Primitive Paths using Geometrical and Annealing Methods

Sachin Shanbhag and Martin Kroger

School of Computational Science, Florida State University
Department of Materials, ETH Zurich

SoR Meeting, Oct 2007
Primitive Path: the shortest path connecting the two ends of the polymer chain subject to the topological constraints imposed by the obstacles.
Length of the primitive path is shorter than the length of the polymer chain
Primitive Paths in Entangled Polymer Melts

- Polymer chains themselves form obstacles for other chains
- Obstacles/constraints are “mobile”
- Recently “annealing” method to obtain the primitive path network

Everaers et al., *Science*, 2004
Annealing to get Primitive Path Network

- Switch-off **intra-chain** excluded volume (keep **inter-chain** EV)
- Decrease the system temperature gradually
- Tension in the chains gradually increases and they shrink to their primitive paths

Everaers et al., *Science*, 2004
Why is this so exciting?

We can now extract the primitive path network from these microscopic simulations. The primitive path network forms a basic ingredient of these successful coarse-grained models.
Different Methods to get Primitive Paths

(1) The original annealing algorithm
   (Everaers et al., 2004)

(2) Lattice-based modified annealing algorithm
   (Shanbhag and Larson, 2005)

(3) Z-code - shortest multiple disconnected path
    (Kroger, 2005)

(4) CReTA - contour reduction topological analysis
    (Tzoumanekas and Theodorou, 2006)

All these methods seek to minimize the total contour length, while preserving “physically relevant” obstacles
Different Methods to get Primitive Paths

1. The original annealing algorithm
   (1000 centiseconds/particle)

2. Lattice-based modified annealing algorithm
   (100 centiseconds/particle)

3. Z-code - shortest multiple disconnected path
   (1 centisecond/particle)

4. CReTA - contour reduction topological analysis
   (10 centiseconds/particle)

In general, geometrical methods are cheaper
## Different Methods to get Primitive Paths

1. The original annealing algorithm  
   (1000 centiseconds/particle)

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   (100 centiseconds/particle)

3. Z-code - shortest multiple disconnected path  
   (1 centiseconds/particle)

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   (10 centiseconds/particle)

Apply these different methods to the same set of equilibrated samples.
Bond Fluctuation Model

Efficient equilibration of chains

Shanbhag and Larson, *PRL*, 2005
Annealing

Procedure

1. Equilibrate \( N_p \) chains, \( N \) beads/chain in a box of \( L_{\text{box}} \times L_{\text{box}} \times L_{\text{box}} \) using BFM

2. Extract their primitive paths: Annealing
   - Anchor ends of all chains
   - Turn off intra-chain excluded volume
   - Favor moves that reduce length

   \[ p_{\text{acc}}(t) = \min\{1, \exp(-A \Delta L (t/t_{\text{anneal}})^2)\} \]

System Parameters

\[ f = 0.5; A \approx 16; \ t_{\text{anneal}} \approx 5 \ t_{\text{Rouse}} \]

Crossing: \( <P(t)> < 0.3 \)
No Crossing: \( <P(t)> < 0.05 \)

\( A \rightarrow \infty, \) annealing approaches quenching

<table>
<thead>
<tr>
<th>( N )</th>
<th>( N_p )</th>
<th>( L_{\text{box}} )</th>
</tr>
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<tr>
<td>10</td>
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<td>20</td>
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<td>55</td>
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<tr>
<td>500</td>
<td>216</td>
<td>60</td>
</tr>
</tbody>
</table>

Movie (Annealing)

Bond Fluctuation Model

Efficient equilibration of chains

Shanbhag and Larson, *PRL*, 2005
Geometrical Method: Z-code

Computation time = 1 s (Kroger, 2005)
Overall Idea

Since network A is on a lattice, while network Z is off-lattice: we expect \( <LppA> \) to be greater than \( <LppZ> \)
Overall Idea

- Anneal $\rightarrow$ PP network (A) $(\text{measure } <\text{LppA}>)$
- Z-code $\rightarrow$ PP network (Z) $(\text{measure } <\text{LppZ}>)$
- PP network (A$\rightarrow$Z) $(\text{measure } <\text{LppA-Z}>)$
Overall Idea

Equilibrated System

Anneal → PP network (A) (measure $<L_{ppA}>$)

Z-code

PP network (A) → PP network (Z) (measure $<L_{ppZ}>$)

PP network (A->Z) (measure $<L_{ppA->Z}>$)

Expect these to be comparable
Results...

A (red); Z (green); A→Z (blue)

Shanbhag and Kroger, 2007
Results...

L_{pp}(A\rightarrow Z) is 15% smaller than L_{pp}(Z), systematically.

Shanbhag and Kroger, 2007
Annealing: Effect of “A” parameter

Quenching leads to longer $L_{pp}$ more entanglements?

$p_{acc}(t) = \min\{1, \exp(-A \Delta L (t/t_{anneal})^2)\}$

$N=300; L_{pp}(t=0)=421; t_A=5\tau_e$

Shanbhag and Kroger, 2007
Annealing: Effect of “A” parameter

\[ N=300; \quad L_{pp}(t=0)=421; \]

representative sample

Shanbhag and Kroger, 2007
Annealing: Effect of “A” parameter

$N=300; \ L_{pp}(t=0)=421;$
representative sample

Shanbhag and Kroger, 2007
Annealing: Effect of “A” parameter

Some entanglements lost during annealing are preserved during quenching

$N=300; L_{pp}(t=0)=421$; representative sample

Shanbhag and Kroger, 2007
How are entanglements lost during annealing?

Constraint Release by End Looping (CR-EL)

Chain Slip

*does not need slack*

Needs chain slack and chain ends

out-of-secant area disentanglement

Zhou and Larson, 2006
Shanbhag and Kroger, 2007
For $A<1000$, most of the slack is lost before $t/t_A=0.02$, where,

$$A(t/t_A)^2 \ll 1$$

If we consider $A > 1/(0.02)^2 \sim 2500$, different picture.

CR-EL is most active during early time.

Zhou and Larson, 2006
Shanbhag and Kroger, 2007
Rings: Prevent CR-EL by design

N=190; Lpp(t=0)=210

For rings beads 1 and N, were immobilized (like linears)
Limiting equivalence: Quenching and $Z$

Quenching: $T=0$, or $A \rightarrow \infty$

$\text{Quenching: }$

$$ F_i = k(u_i - u_{i-1}) + F_{EV} $$

If $F_{EV} = 0$, then
$$ \frac{dr_i}{dt} = \frac{k}{\zeta}(u_i - u_{i-1}) = \frac{2k}{\zeta}(r_{cm} - r_i) $$
Limiting equivalence: Quenching and Z

Quenching:

If $F_{EV}(r)$, is point-like and radially symmetric, with obstacle at $r$

$$\frac{dr_i}{dt} = (2k/\zeta) \,(r_{cm} - r_i) + F_{EV}(|r_i - r|)$$

Stationary solution $r_i$ is a point close to $r$, that is attached to $r_{cm}$ by a spring
Limiting equivalence: Quenching and Z

If the size of the beads is decreased, during quenching, while maintaining the ratio of the bead size to the spring length (to prevent crossing) Z and quenching algorithms become almost identical.
Summary

1. Annealing and Geometrical methods compared

2. \( L_{pp}(A\rightarrow Z) < L_{pp}(Z) < L_{pp}(A) \)

3. About 15\% difference between \( L_{pp}(A\rightarrow Z) \) and \( L_{pp}(Z) \), due to loss of entanglements during annealing

4. Equivalence between quenching (in the limit of vanishing bead size) and geometrical methods demonstrated
Acknowledgements

- PRF and CRC-FYAP for funding
Chain Uncrossability…

Chain crossing *necessarily* involves the intersection of the midpoints of two bonds, if one bead is moved at a time.
Chain Uncrossability…

Secondary lattice (split each original cube to 8 cubes)
Enforce (or don’t enforce) excluded volume of bond midpoints

*red points (bond midpoints occupy positions on the secondary lattice)*