Modeling the Nonlinear Rheology of Reversible Networks

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INITIAL TRAINING NETWORK
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Outline

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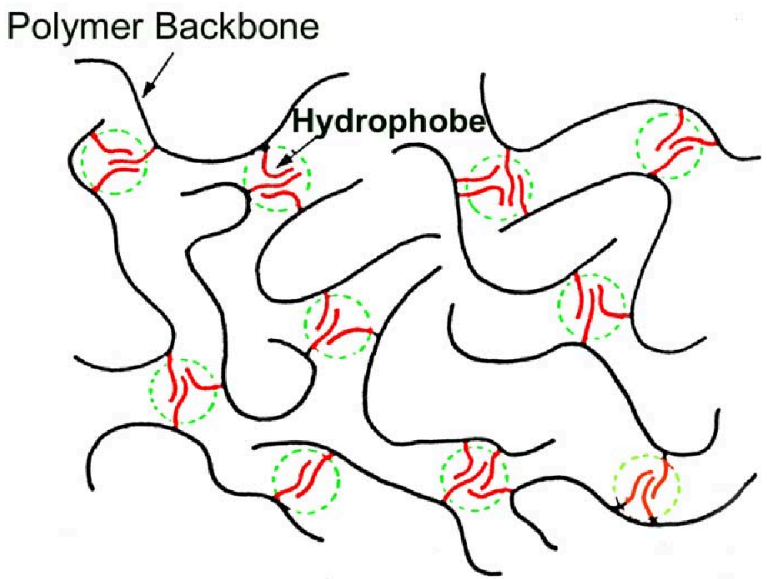
   - ”Classic” Sticky-Rouse Model
   - Stochastic Sticky-Rouse Model
2. Coarse-grained Molecular Simulations
3. Periodic Boundary Conditions (PBC)
4. Sticky-Rouse Model with PBC
5. Conclusions & Questions

Section 1

Background of Associating Polymers

Associating Polymers [1]

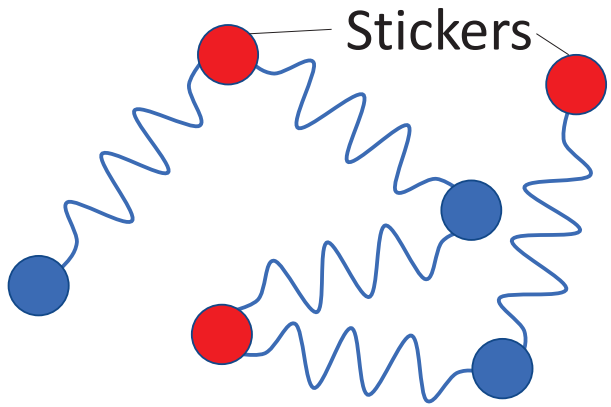
- The existence of '**tunable**' interactions in associating polymers provide a convenient control of the physical properties of these polymers.
- The factors affecting this sort of interactions can be polymer concentration, the number of stickers per chain and the strength of physical bonds.



[1] Rubinstein, M., & Dobrynin, A. V. (1997). Solutions of associative polymers. Trends in Polymer Science.

"Classic" Sticky-Rouse Model

Sticky-Rouse model is based on the idea that stickers along the chain provide an additional effective drag, delaying the terminal relaxation time.



- If the stickers are weak physical bonds, the association lifetime can be defined by

$$\tau_{assoc} = \tau_0 exp(E_a/k_B T), \tag{1}$$

where τ_0 is the relaxation time of a Rouse monomer, E_a is activation energy and $k_B T$ is the thermal energy.

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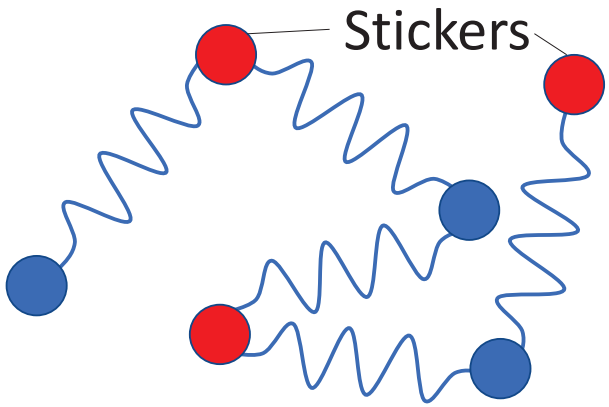

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”Classic” Sticky-Rouse Model

- However, a significant stress relaxation only occurs when the stickers change partners, characterized by an average timescale τ_s, which may be significantly longer than the timescale τ_{assoc}.
- Based on the sticky-Rouse model, *Chen et al.*[2] give the expression of shear relaxation modulus

$$G(t) = \frac{\rho RT}{M}\Big[\sum_{p=1}^{S} \mathrm{EXP}\Big(\frac{-tp^2}{\tau_s S^2}\Big) + \sum_{p=S+1}^{N} \mathrm{EXP}\Big(\frac{-tp^2}{\tau_0 N^2}\Big)\Big] \qquad (2)$$

where S is the number of the stickers per chain and N is the number of the segments per chain and $\frac{\tau_0 N^2}{p^2}$ is the relaxation time of $1/p$ of a chain.

[2] Chen, Q.; Tudryn, G. J.; Colby, R. H. Ionomer dynamics and the sticky Rouse model. Journal of Rheology. 2013.

Stochastic Sticky-Rouse Model

Similarly, *Cui et al.*[3] view the stress relaxation modulus G as the sum of the "fast" Rouse modes and the "slow" sticky modes.

$$G(t) = G_{fast}(t) + G_{sticky}(t), \tag{3}$$

where,

$$G_{fast}(t) = \frac{\rho R T}{M}\left(\tilde{G}_{ends}(t) + \tilde{G}_{trapped}(t)\right)$$

$$\tilde{G}_{ends}(t) = \sum_{\{i=1,S+1\}} \sum_{p=1,p_{odd}}^{N_i} \text{EXP}\left(\frac{-tp^2}{4\tau_0 N_i^2}\right)$$

$$\tilde{G}_{trapped}(t) = \sum_{i=2}^{S} \sum_{p=1}^{N_i} \text{EXP}\left(\frac{-tp^2}{\tau_0 N_i^2}\right)$$

N_i is the number of Rouse monomers in the i-th strand and

[3] Cui, Guanghui, et al. Linear shear and nonlinear extensional rheology of unentangled supramolecular side-chain polymers. Journal of Rheology. 2018

Stochastic Sticky-Rouse Model

$$\tilde{G}_{sticky}(t) = \frac{V}{k_B T}\langle \sigma_{xy}(t+\tau)\sigma_{xy}(\tau)\rangle. \qquad (4)$$

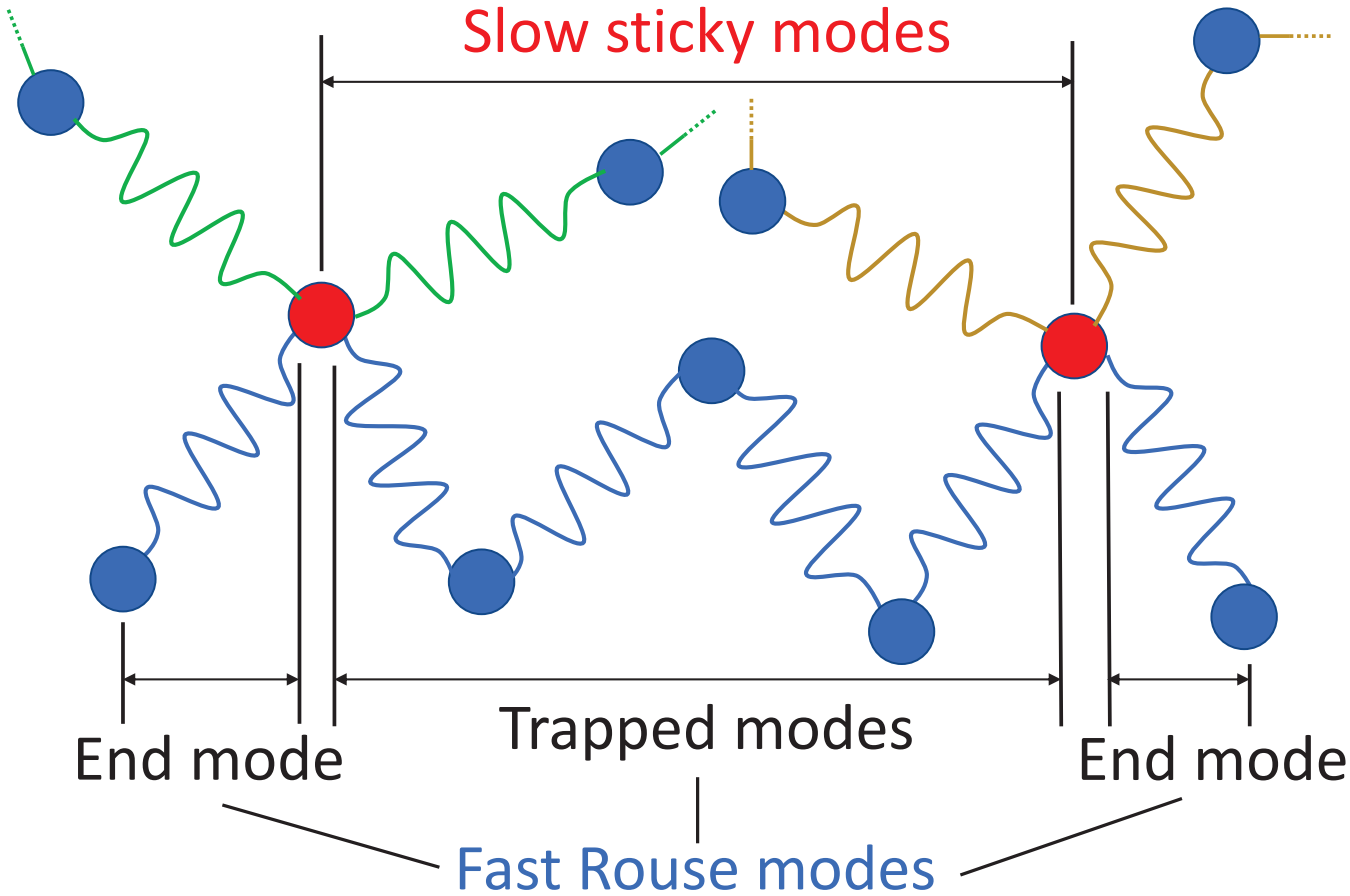
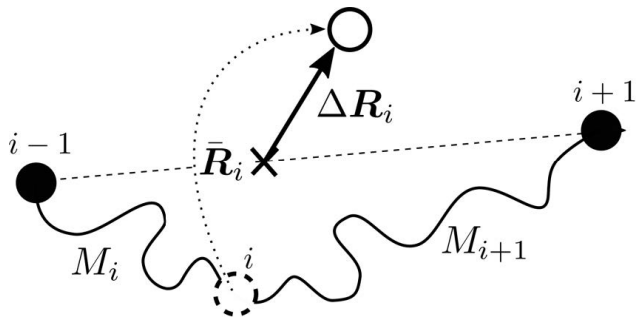


Figure 1: Illustration of shear relaxation modes.

Stochastic Sticky-Rouse Model

In *Cui et al.*'s work, the "slow" stress relaxation is recognized by allowing stickers to take "hops", as shown in the following picture. Sticker i detaches (dashed circle), takes a local "hop," and reattaches to a new position.



However, both Chen and Cui's works only consider the linear viscoelasticity. Our work will focus on the nonlinear behavior of associating polymers.

Section 2

Coarse-grained Molecular Simulations

Dumbbell Model

- Smoluchowski approach

$$\frac{\partial \Psi}{\partial t} = \frac{\partial}{\partial \mathbf{R}} \cdot \left[D \frac{\partial \Psi}{\partial \mathbf{R}} + \Psi D \frac{\partial}{\partial \mathbf{R}} \left(\frac{E}{k_B T} \right) \right] - \frac{\partial}{\partial \mathbf{R}} \cdot (\Psi \mathbb{K} \cdot \mathbf{R}), \qquad (5)$$

where E is the elastic energy, $\mathbb{K}$ is the velocity gradient and D is the diffusion coefficient. At equilibrium, $\Psi(\mathbf{R}, t)$ is isotropic and Gaussian. When D does not vary with $\mathbf{R}$, we can easily compute the term $\langle \mathbf{RR} \rangle$ by

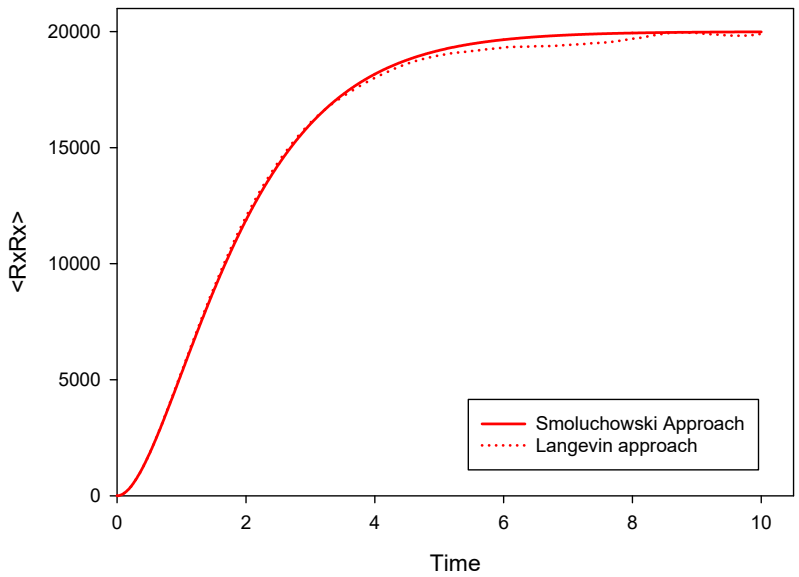
$$\frac{\mathrm{d}\langle \mathbf{RR} \rangle}{\mathrm{d}t} = 2D\mathbb{I} - \frac{6D}{R_0^2} \langle \mathbf{RR} \rangle + \mathbb{K} \cdot \langle \mathbf{RR} \rangle + \langle \mathbf{RR} \rangle \cdot \mathbb{K}^{\mathsf{T}}. \qquad (6)$$

- Langevin approach

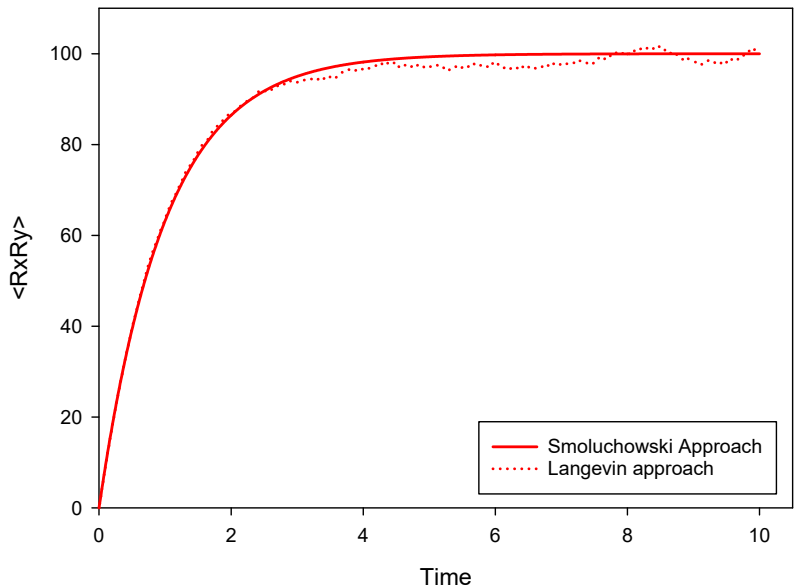
$$\zeta \left(\mathbb{K} \cdot \mathbf{R} - \frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t} \right) - H\mathbf{R} + \mathbf{f} = \mathbf{0}. \qquad (7)$$

Results of Dumbbell Model

Shear start up:



(a)



(b)

Figure 2: Comparisons between Smoluchowski approach and Langevin approach (a) $\langle R_x R_x \rangle$, (b) $\langle R_x R_y \rangle$.(number of molecules:10000, shear rate:100)

Langevin Approach

Solution of Smoluchowski equation is more complicated and Langevin approach is preferable.

- Langevin approach

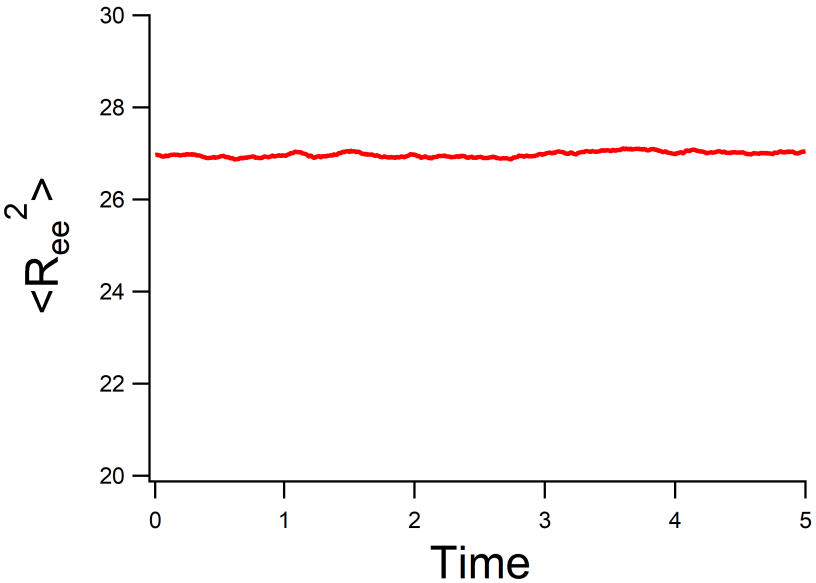
$$\begin{cases} \zeta \frac{\mathrm{d}\mathbf{R}_1}{\mathrm{d}t} = -H(\mathbf{R}_1 - \mathbf{R}_2) + \zeta \mathbb{K} \cdot \mathbf{R}_1 + f_1, \text{if } n = 1 \\ \zeta \frac{\mathrm{d}\mathbf{R}_n}{\mathrm{d}t} = -H(2\mathbf{R}_n - \mathbf{R}_{n+1} - \mathbf{R}_{n-1}) + \zeta \mathbb{K} \cdot \mathbf{R}_n + f_n, \\ \quad \text{if } n = 2, ..., N-1 \\ \zeta \frac{\mathrm{d}\mathbf{R}_N}{\mathrm{d}t} = -H(\mathbf{R}_N - \mathbf{R}_{N-1}) + \zeta \mathbb{K} \cdot \mathbf{R}_N + f_N, \text{if } n = N \end{cases} \tag{8}$$

where $H = 3k_B T / R_0^2$ and R_0 is the end-to-end distance for a subchain at the equilibrium state, f_n is the random force characterized by

$$\begin{aligned} &\langle f_n(t) \rangle = 0, \\ &\langle f_{n\alpha}(t) f_{m\beta}(t') \rangle = 2\zeta k_B T \delta_{nm} \delta_{\alpha\beta} \delta(t - t'). \end{aligned} \tag{9}$$

Results of Langevin Approach

- Static problem
  $\langle \mathbf{R}_{ee}^2 \rangle = (N-1)R_0$, where $\mathbf{R}_{ee}$ is the end-to-end vector and N is the number of the beads per molecule.
- Dynamic problem
  $\langle (\mathbf{R}_{cm}(t) - \mathbf{R}_{cm}(0))^2 \rangle = 6Dt$, where $\mathbf{R}_{cm}$ is the center mass vector.



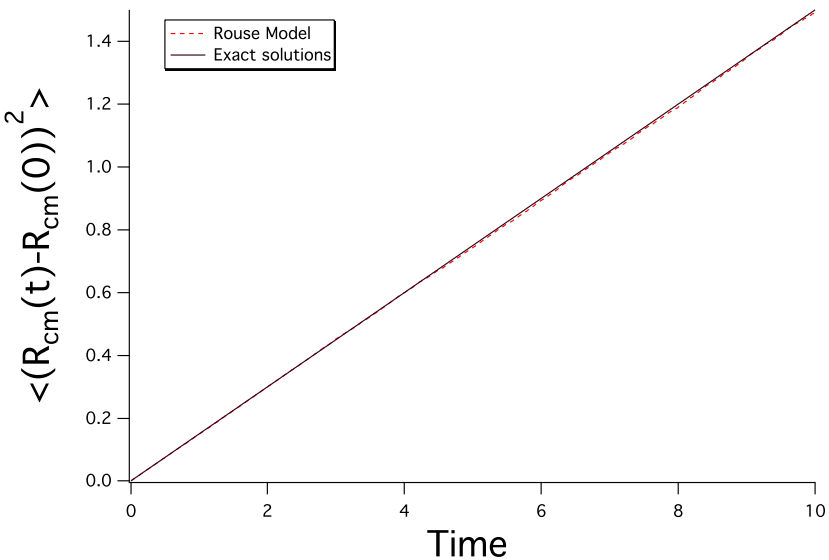


Figure 3: Results of Rouse model at equilibrium state: (number of molecules: 10000, number of beads per molecule N: 10).

Section 3

Periodic Boundary Conditions (PBC)

Periodic Boundary Conditions

- Periodic Boundary Conditions are used when we have interacting molecules (polymer network, for example).

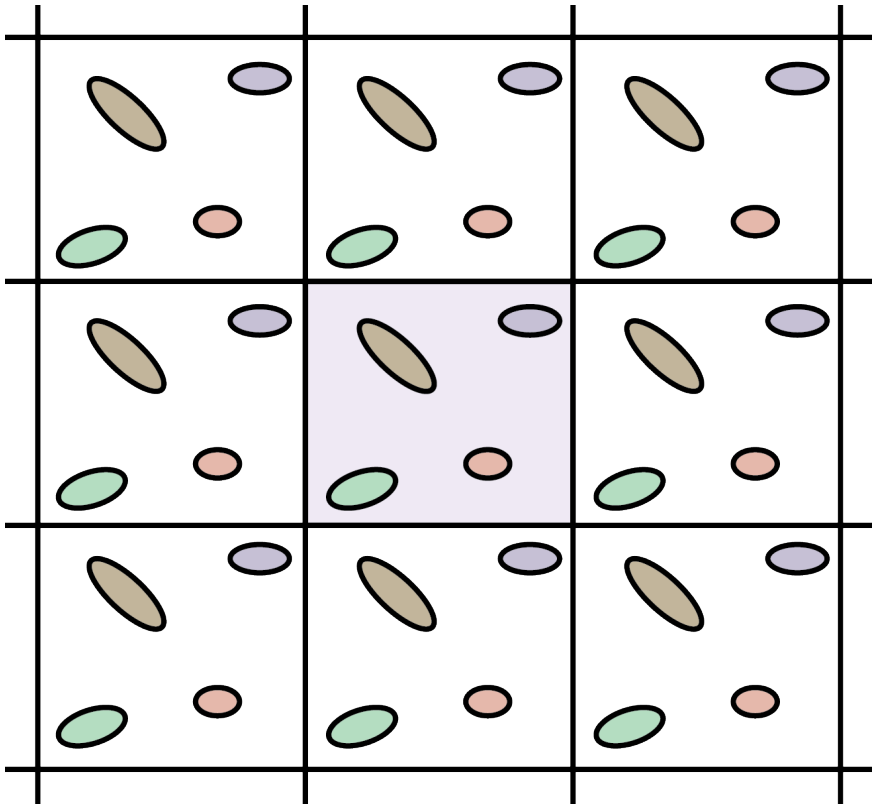
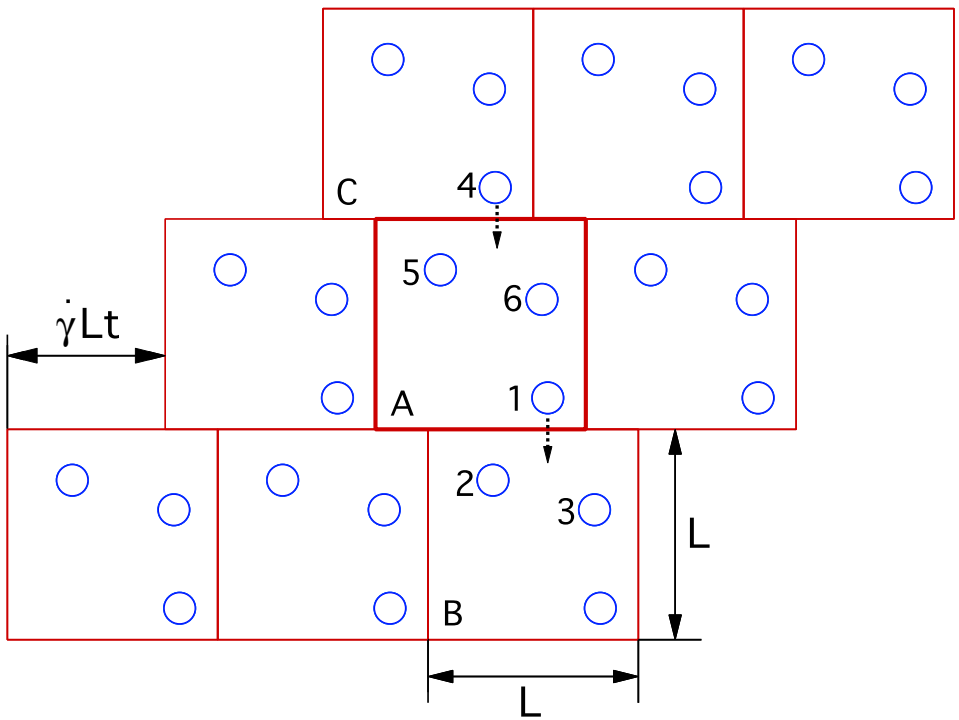


Figure 4: Illustration of Periodic Boundary Conditions in 2D.

Periodic Boundary Conditions

- For the non-equilibrium state, Lees and Edwards proposed a sliding periodic box model.[4]



[4] Lees, A. W., and S. F. Edwards. The computer study of transport processes under extreme conditions. Journal of Physics C: Solid State Physics. 1972.

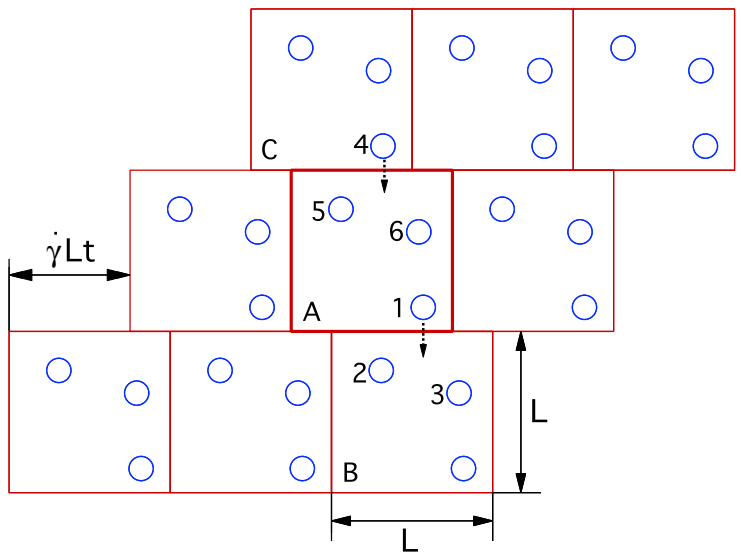
Periodic Boundary Conditions

- The kinematic relation for the horizontal periodicity is

$$v_x(x + nL, y) = v_x(x, y), \quad x \in (0, L), \quad y \in (0, L), \quad n \in N. \tag{10}$$

- The kinematic relation for the sliding periodicity is

$$\begin{aligned} v_x(x + n\dot{\gamma}Lt, y + nL; t) = v_x(x, y; t) + n\dot{\gamma}L, \\ x \in (0, L), \quad y \in (0, L), \quad n \in N. \end{aligned} \tag{11}$$



Results of Classic Rouse Chain with PBC

- Microscopic expression for the stress tensor

$$\sigma = \nu H \langle \sum_{n=1}^{N-1} (\mathbf{R}_{n+1} - \mathbf{R}_n) \otimes (\mathbf{R}_{n+1} - \mathbf{R}_n) \rangle. \qquad (12)$$

  where ν is the number density of molecules.

- Shear relaxation modulus (excluding the solvent contribution) of a Rouse chain

$$G(t) = \frac{V}{k_B T} \langle \sigma_{xy}(t+\tau) \sigma_{xy}(\tau) \rangle_\tau = \nu k_B T \sum_{p=1}^{N-1} \exp(-2t/\tau_p), \qquad (13)$$

where $H = 3k_B T / R_0^2$ and τ_p is

$$\tau_p = \frac{2\zeta}{H} \left[4 \sin^2 \left(\frac{p\pi}{2N} \right) \right]^{-1}. \qquad (14)$$

Results of Classic Rouse Chain with PBC

- At the equilibrium state, we apply the Rouse model to simulate the shear relaxation modulus using the periodic boundary conditions and compare the results with the exact results.

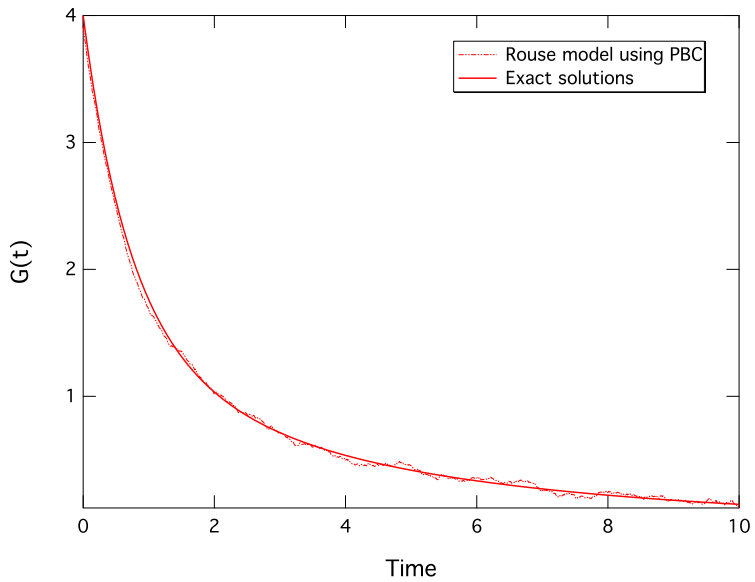


Figure 5: Shear relaxation modulus (molecules:10000, beads for every molecule:5).

Results of Classic Rouse Chain with PBC

- At the non-equilibrium state, stress tensor is computed by Rouse model using PBC.

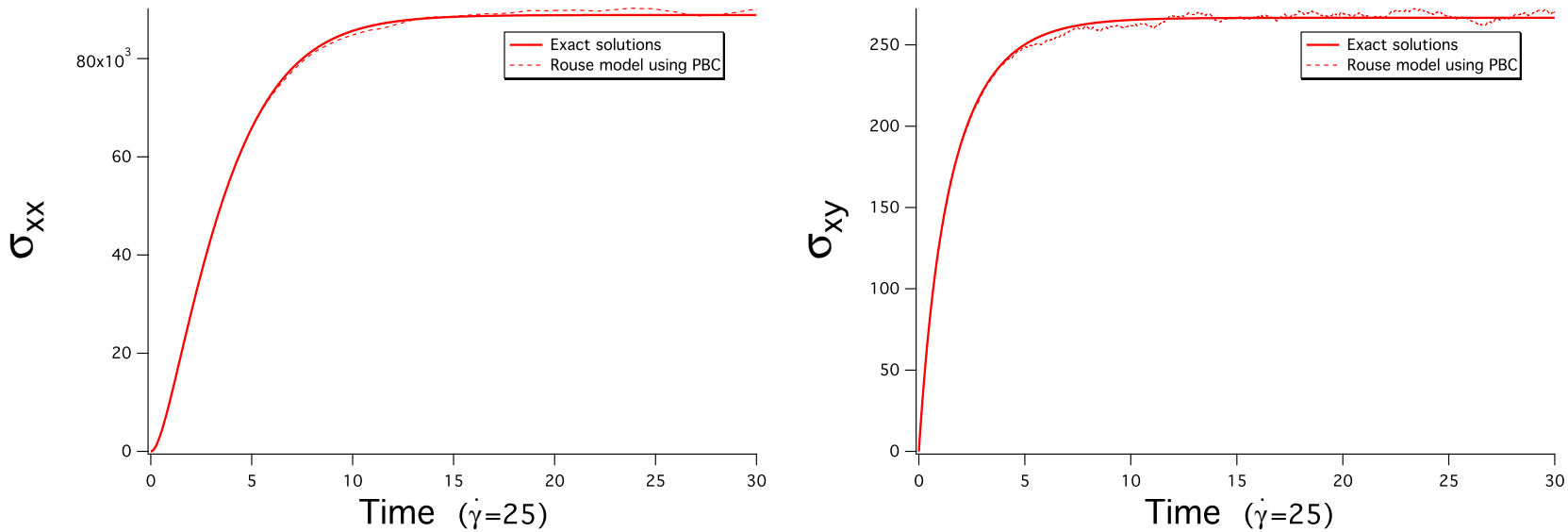


Figure 6: Stress tensor (molecules:10000, beads for every molecule:5).

Section 4

Sticky-Rouse Model with PBC

Sticky-Rouse Model

The idea behind sticky-Rouse model is viewing part of the beads of the Rouse model as stickers. When two stickers are closed enough, they will be associated.

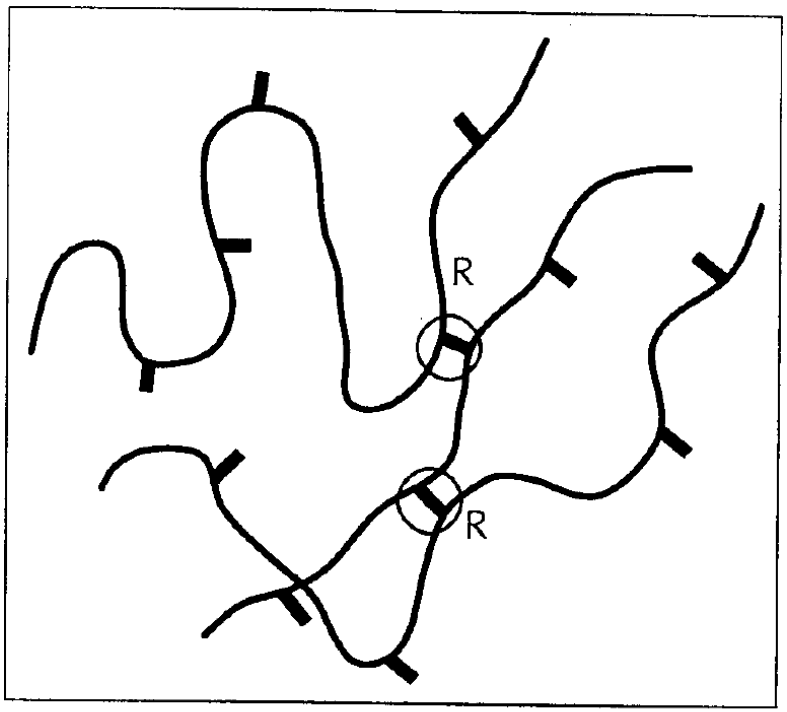


Fig. 3 *A simple model of associative polymers: molecules carrying several stickers each. Stickers can form reversible bonds (denoted by R).*

Key Parameters

In this section, we try to apply the Langevin methods to simulate the Sticky-Rouse model. To begin with, we should propose the following parameters, which will help us simulate the reversible process.

- Number of beads per molecule N.
- Number of stickers per molecule S.
- Lifetime of stickers τ_s.
- The minimum distance d_c between two stickers which are going to be associated.
- The 'hop' distance d_h ($d_h > d_c$).

Protocol: Compute the coordinates of every bead using the Langevin equations. Then determine the distance of two stickers. If it is less than d_c, we will associate the two beads. After time τ_s, we separate them by assigning the 'hop' distance to them.

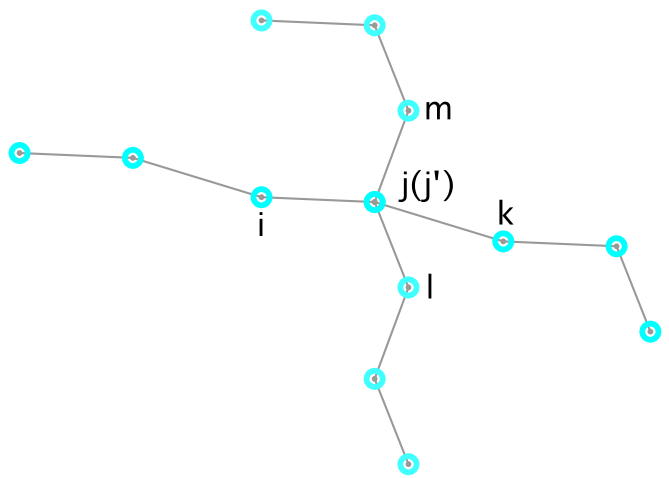
Langevin Approach for Sticky-Rouse Model

- If the distance of two stickers, say beads $R_j, R_{j'}$, is smaller than d_c, they will be associated as Fig. **??**, the coordinates of R_j (assume $R_j = R_{j'}$) can be computed by

$$2\zeta \frac{\mathrm{d}\mathbf{R}_j}{\mathrm{d}t} = -H(4\mathbf{R}_j - \mathbf{R}_i - \mathbf{R}_l - \mathbf{R}_k - \mathbf{R}_m) + 2\zeta \mathbb{K} \cdot \mathbf{R}_j + f_j,$$

where f_j is the random force characterized by

$$\langle f_j(t) \rangle = 0, \quad \langle f_j(t) f_j(t') \rangle = 4\zeta k_B T \delta(t - t'). \tag{15}$$



Section 5

Conclusions & Questions

Conclusions & Questions

- We have successfully simulated the Rouse-model with periodic boundary conditions, not only for the static problems but also for the dynamic problems.
- At present, we almost finished the programming on the sticky-Rouse model. In the next step, we will compare the results with the analytical solutions, like Chen or Cui's works, and some experimental results. In the future, we should also consider nonlinear rheology and double networks with stickers having different strength.