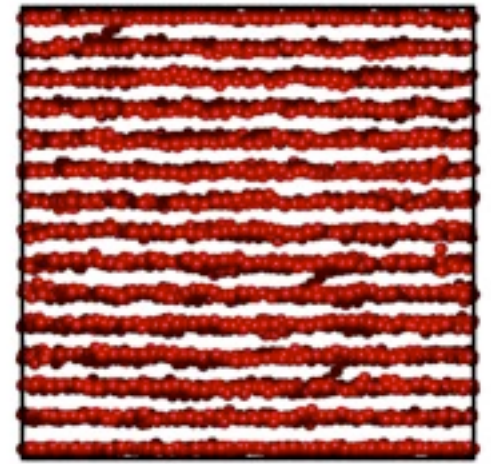# Diffusion coefficient as a function of concentration for different building blocks

Diffusion coefficient as a function of concentration for different building blocks. Plot of D versus $1/C$ wt % (log-log scale) for Trimer, Tetramer, and Pentamer.
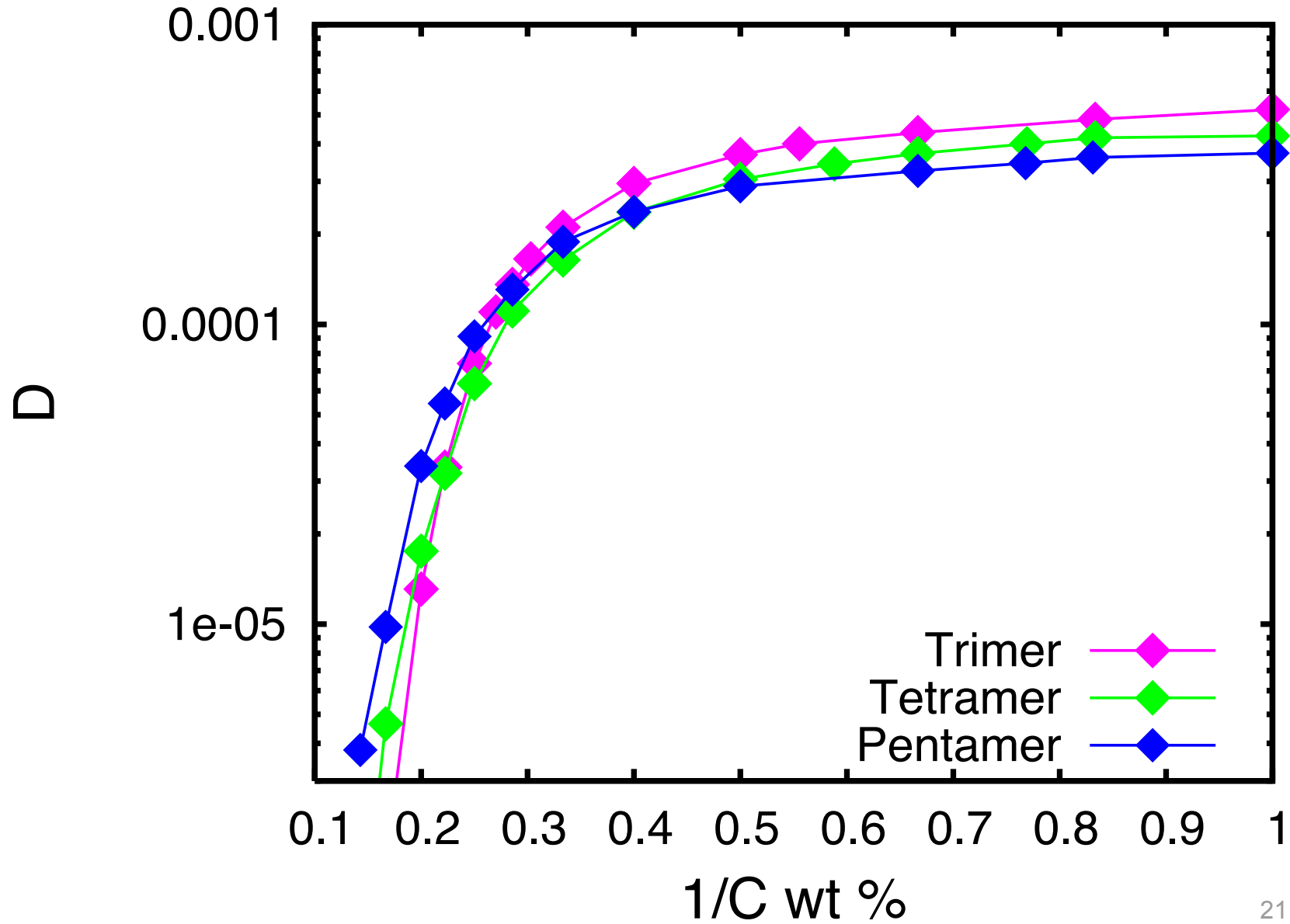
Trimer
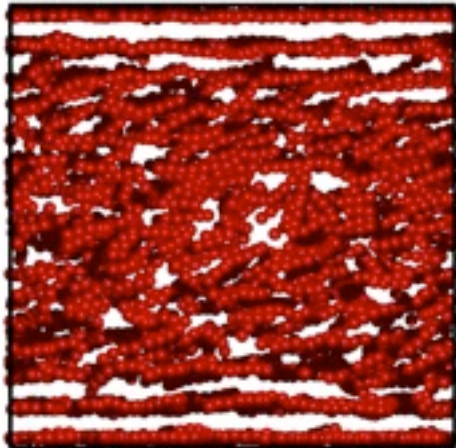

$a_1 = a_2 = 0.1$

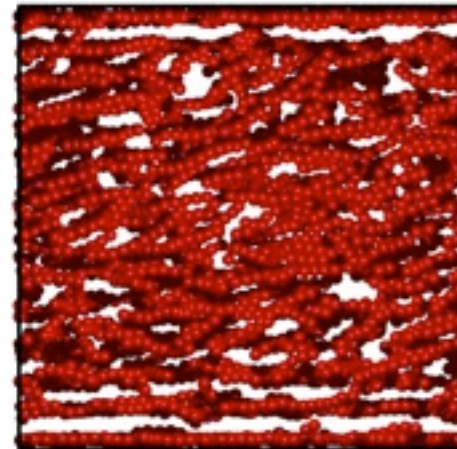$a_1 = a_2 = 0.5$

$a_1 = a_2 = 1.0$

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 ~ 10^3** for a liquid] is obtained)

(1) $\vec{v}_i \longleftarrow \vec{v}_i + \frac{1}{2}\frac{1}{m}\vec{F}_i^C \Delta t$

(2) $\vec{r}_i \longleftarrow \vec{r}_i + \vec{v}_i \Delta t$

(3) Calculate $\vec{F}_i^C \{\vec{r}_j\}$

(4) $\vec{v}_i \longleftarrow \vec{v}_i + \frac{1}{2}\frac{1}{m}\vec{F}_i^C \Delta t$

(5) For all pairs of particles for which $r_{ij} < r_c$

   (i)   Generate $\vec{v}_{ij}^{\circ} \cdot \vec{e}_{ij}$ from a distribution $\xi_{ij}^{(g)} \sqrt{2k_B T^*/m}$

   (ii) $2\vec{\Delta}_{ij} = \vec{e}_{ij}(\vec{v}_{ij}^{\circ} - \vec{v}_{ij}) \cdot \vec{e}_{ij}$

   (iii) $\vec{v}_i \longleftarrow \vec{v}_i + \vec{\Delta}_{ij}$

   (iv) $\vec{v}_j \longleftarrow \vec{v}_j - \vec{\Delta}_{ij}$

with probability $\Gamma \Delta t$

(6) Calculate physical quantities

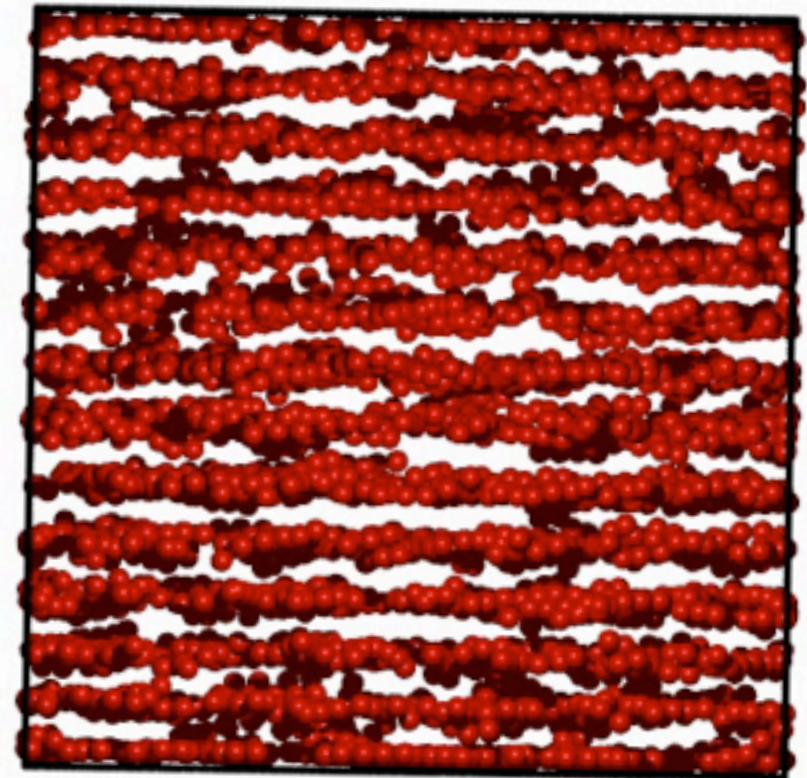*C. P. Lowe, *Europhys. Lett.* **47** (1999) 145
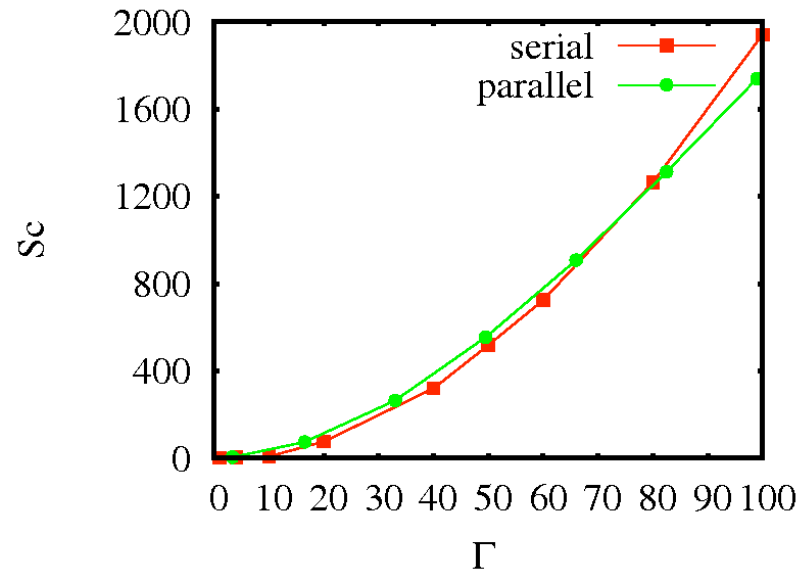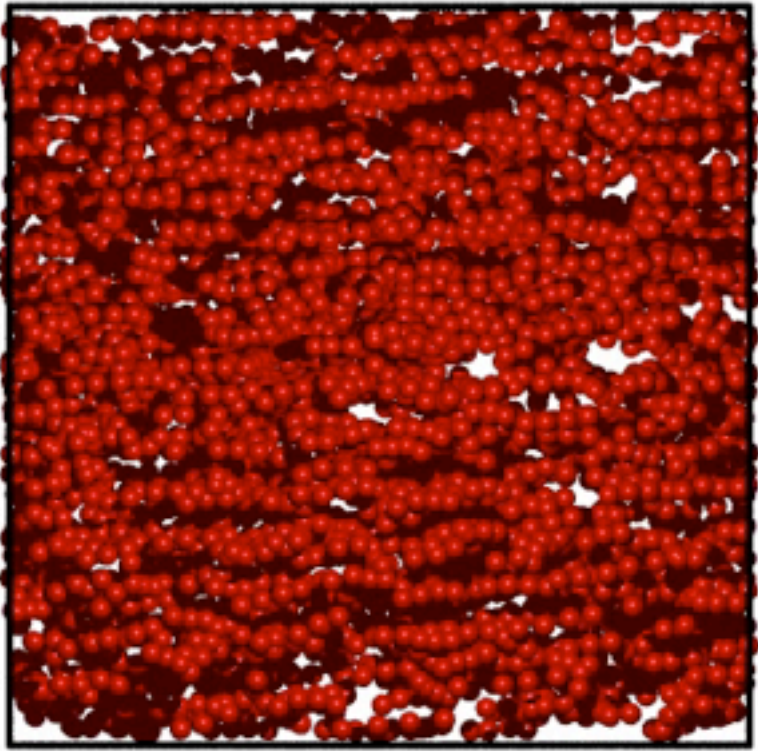
Early stage

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

steady state

Summary of living polymer results

- 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, scission and recombination kinetics and stress correlation function shows that the model reproduces expected results.

- We show the emergence of lamellar and columnar phase when the solution is subjected to simple shear

- The gelation point (as evident from the cluster size distribution) shifts to lower monomer concentration as the size of the basic building block (molecular weight) is increased.

- For larger molecular weight, higher shear stress was required to obtain the layering transition

We now switch to polyelectrolytes