Entangled Polymer Melts with Dissipative Particle Dynamics

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

Army Research Laboratory
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How to prevent chain crossing, and still be fast? ...apply force between bonds

Yelena Sliozberg, unpublished
Dissipative Particle Dynamics

\[ \mathbf{F}_i = \sum_{j \neq i} \left( \mathbf{F}^C_{ij} + \mathbf{F}^D_{ij} + \mathbf{F}^R_{ij} + \mathbf{F}^{SRP}_{ij} + \mathbf{F}^H_{ij} \right) \]

**Total Force**

\[ \mathbf{F}^C_{ij} = \begin{cases} a_{ij} \left( 1 - \frac{r_{ij}}{r_c} \right) \mathbf{r}_{ij} & (r_{ij} < r_c) \\ 0 & (r_{ij} \geq r_c) \end{cases} \]

\[ \mathbf{F}^D_{ij} = -\gamma \omega^D(r_{ij}) \left( \mathbf{r}_{ij} \cdot \mathbf{v}_{ij} \right) \mathbf{r}_{ij} \]

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

\[ \sigma^2 = 2\gamma k_B T \]

\[ \mathbf{F}^{SRP}_{ij} = a_{ij}^{\tilde{c}} \left( 1 - \frac{d_{ij}}{d_c} \right) \mathbf{d}_{ij} \begin{cases} (d_{ij} < d_c) \\ 0 \qquad (d_{ij} \geq d_c) \end{cases} \]

\[ \mathbf{F}^H_{ij} = -K(r_{ij} - r_0) \mathbf{r}_{ij} \]

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

**DPD**


**SRP**

Segmental Repulsive Potential


**Bond & Angle**

**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**

**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

Parameterization: Chain Crossings

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

DPD without SRP:
Chains cross freely

\[ F_{ij} = a_{ij} \left( 1 - \frac{d_{ij}}{d_c} \right) \]

Vary potential parameters: \( a_{ij}, d_c \)
Count bond crossing
Check thermodynamics
Choose \( a_{ij}, d_c \)

Test system: 78 chains of N=30, 2*10^6 timesteps
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 $\gamma > 4.5$

**Minimum Distance (Goujon et. al)**

- Larger PE and pressure
- Thermostat struggles with low temp
- Restricted to $\gamma \approx 50$ for $T=1.0$

\[
P = \frac{Nk_BT}{V} + \sum_{i}^{N} \frac{r_i \cdot f_i}{dV}
\]
**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

\[ E = K[1 + \cos(\theta)] \]

Vary parameter: $K$

Check chain structure

Choose $K$

\[ C_n = \frac{<R^2>}{Nl^2} \]

Goujon et al. is less than regular DPD chain due to “kinks”
**Diffusion**

### Equilibration

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

2. **Time:** not straightforward
   1. MSD$_{g_1}$ = MSD$_{g_3}$ won’t happen for long chains
   2. At least move a radius of gyration
   3. Better to wait for $0.90 \times d(g_1)/dt = d(g_3)/dt$

3. **Shortcut:** measure characteristic ratio, prebuild the equilibrium structure

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**Analytical Correction**

inner monomers

center of mass (COM)

inner monomers wrt COM of chain

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**D vs. 1/L**

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**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

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**Graph**

- Dynamics of chains from DPD+ entanglements reaches reptation limit!

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**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

\[ b = \frac{1}{2} \left( \lambda_z^2 + \lambda_x^2 + \lambda_y^2 \right) \]

Graphs showing stress-strain curves for long, short, and mixed DPD+mSRP simulations.
Timothy Sirk
Army Research Laboratory

tim.sirk@us.army.mil