Primitive Paths using Geometrical and Annealing Methods

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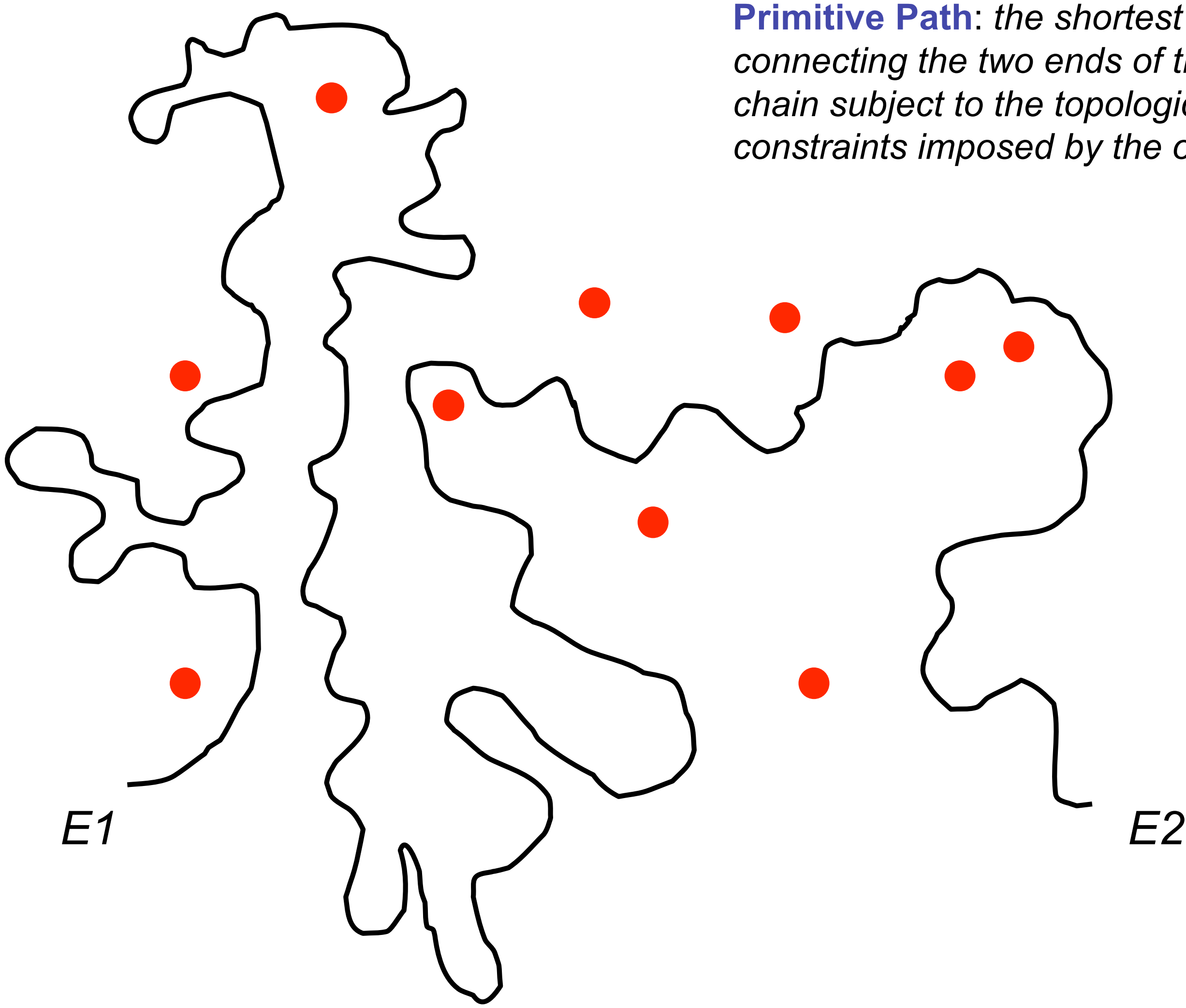
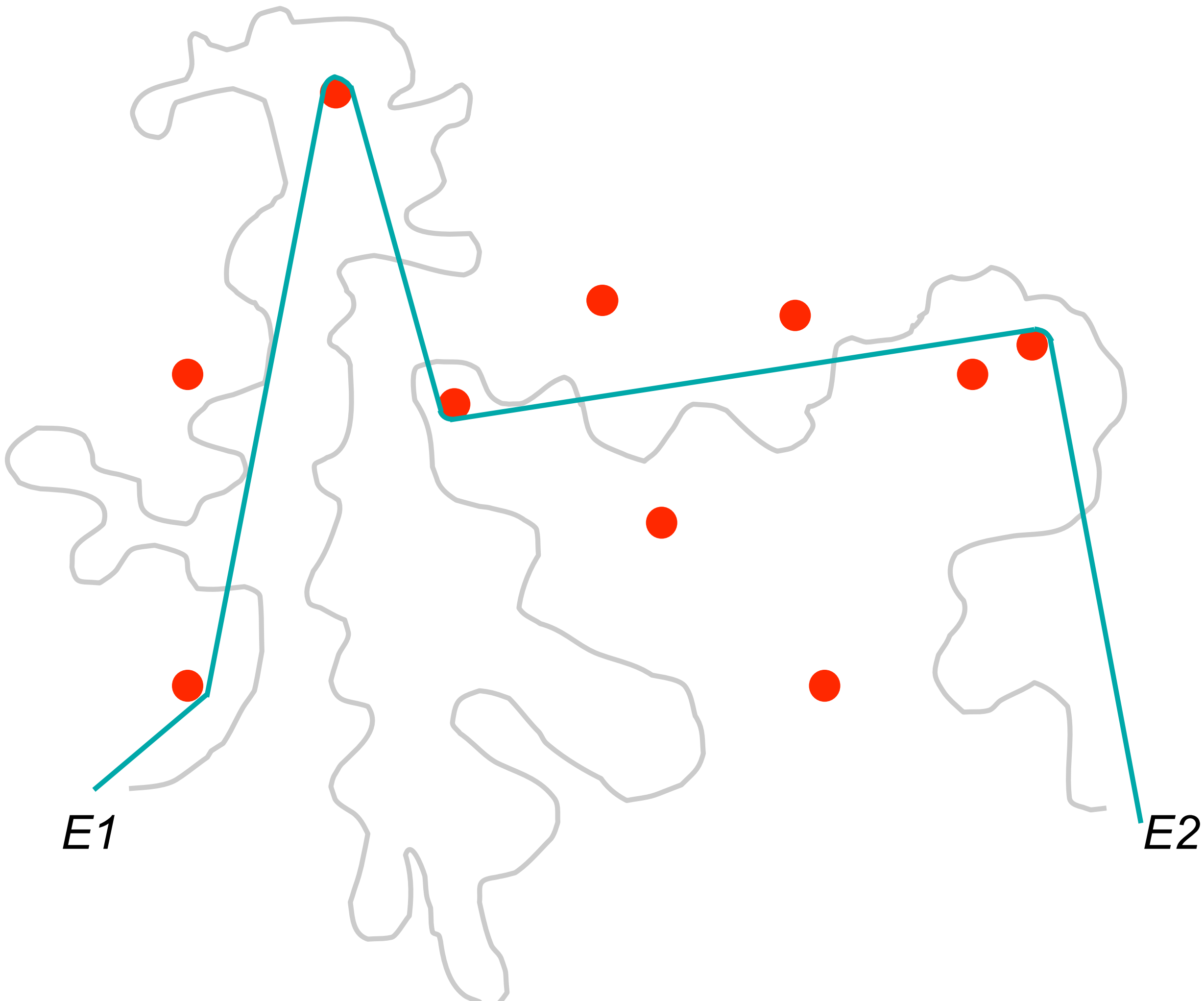
Primitive Path



Primitive Path: *the shortest path connecting the two ends of the polymer chain subject to the topological constraints imposed by the obstacles*

Primitive Path



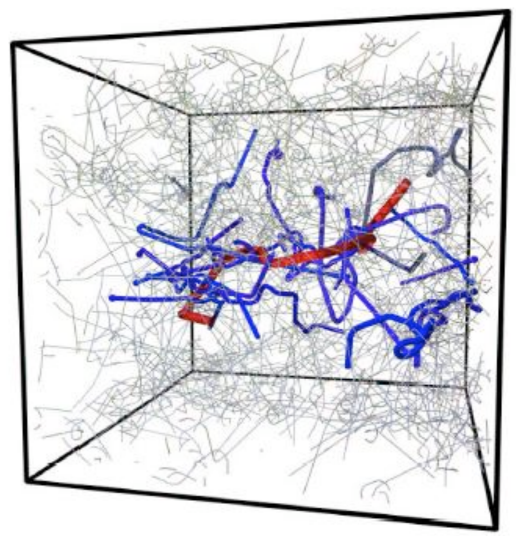
Length of the primitive path is shorter than the length of the polymer chain

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



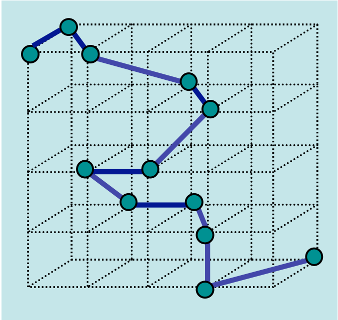
❖ Switch-off **intra-chain** excluded volume (keep **inter-chain** EV)

❖ Decrease the system temperature gradually

❖ Tension in the chains gradually increases and they shrink to their primitive paths

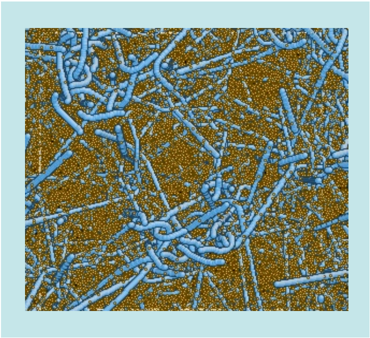
Everaers et al., *Science*, **2004**

Why is this so exciting?

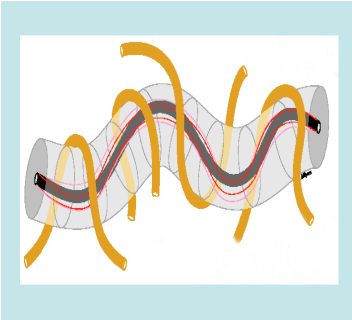


lattice models

molecular dynamics

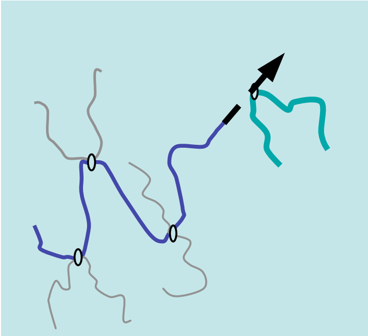


we can now extract the primitive path network from these microscopic simulations



tube model

slip-link models



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)

ANNEALING

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

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

GEOMETRICAL

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 centiseconds/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)

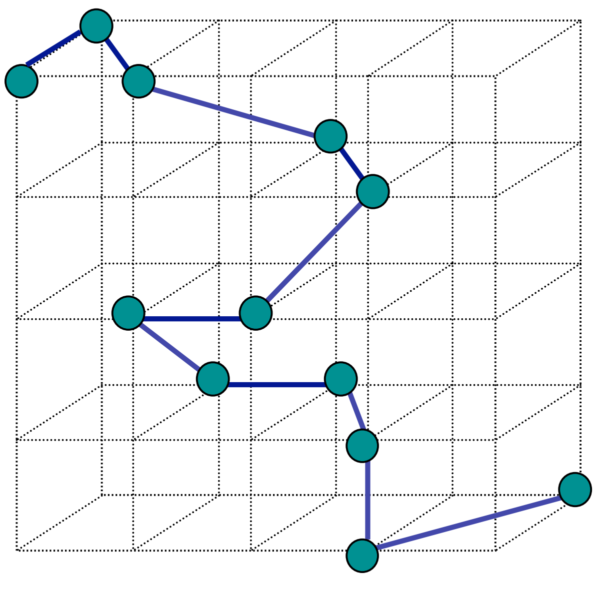
(3) Z-code - shortest multiple disconnected path
(1 centiseconds/particle)

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

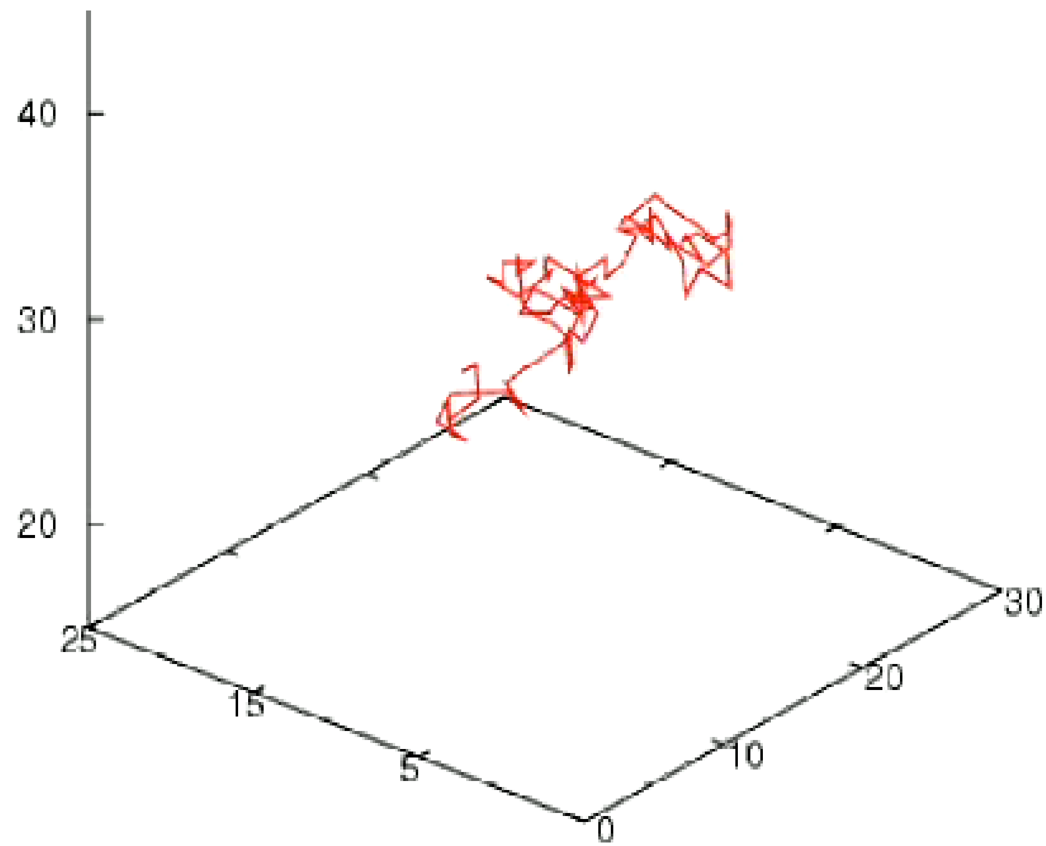
Apply these different methods to the same set of equilibrated samples

Movie (Equilibration)

Bond Fluctuation Model



Efficient equilibration of chains



Shanbhag and Larson, *PRL*, **2005**

Shaffer, *J. Chem Phys.*, **1994**

Annealing

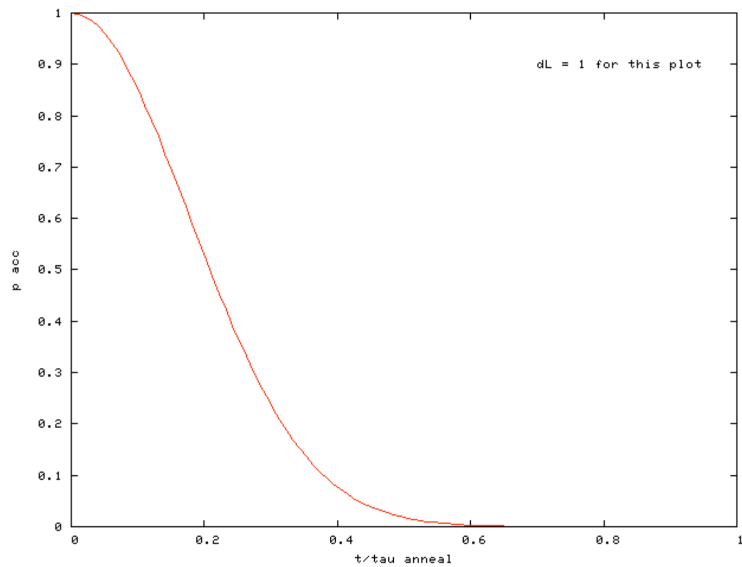
Procedure

1. Equilibrate N_p chains, N beads/chain in a box of $L_{box}*L_{box}*L_{box}$ using BFM

2. Extract their primitive paths: Annealing

- Anchor ends of all chains
- Turn off intra-chain excluded volume
- Favor moves that reduce length

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



N	N_p	L_{box}
10	400	20
32	125	20
75	180	30
125	364	45
300	277	55
500	216	60

System Parameters

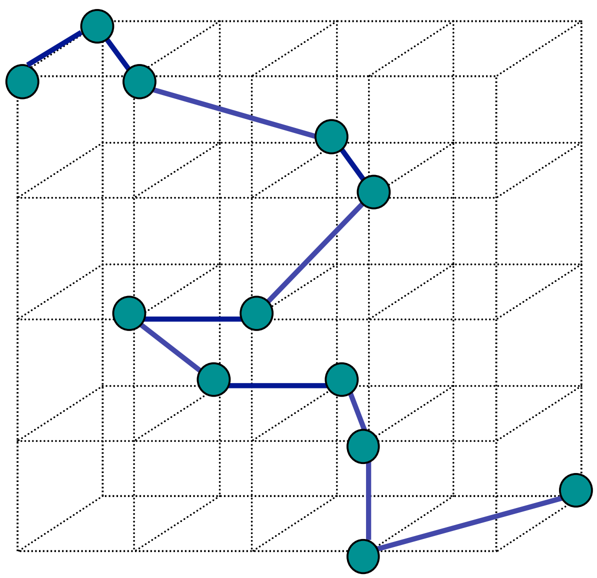
f = 0.5; A≈16; $t_{anneal} \approx 5\, t_{Rouse}$
Crossing: <**P**(t)> < 0.3
No Crossing: <**P**(t)> <0.05

A -> infinity, annealing approaches quenching

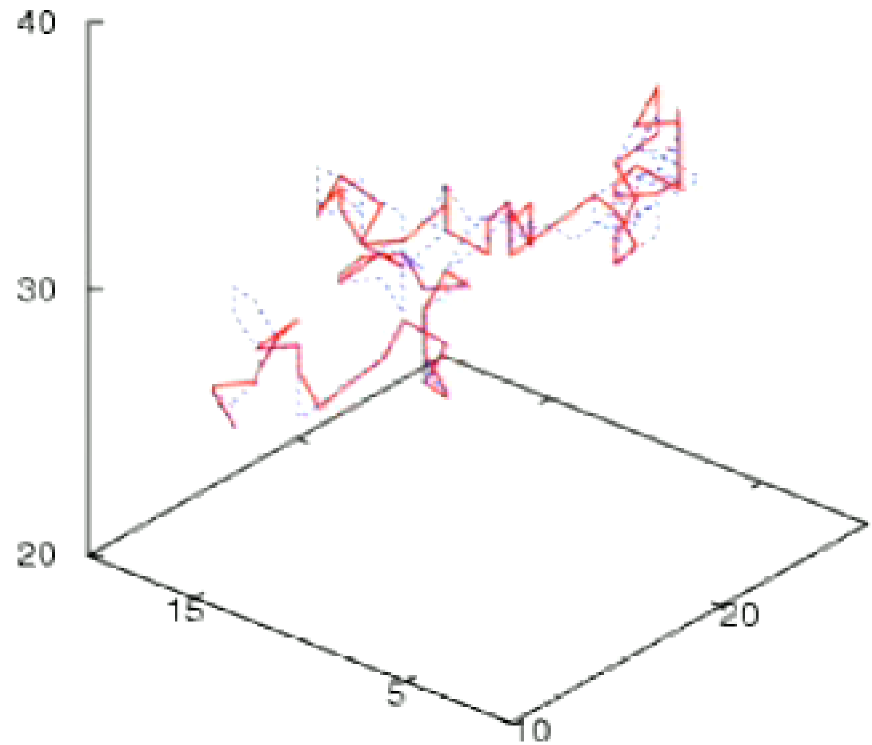
S. Shanbhag and R. G. Larson, ***PRL***, 2005

Movie (Annealing)

Bond Fluctuation Model



Efficient equilibration of chains



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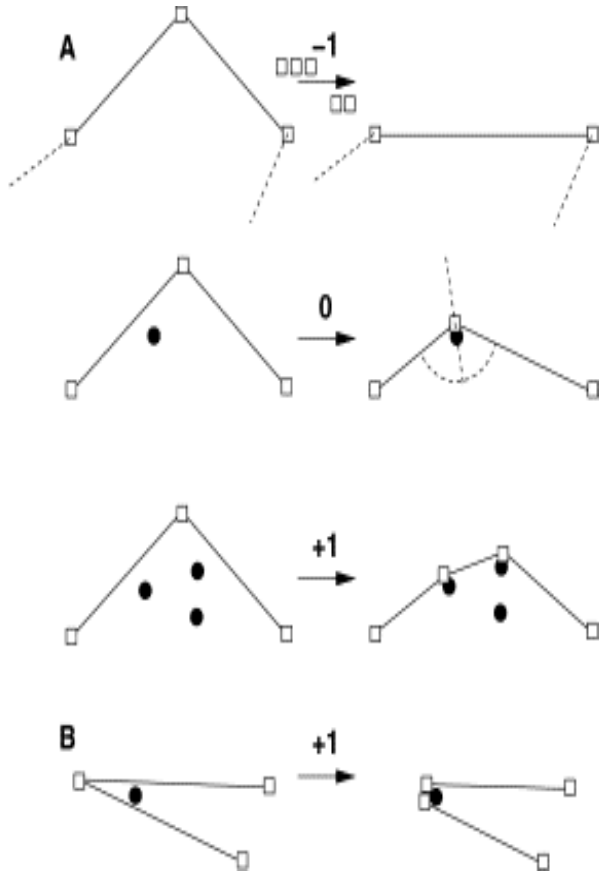
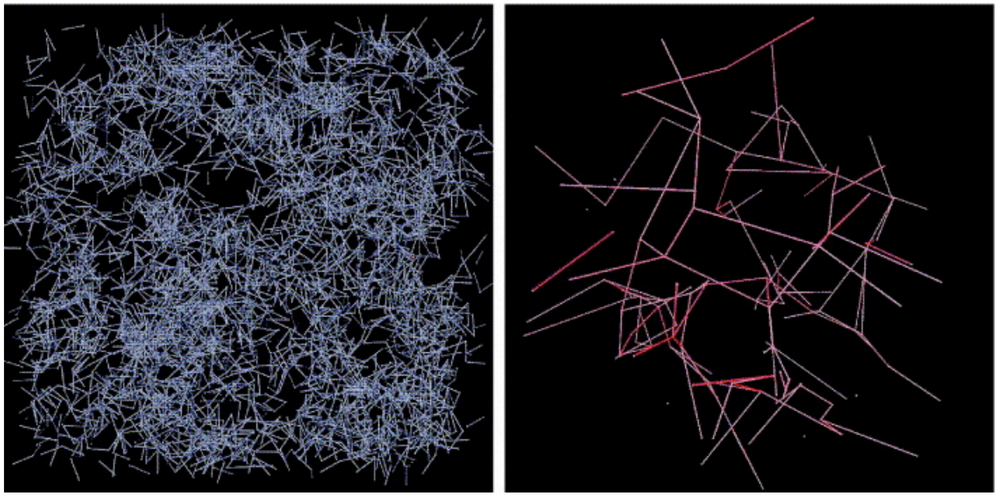
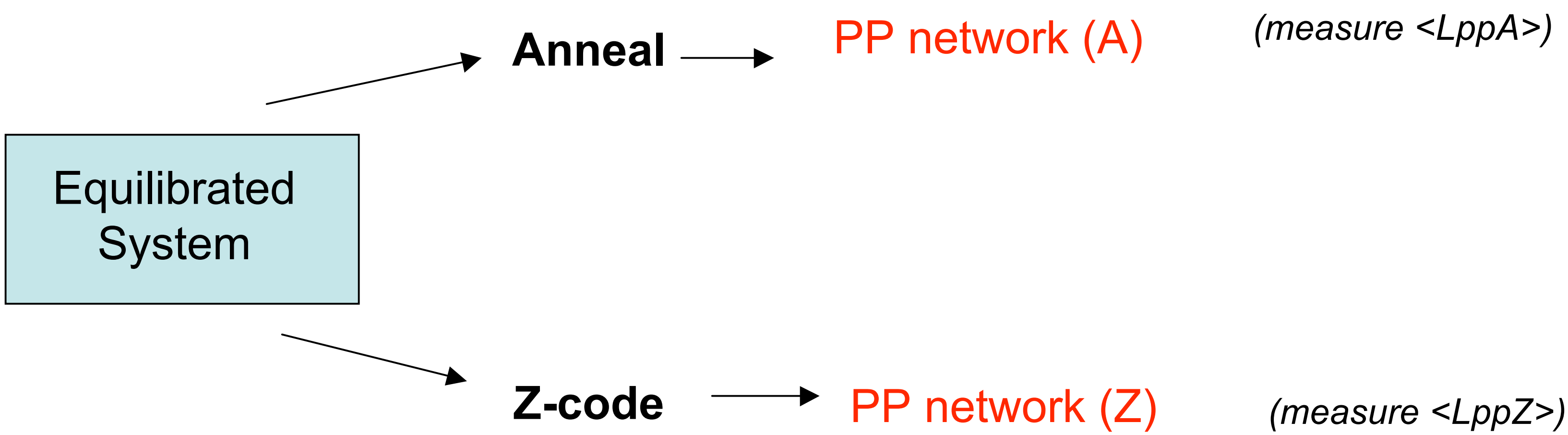
Geometrical Method: Z-code





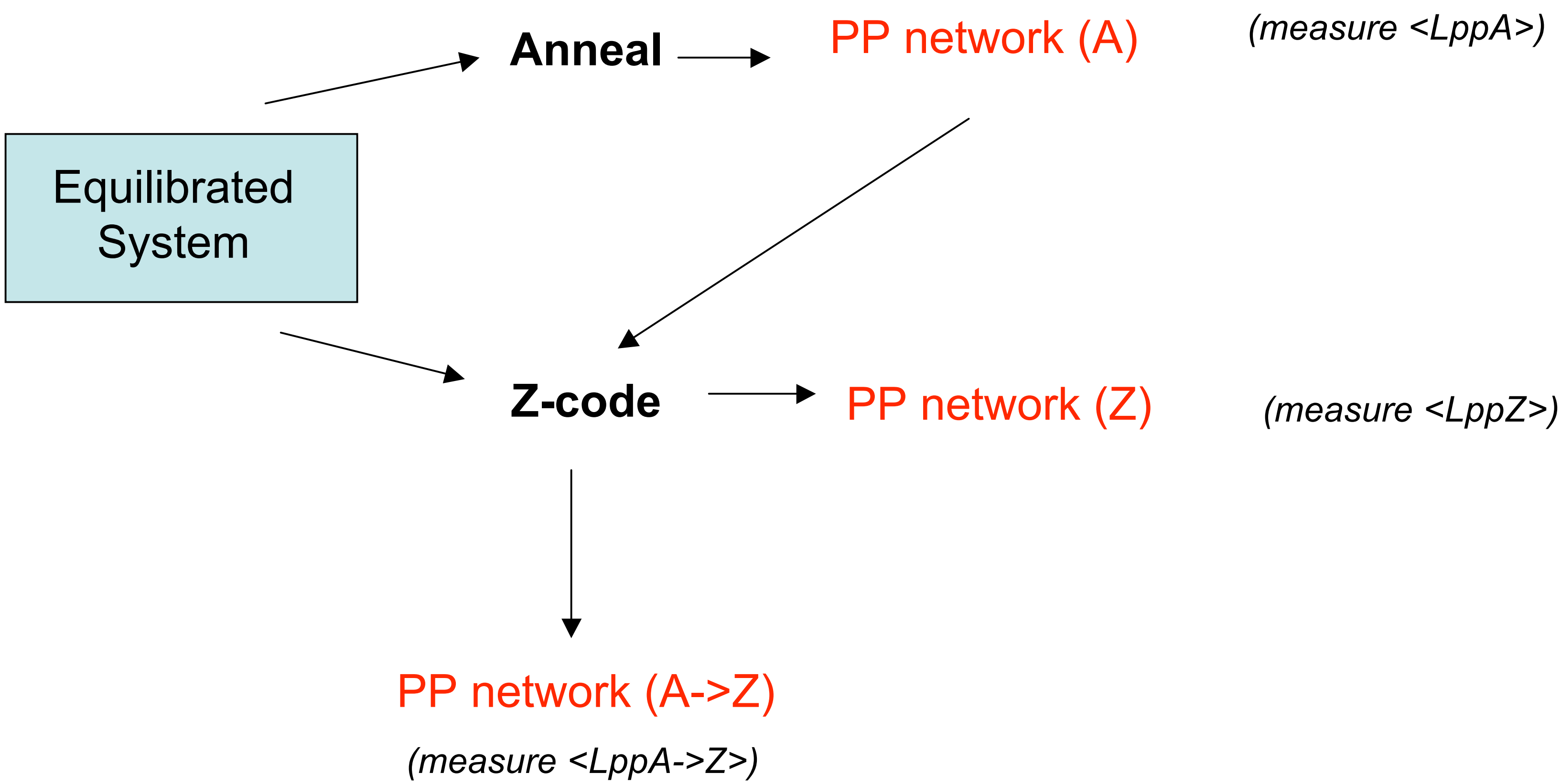
Computation time = 1 s (Kroger, 2005)

Overall Idea

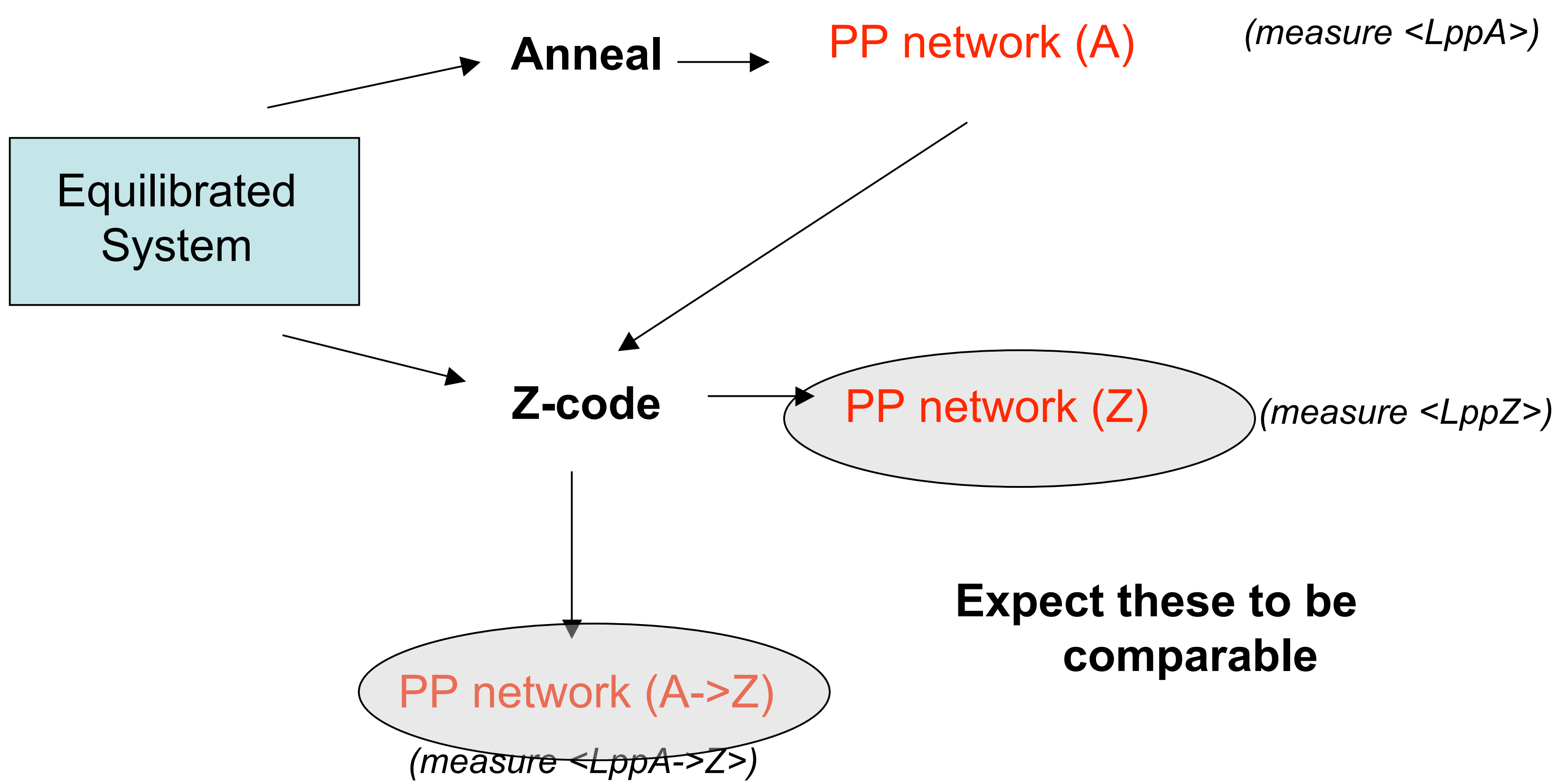


Since network A is on a lattice, while network Z is off-lattice: we expect <LppA> to be greater than <LppZ>

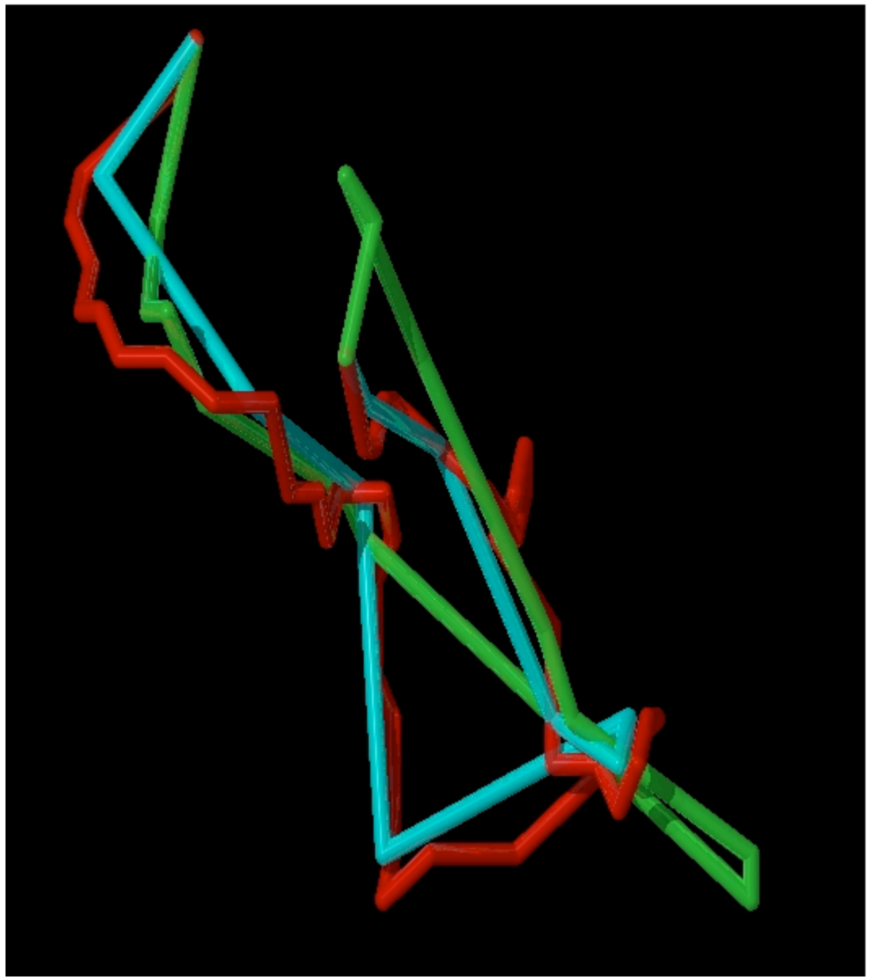
Overall Idea



Overall Idea



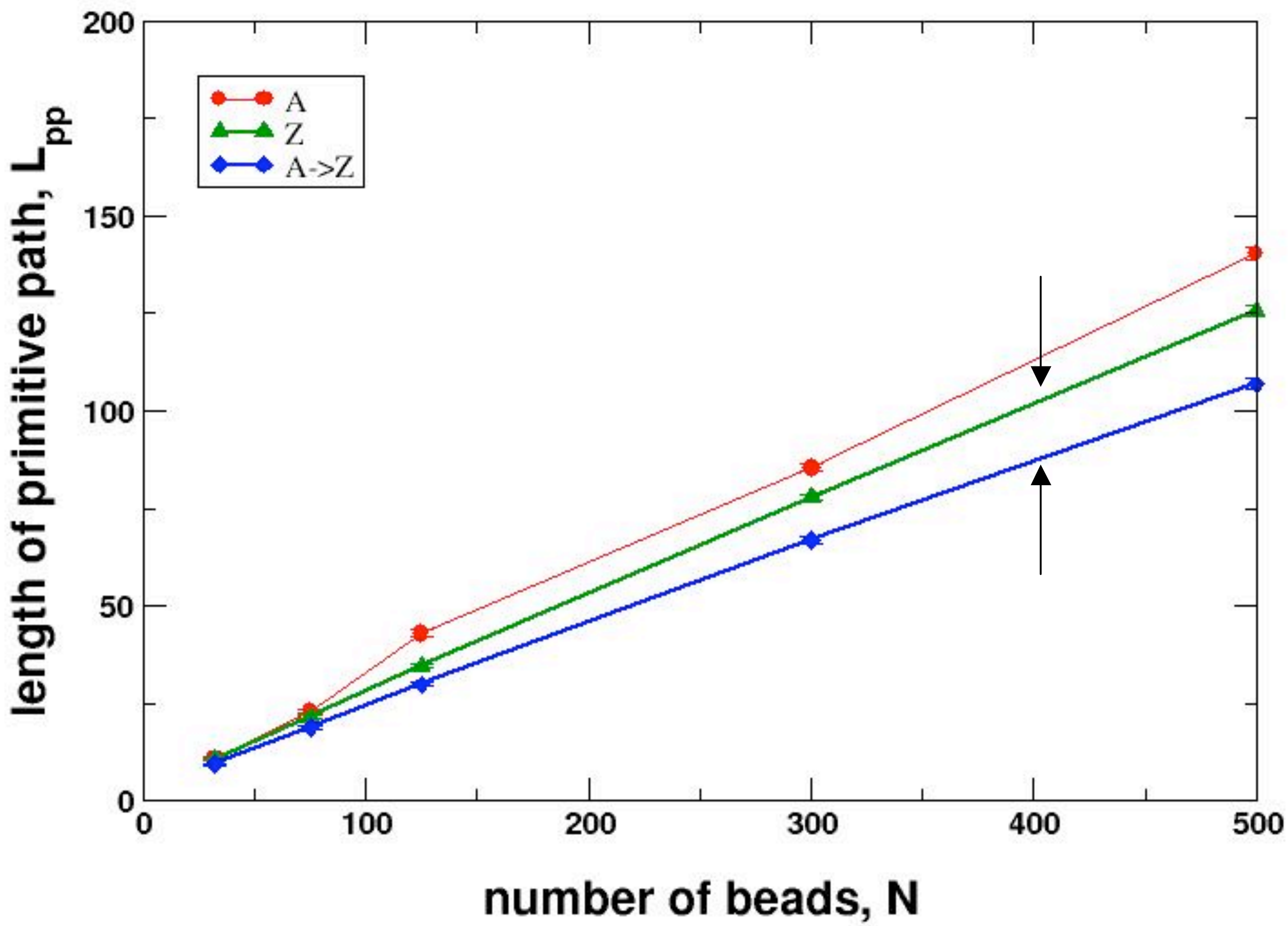
Results…



A (red); **Z** (green); **A->Z** (blue)

Shanbhag and Kroger, 2007

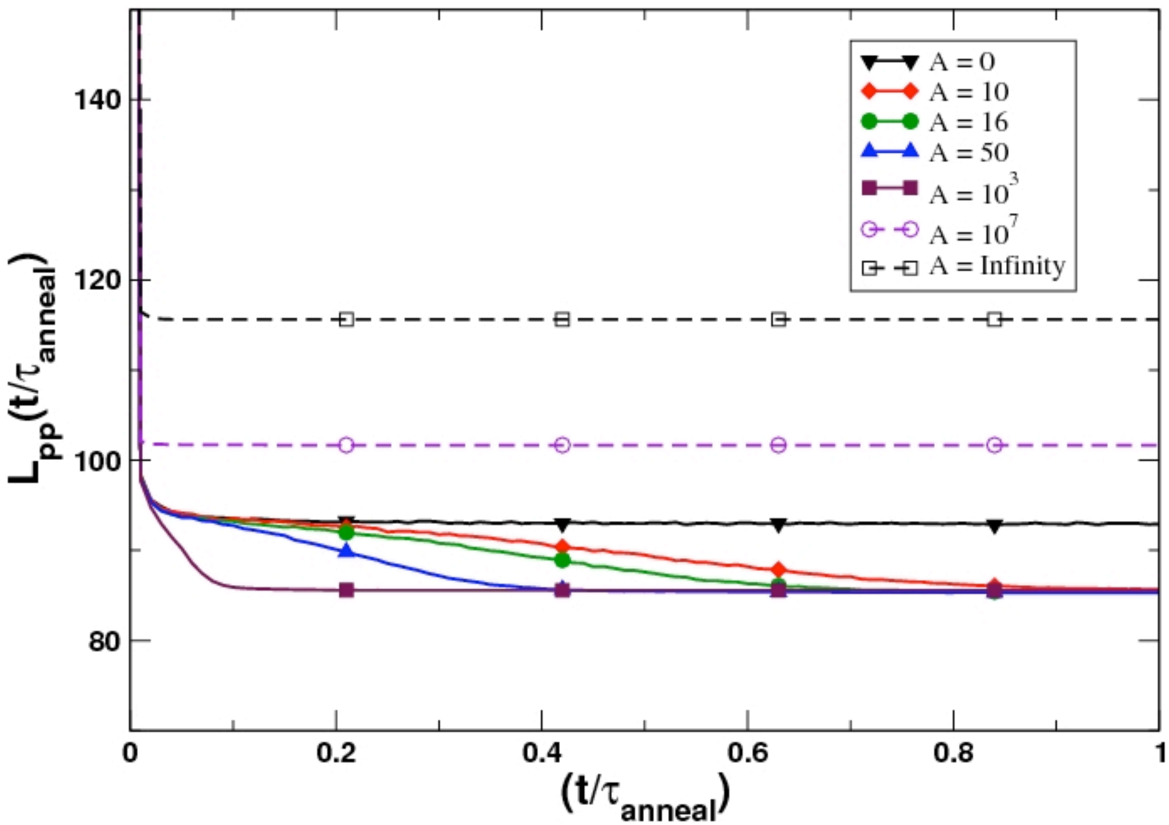
Results…



Lpp(A->Z) is 15% smaller than Lpp(Z), systematically.

Shanbhag and Kroger, 2007

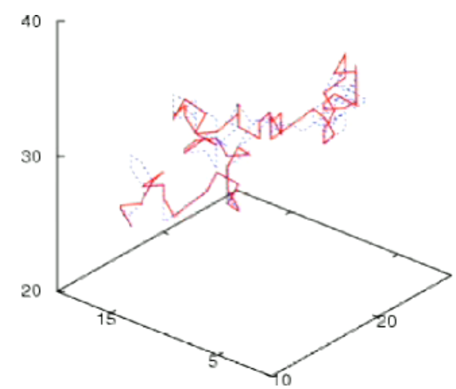
Annealing: Effect of "A" parameter



N=300; Lpp(t=0)=421; $t_A=5\tau_e$

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

Quenching leads to longer L_{pp} more entanglements?



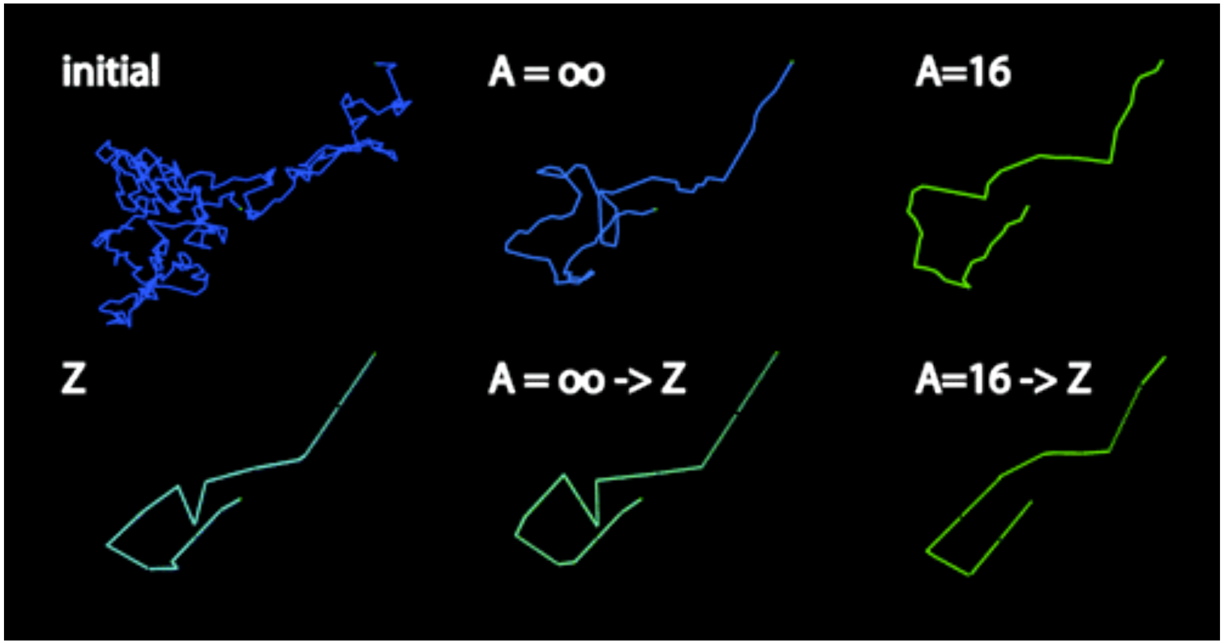
Shanbhag and Kroger, 2007

Annealing: Effect of "A" parameter

N=300; Lpp(t=0)=421;
representative sample

Shanbhag and Kroger, 2007

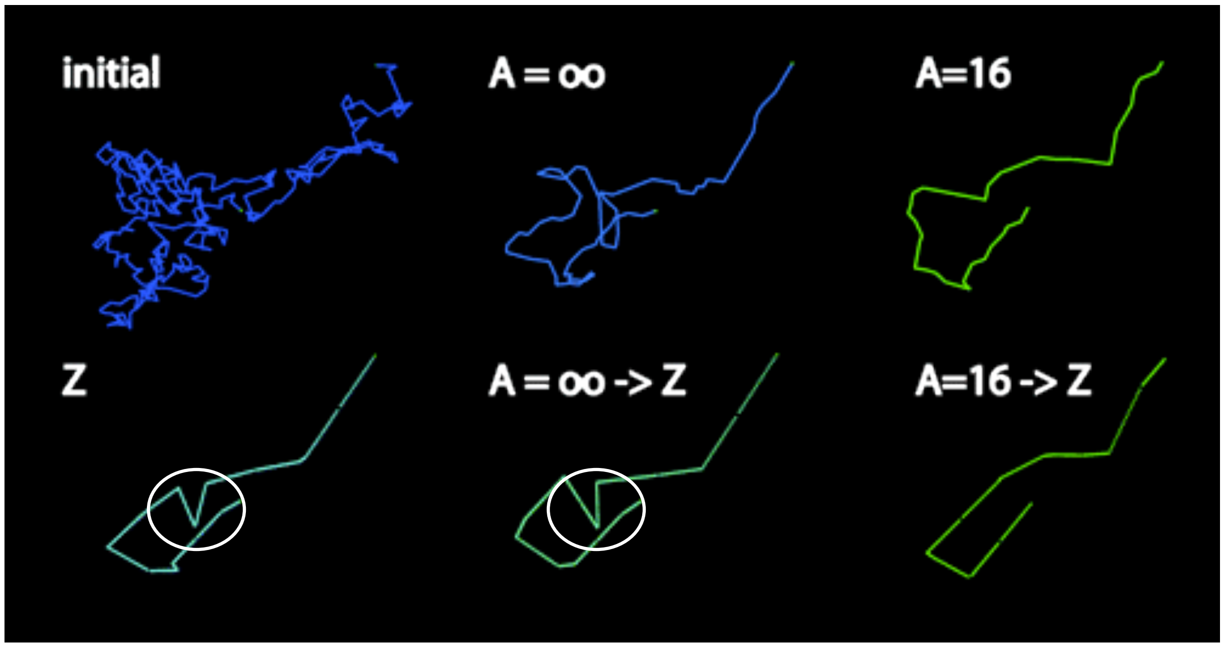
Annealing: Effect of “A” parameter



N=300; Lpp(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; Lpp(t=0)=421;
representative sample

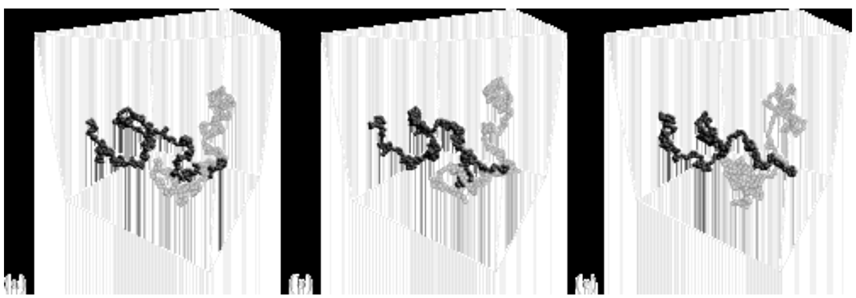
Shanbhag and Kroger, 2007

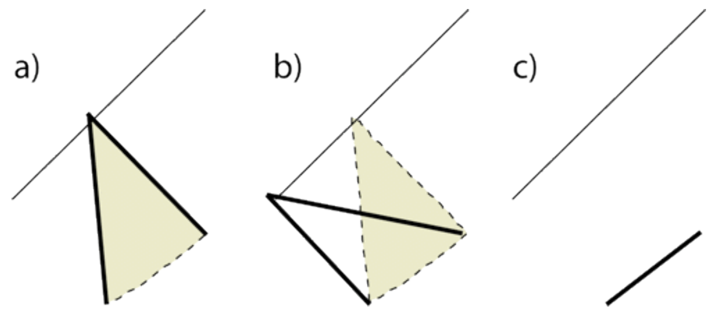
How are entanglements lost during annealing?

Constraint Release
by End Looping
(CR-EL)

Chain Slip

does not need slack



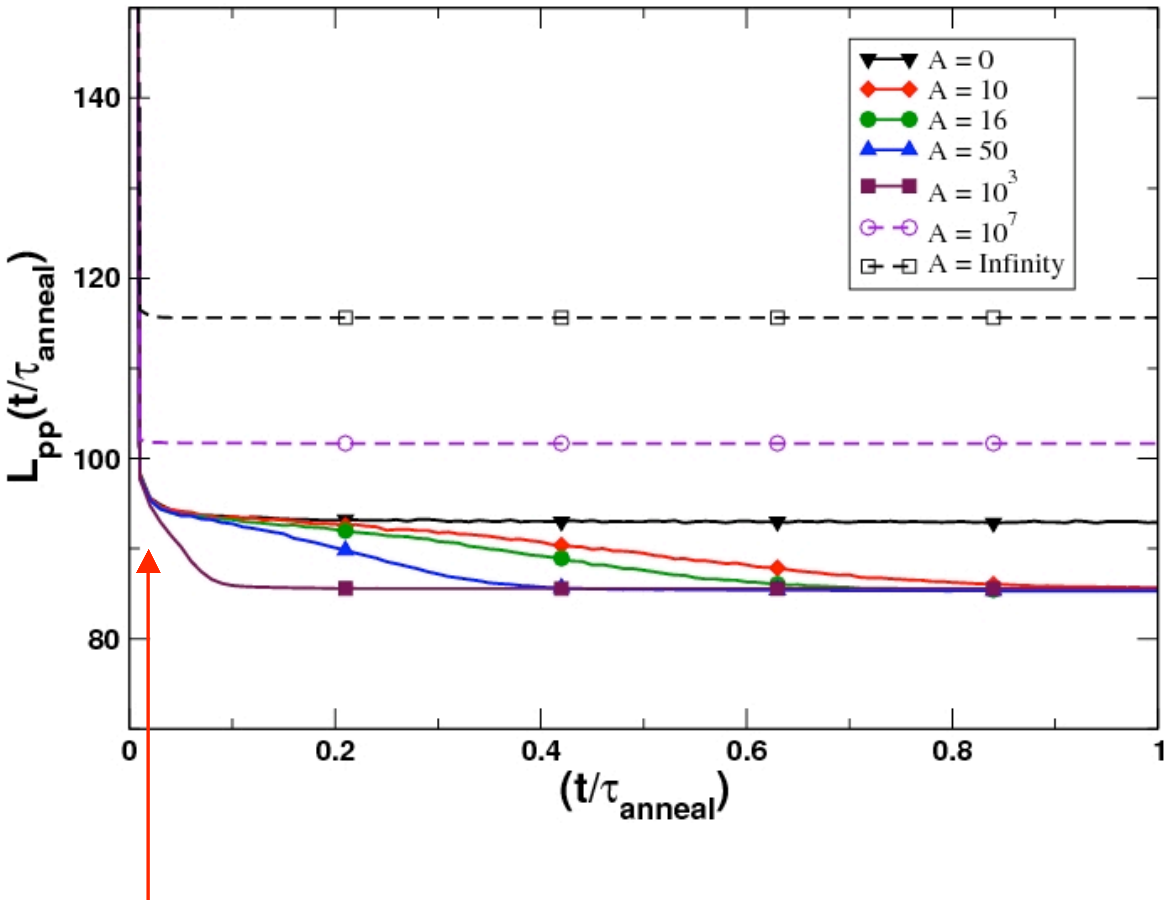


Needs chain slack and chain ends

out-of-secant area disentanglement

Zhou and Larson, 2006
Shanbhag and Kroger, 2007

End Looping



For A<1000, most of the slack is lost before t/t_{Al}=0.02, where,

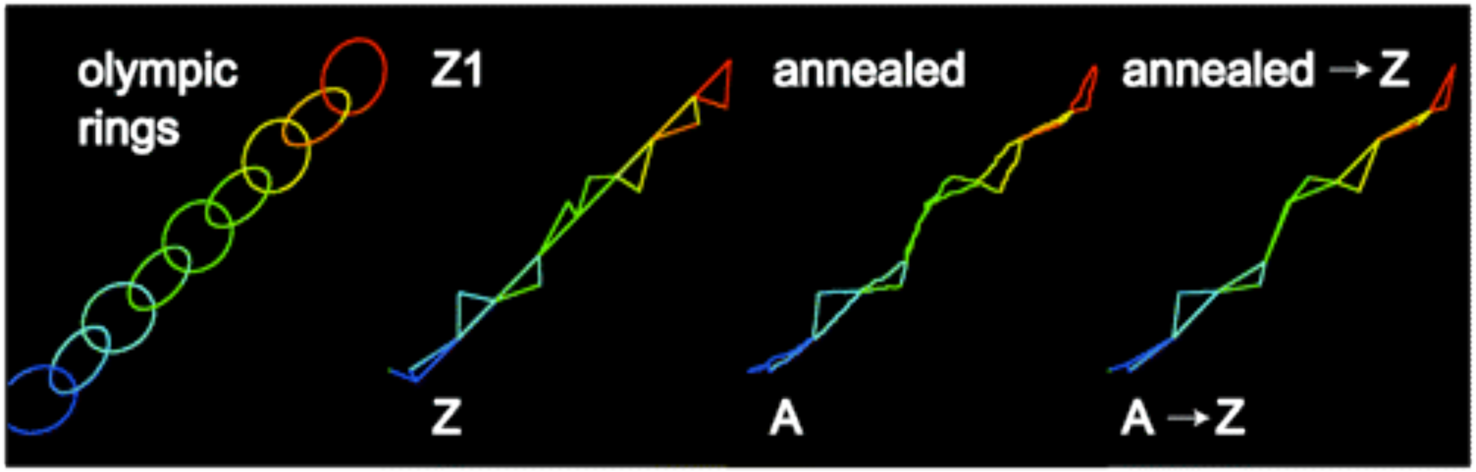
$$A(t/t_A)^2 << 1$$

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



Lpp=109 Lpp=106 Lpp=98

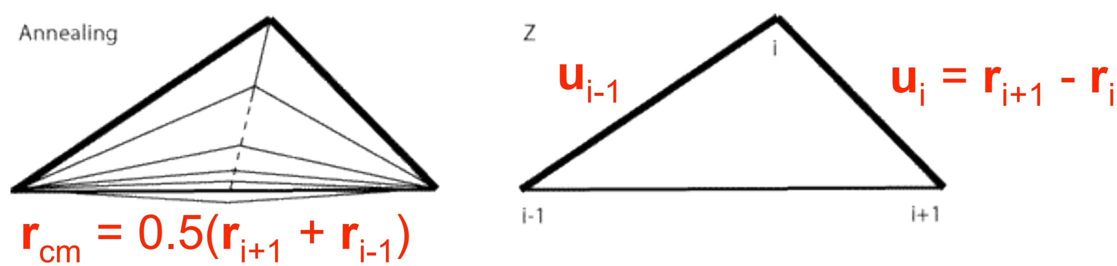
7.7% difference persists

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 -> infinity

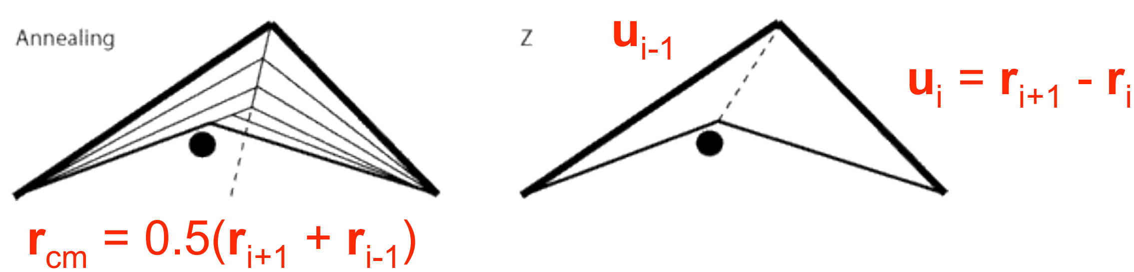


Quenching:

$\mathbf{F}_i = k(\mathbf{u}_i - \mathbf{u}_{i-1}) + \mathbf{F}_{EV}$

If $\mathbf{F}_{EV} = 0$, then $d\mathbf{r}_i/dt = (k/\zeta)\,(\mathbf{u}_i - \mathbf{u}_{i-1}) = (2k/\zeta)\,(\mathbf{r}_{cm} - \mathbf{r}_i)$

Limiting equivalence: Quenching and Z



Quenching:

If $\mathbf{F}_{EV}(\mathbf{r})$, is point-like and radially symmetric, with obstacle at $\mathbf{r}$

$d\mathbf{r}_i/dt = (2k/\zeta)\ (\mathbf{r}_{cm} - \mathbf{r}_i) + \mathbf{F}_{EV}(|\mathbf{r}_i - \mathbf{r}|)$

Stationary solution $\mathbf{r}_i$ is a point close to $\mathbf{r}$, that is attached to $\mathbf{r}_{cm}$ 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

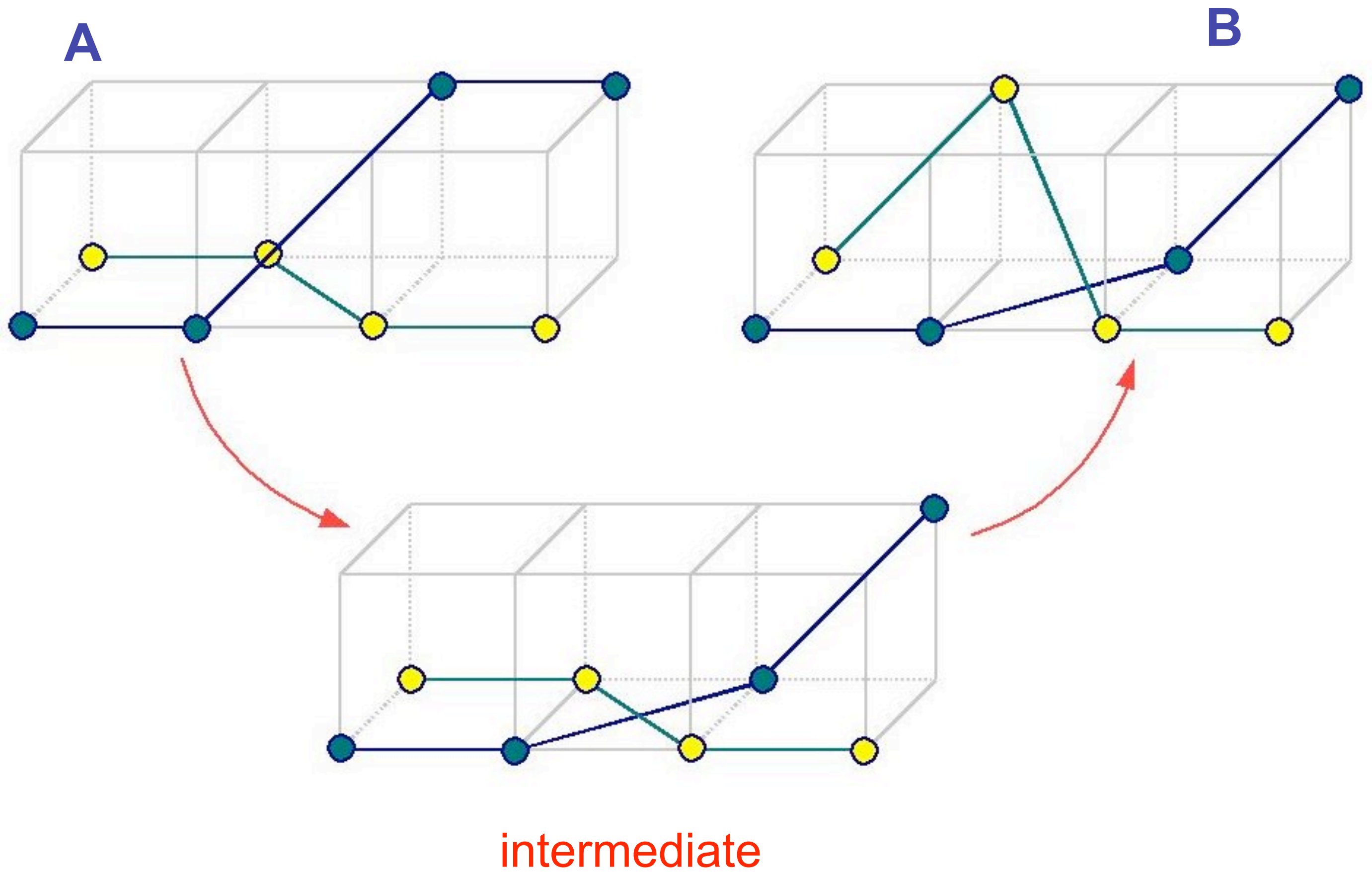
1. Annealing and Geometrical methods compared
2. Lpp(A->Z) < Lpp(Z) < Lpp(A)
3. About 15% difference between Lpp(A->Z) and Lpp(Z), due to loss of entanglements during annealing
4. Equivalence between quenching (in the limit of vanishing bead size) and geometrical methods demonstrated

Acknowledgements

- PRF and CRC-FYAP for funding

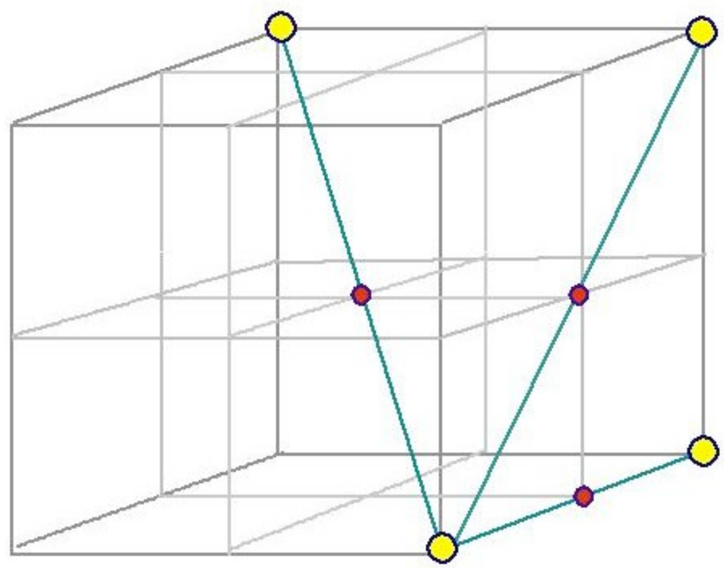
Chain Uncrossability…

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)