Entangled Polymer Melts with Dissipative Particle Dynamics

Timothy Sirk, Yelena Sliozberg, John Brennan,
and Jan Andzelm

Army Research Laboratory
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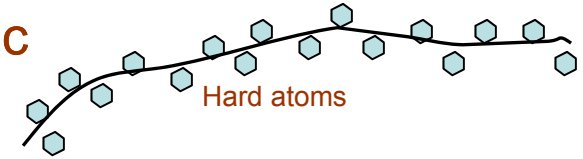
Background

Atomistic

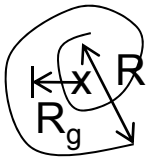


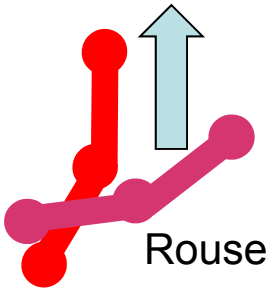
K-G

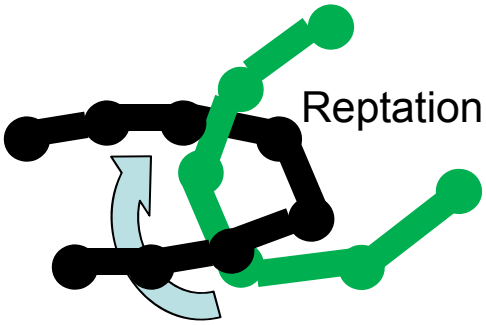
DPD

$t_d \sim N^{3.5}$

$t \sim N^{3*(1/2)}$





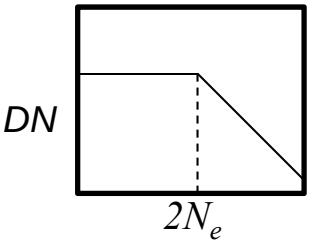


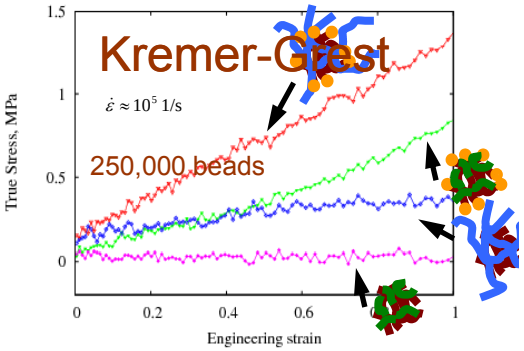
How to prevent chain crossing, and still be fast?

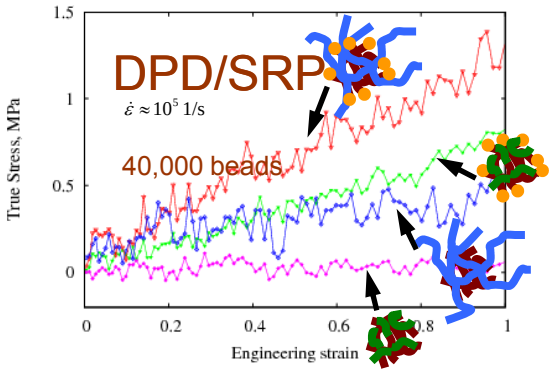
…apply force between bonds

$$N_e = \lim_{N\to\infty} \frac{N}{\langle Z \rangle}$$

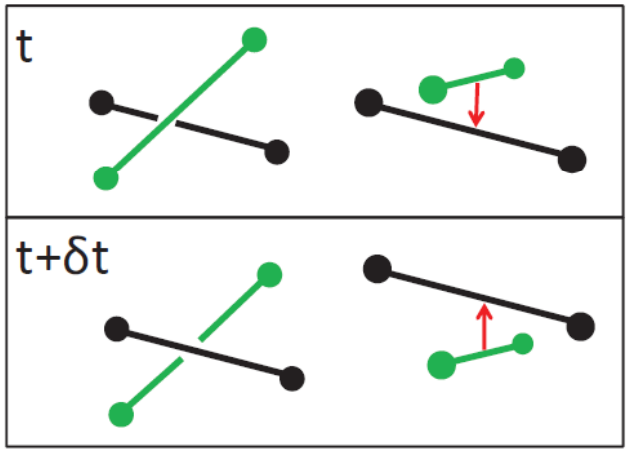
$$N_e = N_e(\rho, R, N)$$







Yelena Sliozberg, unpublished



Dissipative Particle Dynamics

$$\mathbf{F}_i = \sum_{j \neq i} \left(\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R + \mathbf{F}_{ij}^{SRP} + \mathbf{F}_{ij}^H + \mathbf{F}_{ij}^{\prime} \right)$$

Total Force

$$\mathbf{F}_{ij}^C = \begin{cases} a_{ij}\left(1 - r_{ij}/r_c\right)\hat{\mathbf{r}}_{ij} & \left(r_{ij} < r_c\right) \\ 0 & \left(r_{ij} \geq r_c\right) \end{cases}$$

$$\mathbf{F}_{ij}^D = -\gamma \omega^D\left(r_{ij}\right)\left(\hat{\mathbf{r}}_{ij}\mathbf{v}_{ij}\right)\hat{\mathbf{r}}_{ij}$$

$$\mathbf{F}_{ij}^R = \sigma \omega^R \frac{\xi_{ij}}{\sqrt{\Delta t}}\hat{\mathbf{r}}_{ij}$$

$$\omega^D(r) = \left[\omega^R(r)\right]^2$$

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

DPD

Groot and Warren, J. Chem. Phys. 1997

$$\mathbf{F}_{ij}^{SRP} = \begin{cases} a_{ij}^E\left(1 - d_{ij}/d_c\right)\hat{\mathbf{d}}_{ij} & \left(d_{ij} < d_c\right) \\ 0 & \left(d_{ij} \geq d_c\right) \end{cases}$$

SRP

Segmental Repulsive Potential Goujon et. al, J. Chem. Phys. **129**, 034902 (2008)

$$\mathbf{F}_{ij}^H = -K(r - r_0)\hat{\mathbf{r}}_{ij}$$

$$\mathbf{E}_{ijk} = K\cos(\theta)$$

Bond & Angle

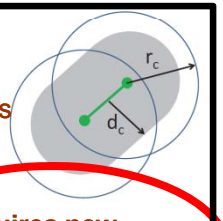
DPD + SRP + Bond + Angles

SRP implemented in LAMMPS

- communicate 'ghost bonds' with forward_pair_comm()
- build a bond neighbor list
- newton bond off, apply force to local atoms

Current SRP

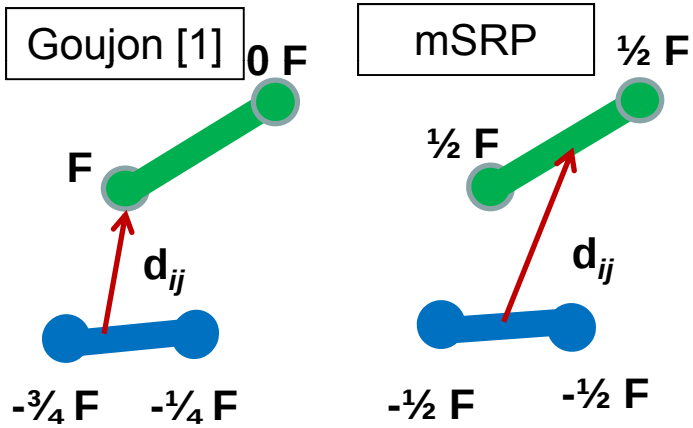
- minimum distance between two bonds
- distribute force unevenly between atoms
- slow, sometimes overshoots d_{ij}



mSRP (new)

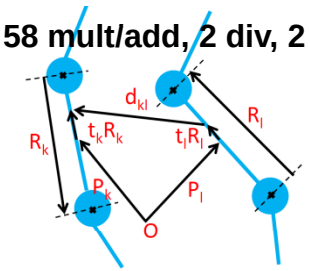
- midpoint distance between bonds
- distribute force evenly
- faster, accurate

Requires new parameters for SRP, angle potentials



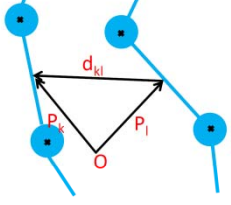
58 mult/add, 2 div, 2 if

18 mult/add



$d_{kl}=P_k+t_kR_k-P_l-t_lR_l$

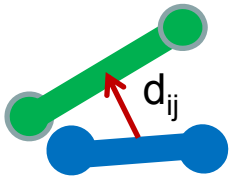
$d(d_{kl})/d(R_k)=d(d_{kl})/d(R_l)=0$



$d_{kl}=P_k-P_l$

1. J. Chem. Phys. **129**, 034902, 2008
2. J. Chem. Phys. **114** (15) p6937, 1997

Parameterization: Chain Crossings



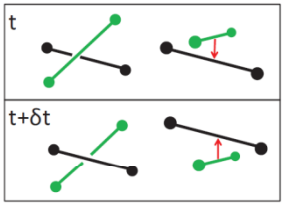
$$\mathbf{F}_{ij} = a_{ij}\left(1-\frac{d_{ij}}{d_c}\right)$$

Vary potential parameters: a_{ij}, d_c

Count bond crossing

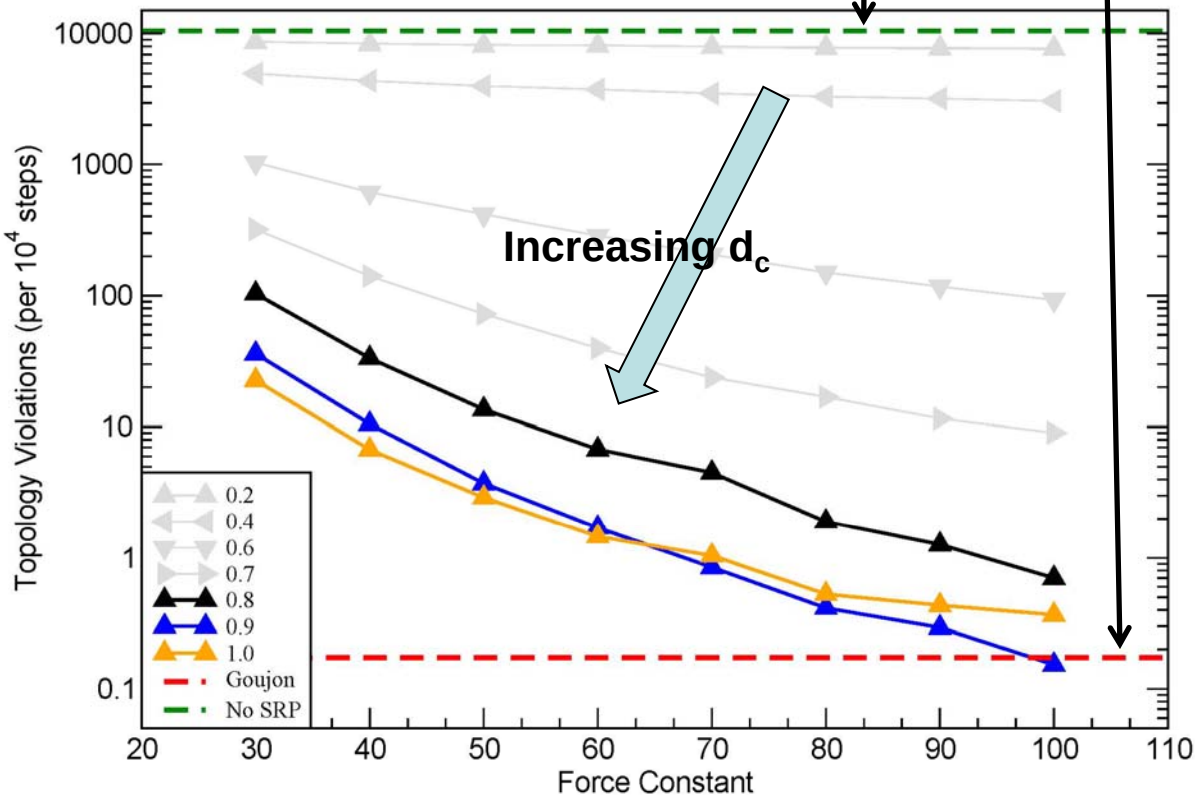
Check thermodynamics

Choose a_{ij}, d_c



DPD with Goujon SRP:
Few chain crossings, large energy contribution

DPD without SRP: Chains cross freely



Test system: 78 chains of N=30, $2*10^6$ timesteps

Thermodynamic Properties

Prevent bond crossings and minimize the effect of SRP

Midpoint Distance

Want low P, PE contributions, and few bond crossings -> choose a=100, r=0.8

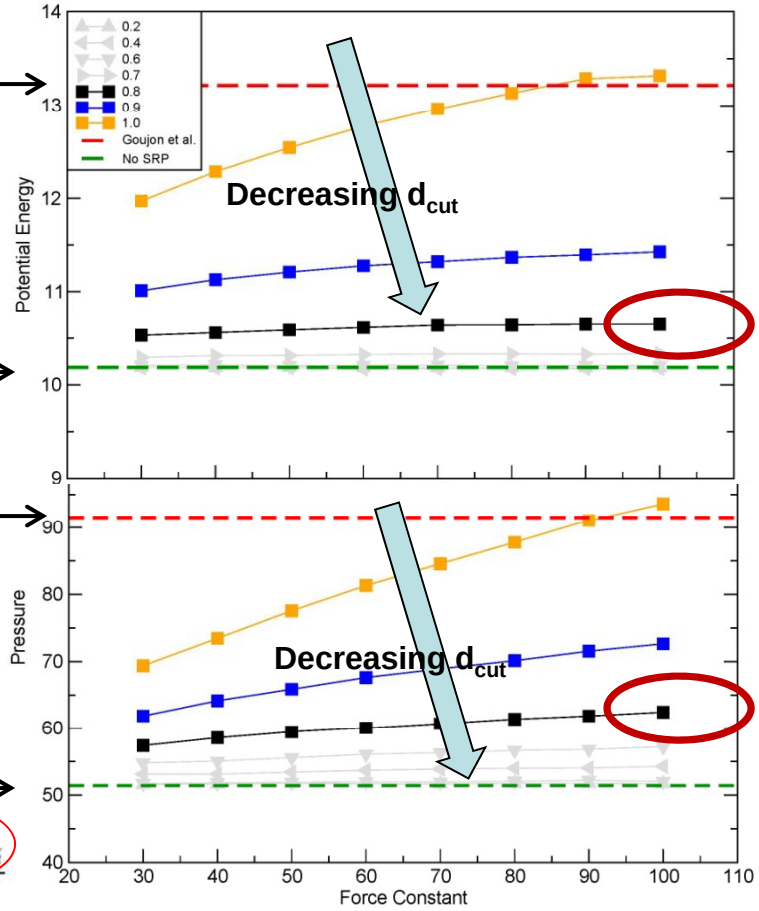
- Small pressure increase over DPD
- Thermostat stable at low temp
- Any γ>4.5

Minimum Distance (Goujon et. al)

- Larger PE and pressure
- Thermostat struggles with low temp
- Restricted to γ~50 for T=1.0

DPD with Goujon SRP: Large PE and pressure

DPD without SRP: Lower limit

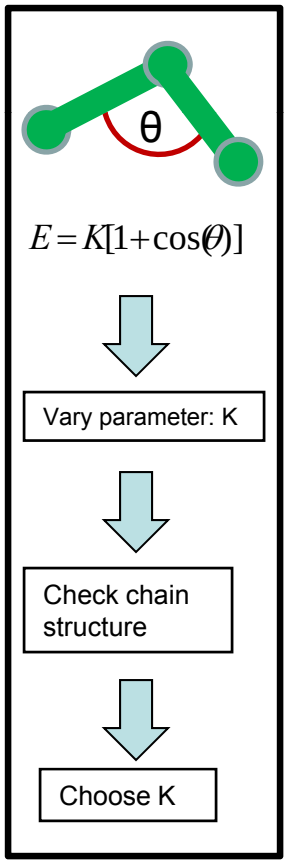


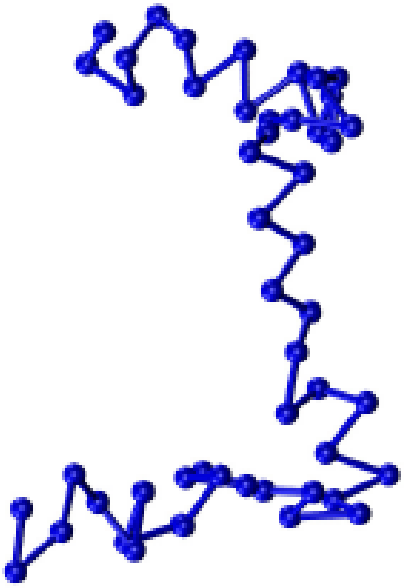
$$P = \frac{Nk_BT}{V} + \frac{\sum_i^N r_i \bullet f_i}{dV}$$

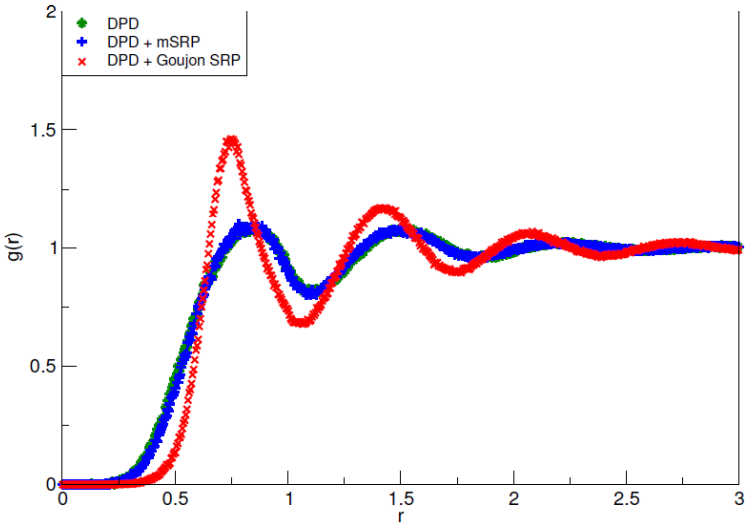
Angle potential and chain structure

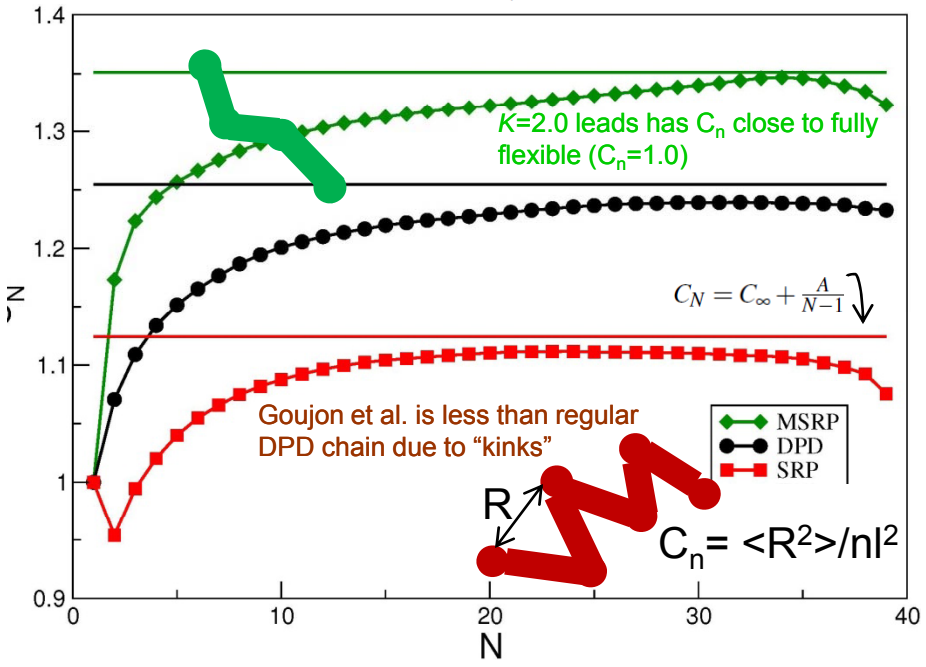
Problem
- Neighboring bonds do not interact
- Favorable for chain to "fold"
- Not good for structure
- Quantify by characteristic ratio, C_n

Solution
- Add angular potential to maintain structure
- Optimize *K* using C_n
- Too weak = poor structure
- Too much = polymer is stiff









Diffusion

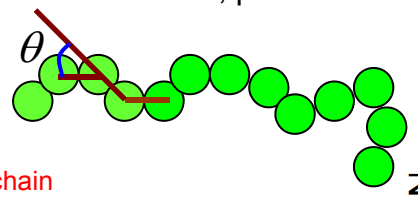
Equilibration

1. Box Size: depends your needs
   1. Structure
   2. Stress/Strain
   3. Diffusion

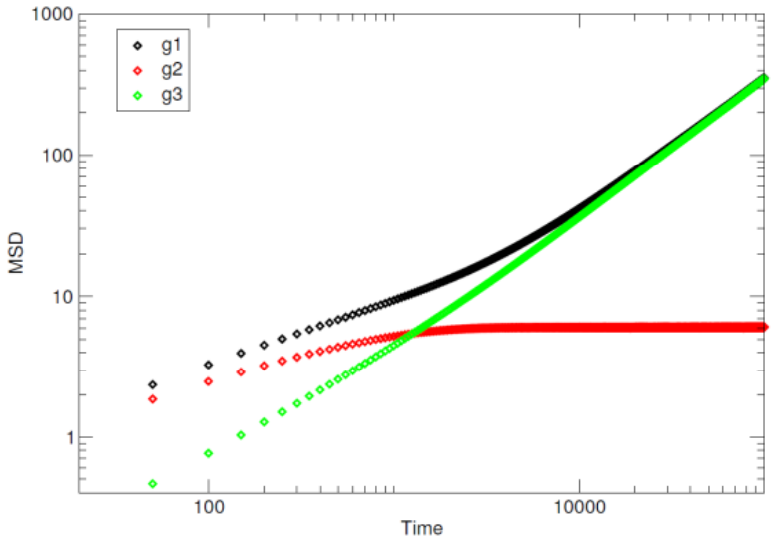
D vs. 1/L

Analytical Correction

2. Time: not straightforward
   1. $MSD_{g1} = MSD_{g3}$ won't happen for long chains
   2. At least move a radius of gyration
   3. Better to wait for $0.90*d(g_1)/dt = d(g_3)/dt$
3. Shortcut: measure characteristic ratio, prebuild the equilibrium structure

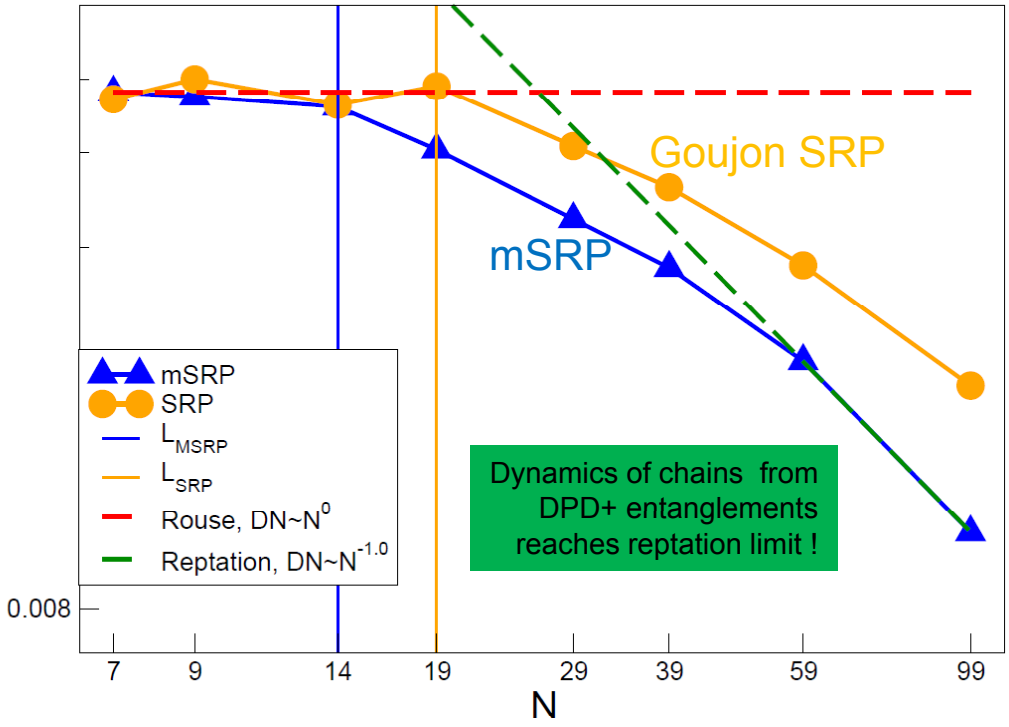


inner monomers
center of mass (COM)
inner monomers wrt COM of chain



Chain Length and Entanglements

1. Identify entanglements with diffusion
   - onset of entangled behavior
   - chain length for one entanglement
2. Check mechanical behavior of entangled chains

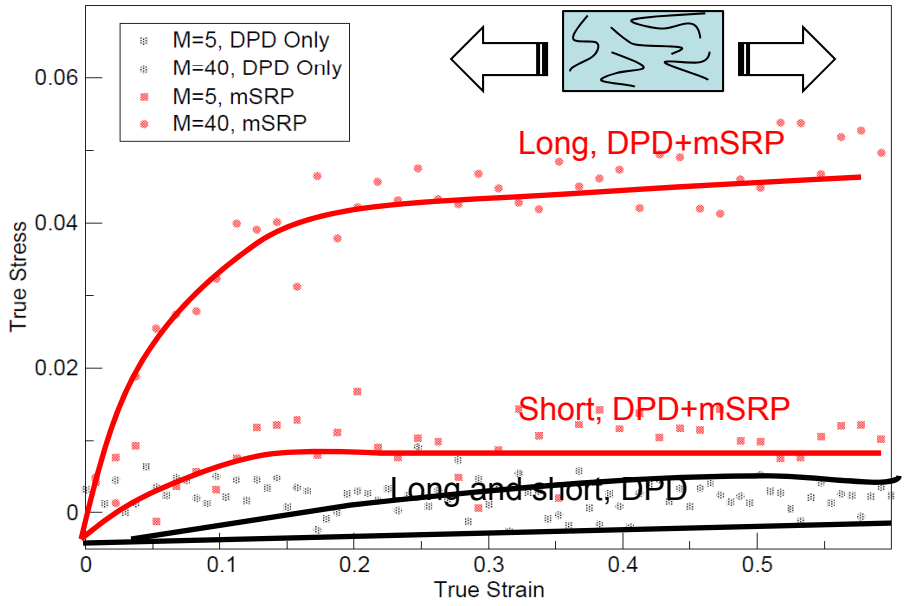


To calculate chain diffusion (DN): Equilibrate until monomers move together with chains

Mechanical Behavior

- tensile test – a fundamental mechanical test
- create stress by deforming simulation box
- compute normal stress as the box is deformed

$$\sigma = -P_{zz} + \frac{1}{2}(P_{xx} + P_{yy})$$



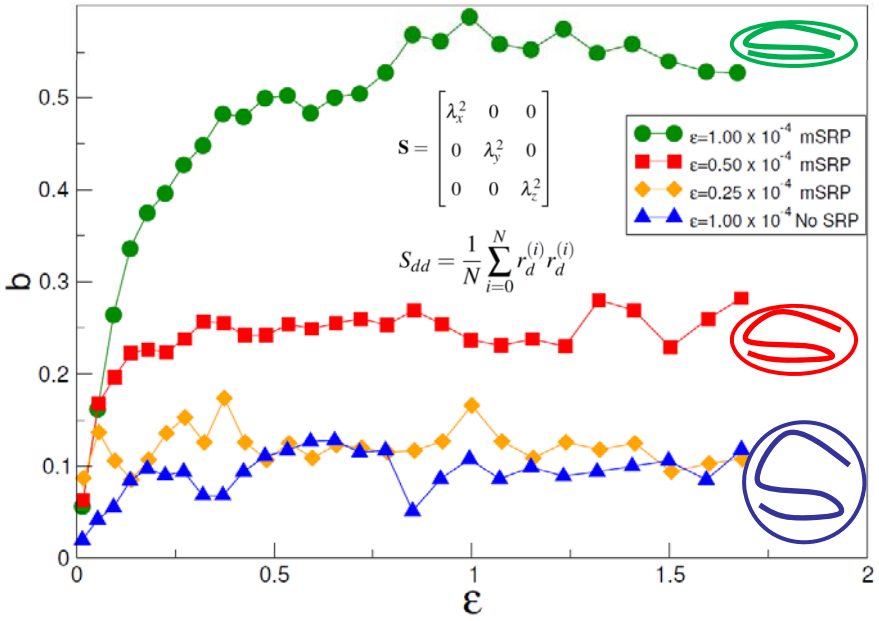
Unentangled chains

- short DPD chains with mSRP
- short/long standard DPD
- less relative motion when stress is applied

Entangled chains

- long DPD chains with mSRP
- entanglements resist relative movement of chains
- relax more slowly than short chains

$$b = \lambda_z^2 - \frac{1}{2}(\lambda_x^2 + \lambda_y^2)$$



Timothy Sirk
Army Research Laboratory

tim.sirk@us.army.mil