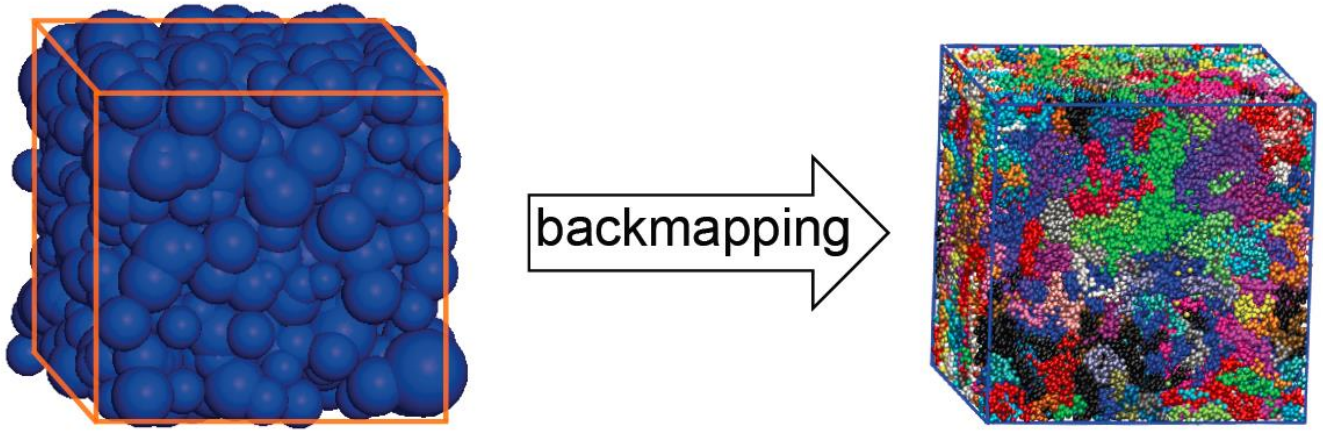
EQUILIBRATING HIGH MOLECULAR-WEIGHT POLYMER MELTS USING HIERARCHICAL STRATEGIES

Guojie Zhang, Takahiro Ohkuma, Hsiao-Ping Hsu, Torsten Stuehn, Kostas Daoulas, and Kurt Kremer



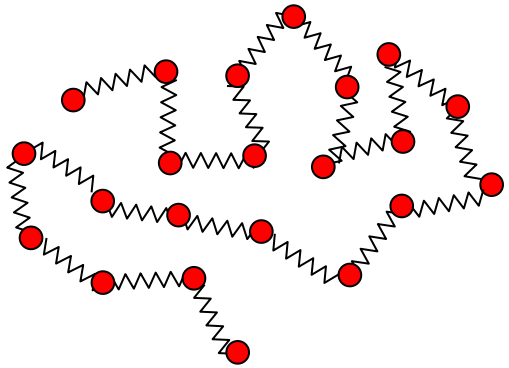
THEORY GROUP

OUTLINE

- Reminder: Rouse and reptation models. Why modeling polymer melts is challenging ?
- Hierarchical modeling of generic and chemistry-specific systems
- “Material genomic” approach to blob-based models
- Hierarchical modeling of multicomponent systems → symmetric blends
- Concluding comments

DYNAMICS IN MELTS OF SHORT POLYMERS: ROUSE MODEL

- Originally developed for dilute polymer solution



N monomers

- Assumption → solvent treated as immobile "background"
- Brownian motion of N linked beads

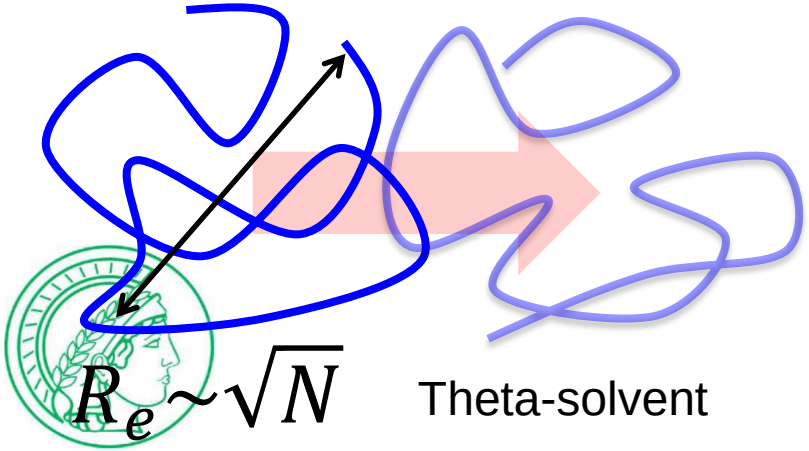
$$\zeta_R = N\zeta$$

friction coefficient of whole Rouse chain

$$D_R = \frac{kT}{N\zeta}$$

diffusion coefficient of whole Rouse chain

- Largest chain-relaxation time ~ chain must diffuse a length comparable to chain size



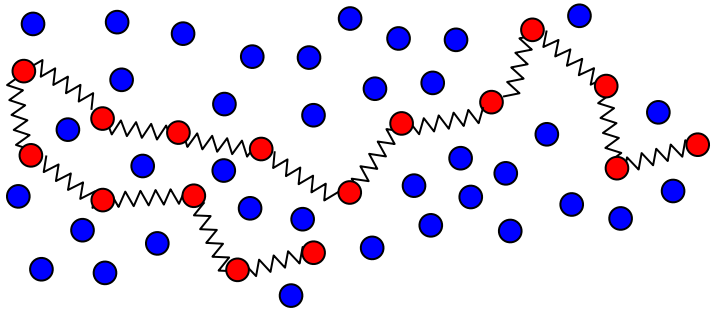
$R_e \sim \sqrt{N}$ Theta-solvent

$$R_e{}^2 \sim D_R \tau_R \Rightarrow \tau_R \sim \frac{\zeta N^2}{kT}$$

Rouse time

DYNAMICS IN MELTS OF SHORT POLYMERS: ROUSE MODEL

- Rouse model neglects hydrodynamic interactions →
  Long-range forces arising from motion of one particle



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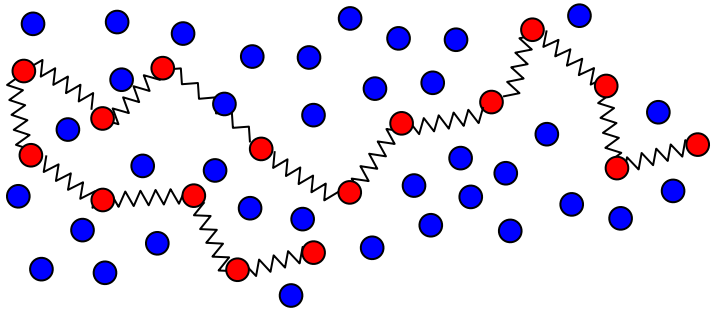


- For dilute solutions Zimm model is appropriate
- In melts of short polymers hydrodynamic interactions are screened and Rouse model becomes valid
- To remember from Rouse model

$$\tau_R \sim \frac{\zeta N^2}{kT} \qquad D_R = \frac{kT}{N\zeta}$$

See also:

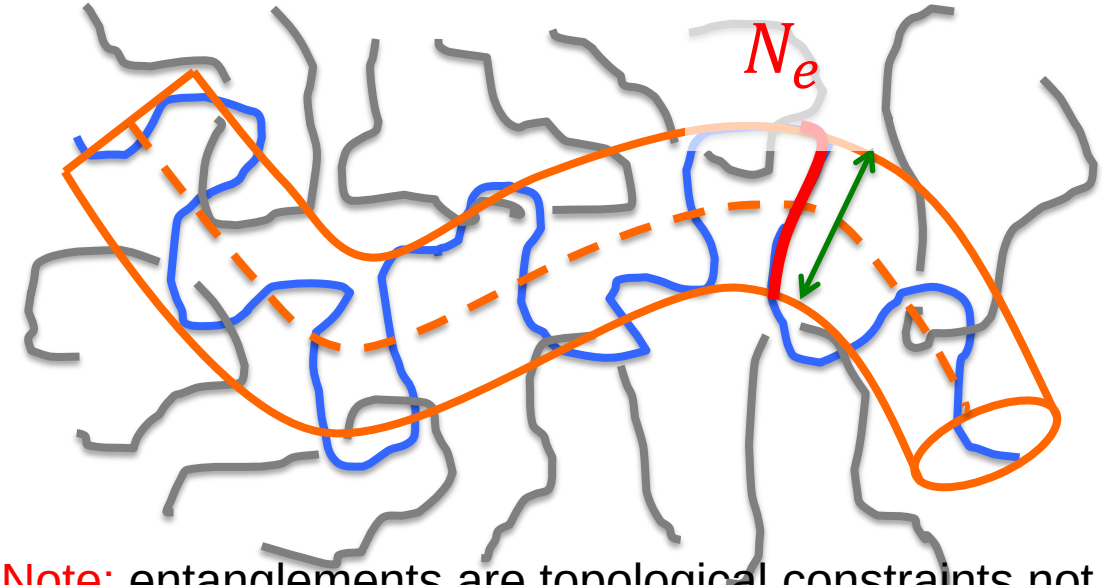
Doi & Edwards, The Theory of Polymer Dynamics 1986

Grosberg & Khokhlov,
Statistical Physics of Macromolecules 1997

Rubinstein & Colby, Polymer Physics 2003

DYNAMICS IN MELTS OF LONG POLYMERS: REPTATION MODEL

- Topological entanglements create an effective tube
- Chain motion on large length scales corresponds to 1D reptation along tube-axis

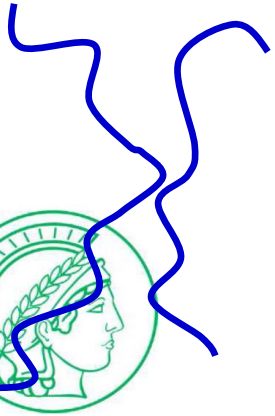


Presentation follows:

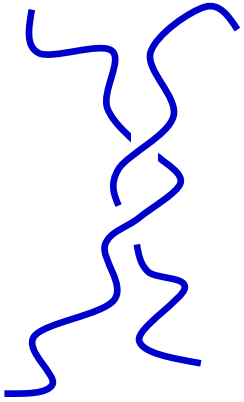
Grosberg & Khokhlov, Statistical Physics of Macromolecules 1997

- Note: entanglements are topological constraints not just monomer / monomer contacts

Contact not entangled



Contact entangled



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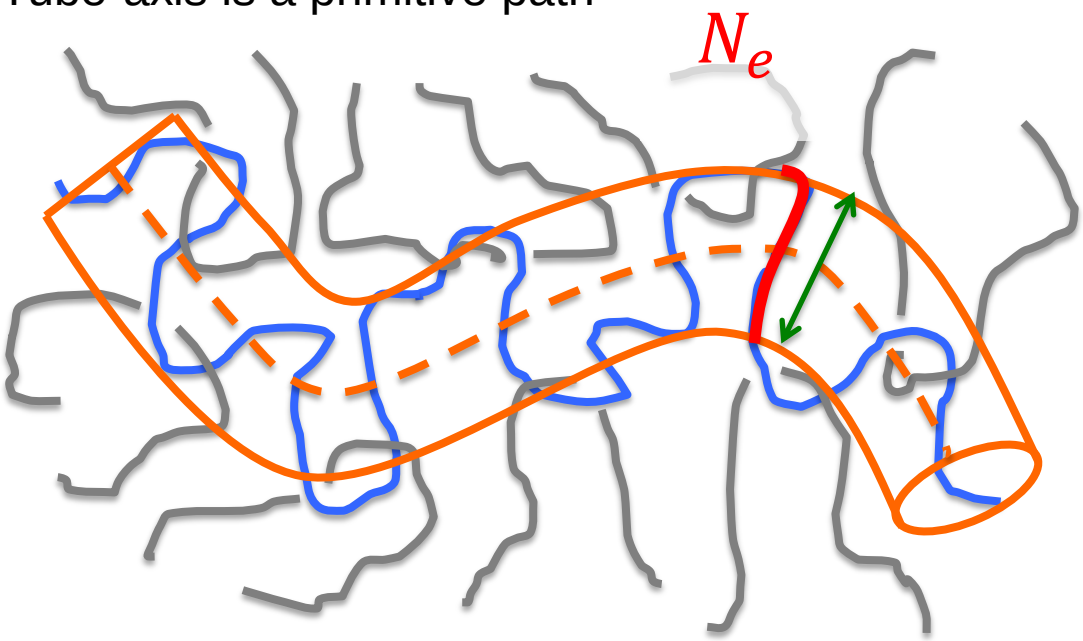
DYNAMICS IN MELTS OF LONG POLYMERS: REPTATION MODEL

- Tube-axis is a primitive path



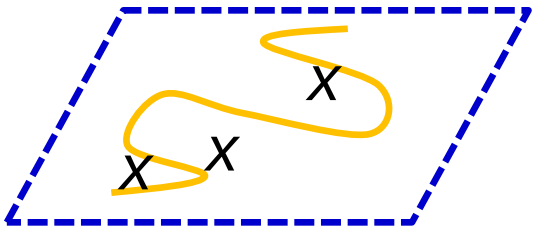
Tube diameter: $d \sim \sqrt{N_e}$

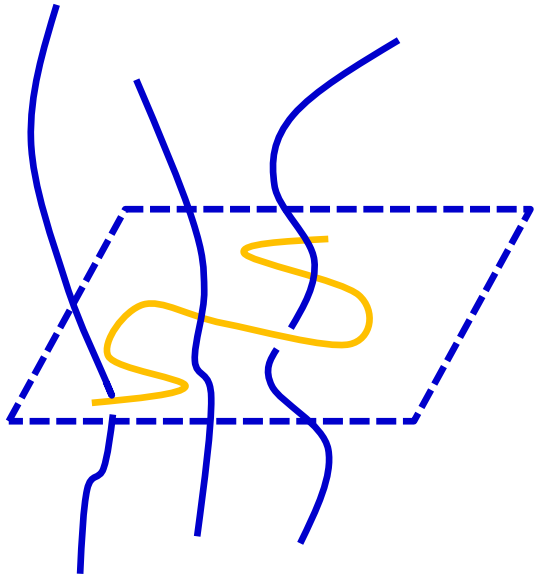
Presentation follows:

Grosberg & Khokhlov, Statistical Physics of Macromolecules 1997

- Primitive path:

Shortest line between chain-ends which preserves the chain-topology with respect to surrounding chains





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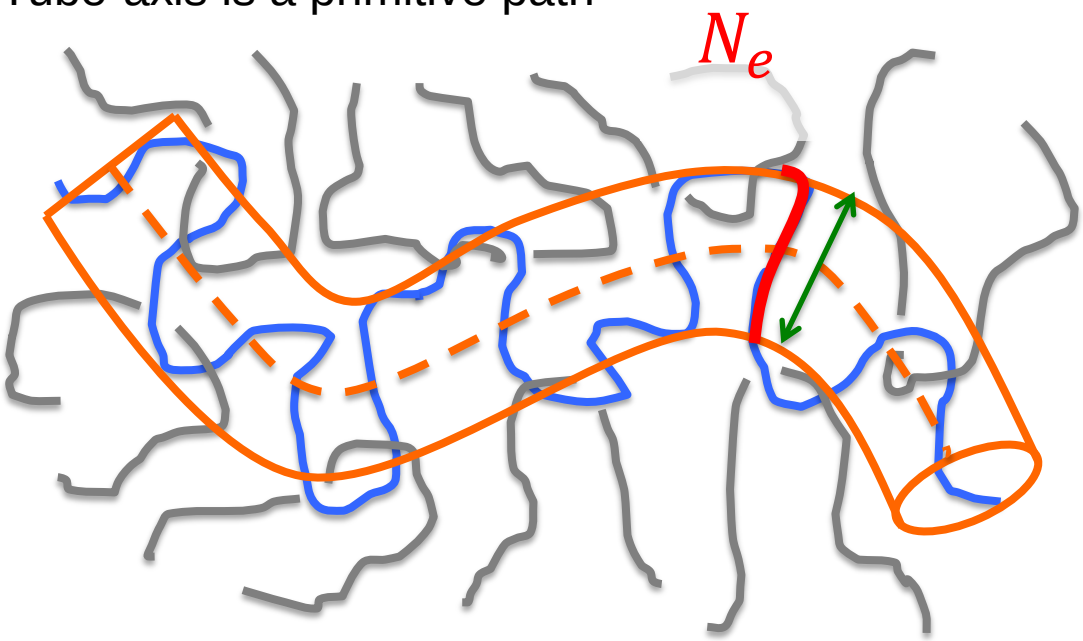

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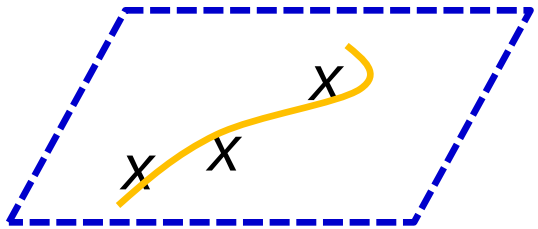
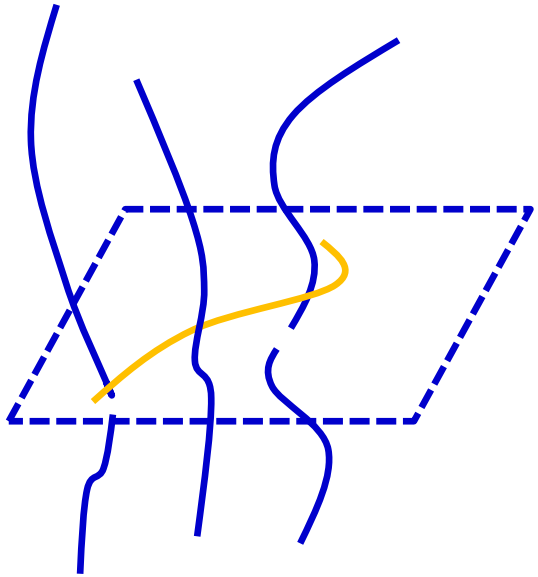
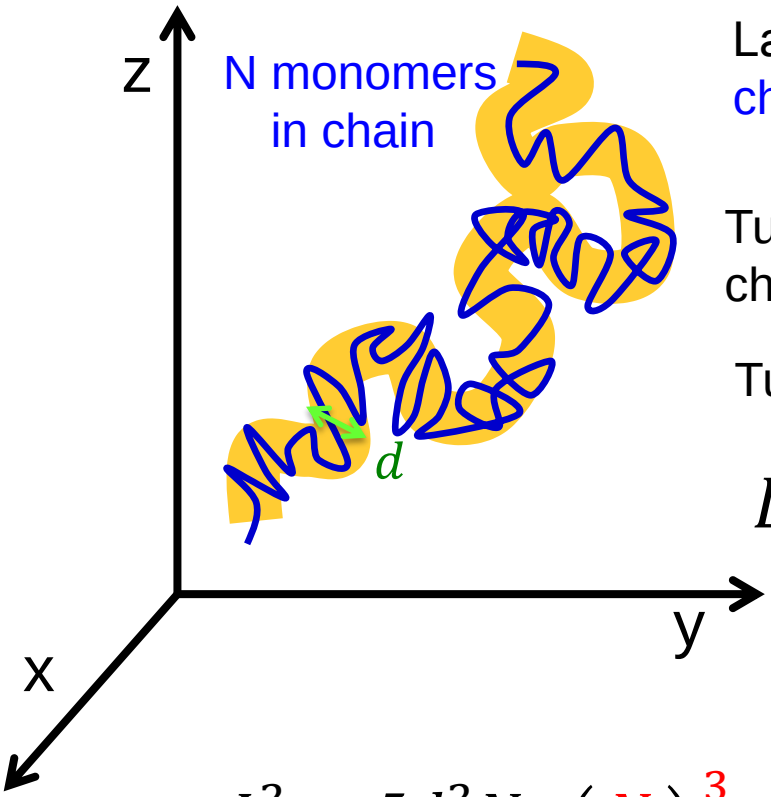


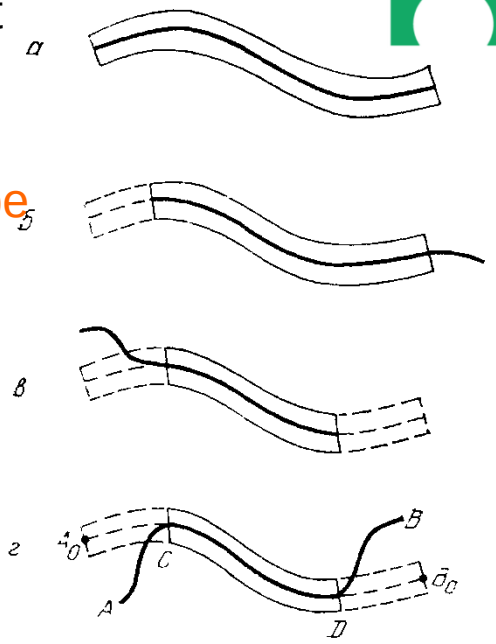


DYNAMICS IN MELTS OF LONG POLYMERS: REPTATION MODEL

- Simple estimations of relaxation time and diffusion coefficient



Largest relaxation time → chain reptates out of the tube



Tube is a random walk
characteristic scale d

Tube contour length

$$L = d\frac{N}{N_e}$$

1D diffusion coefficient along tube $D_t = \frac{kT}{\zeta N}$

$$\tau = \frac{L^2}{D_t} = \frac{\zeta d^2 N_e}{kT}\left(\frac{N}{N_e}\right)^3 \sim \frac{\zeta N_e^2}{kT}\left(\frac{N}{N_e}\right)^3$$

Rouse time of entanglement strand $\tau_e \sim \frac{\zeta N_e^2}{kT}$

3D diffusion coefficient $D = \frac{\langle R^2 \rangle}{t} = \frac{1}{\tau}\frac{N}{N_e}d^2 = \frac{N_e}{N^2}\frac{kT}{\zeta}$

STUDYING HIGH-MOLECULAR POLYMER MELTS IS CHALLENGING AND IMPORTANT

- Equilibrating melts of long polymers described with microscopic detail is challenging:

Largest relaxation time: $\tau \sim \tau_e \left(\frac{N}{N_e}\right)^3$ Chain diffusion: $D = \frac{N_e}{N^2}\frac{kT}{\zeta}$

- Modeling high-molecular weight polymers is crucial for industry where $\frac{N}{N_e} \sim 100$

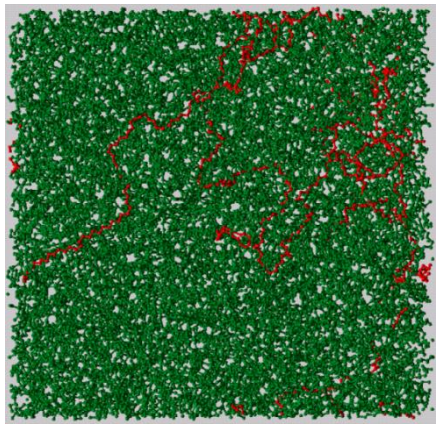
Example:
Processing requires detailed understanding of polymer dynamics and rheology

Classical and modern applications,
e.g. printing polymer inks with useful optical and electronic properties

STRATEGIES FOR EQUILIBRATING LONG POLYMER MELTS

❑ Single-scale techniques:

- Re-bridging Monte Carlo moves

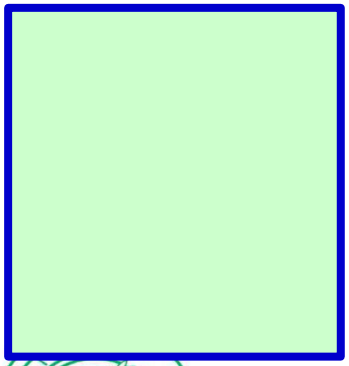


PE melts:
32 chains, C6000

Uhlherr et al,
Europhys. Lett. 2002

Pant & Theodorou, *Macromolecules* 1995

- Configuration assembly procedures



Bead spring melts:
320 chains N = 3500

Hou et al,
Phys. Rev. Lett. 2010

Auhl et al, *J. Chem. Phys.* 2003

❑ Multiscale techniques:

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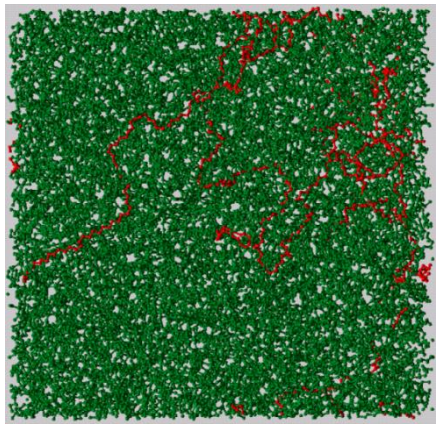

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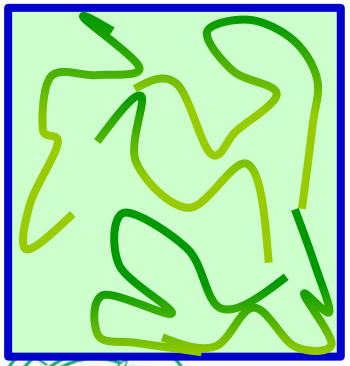

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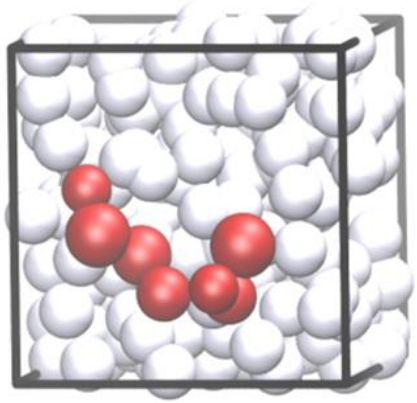

blob model

- Opportunities:

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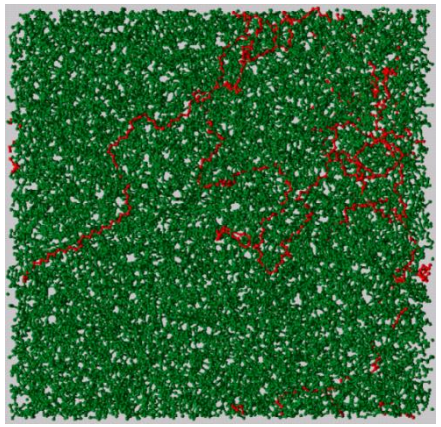

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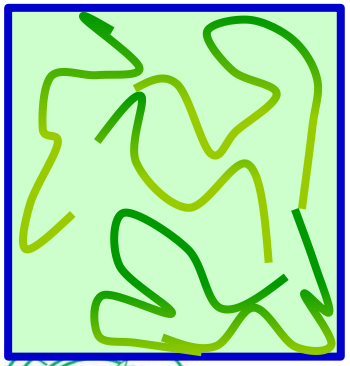

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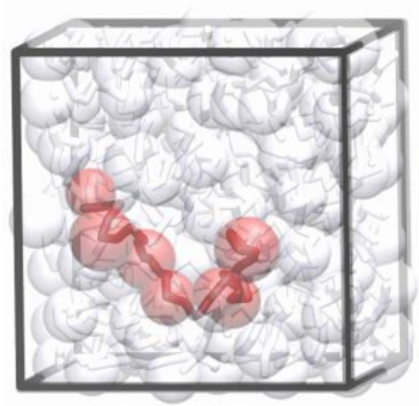

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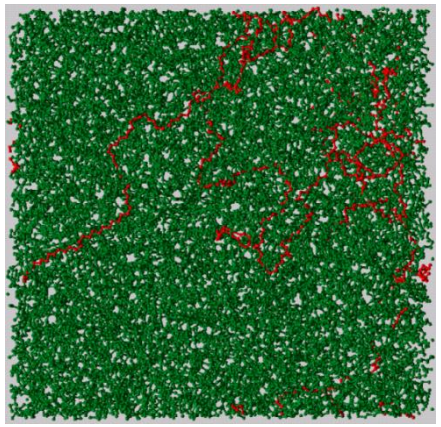

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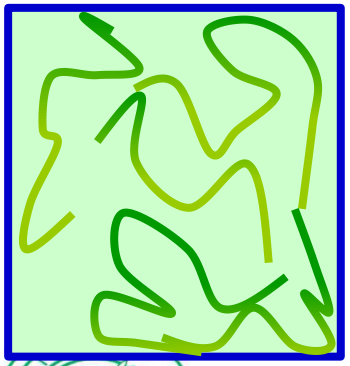

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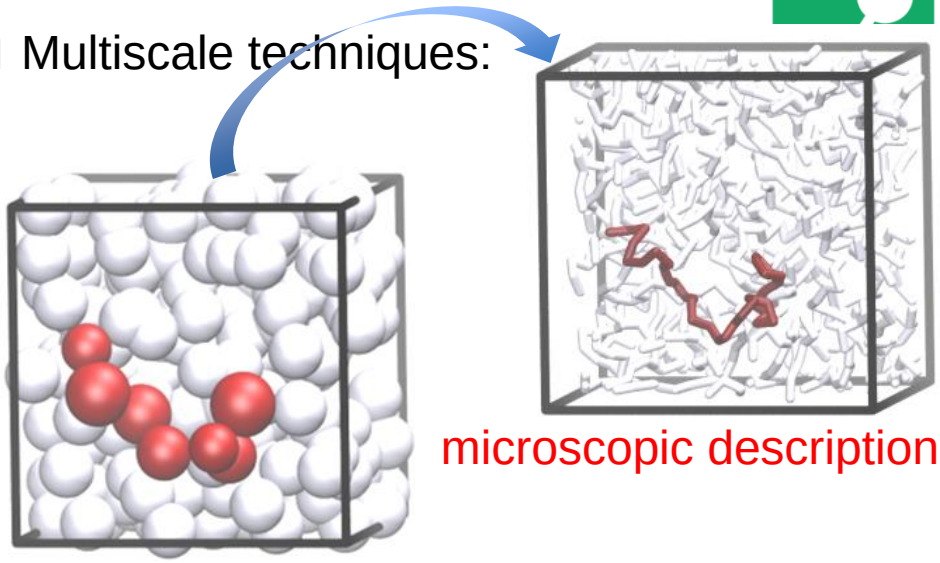

microscopic description

- Opportunities:
  - Equilibrate samples of unprecedented size / chain length

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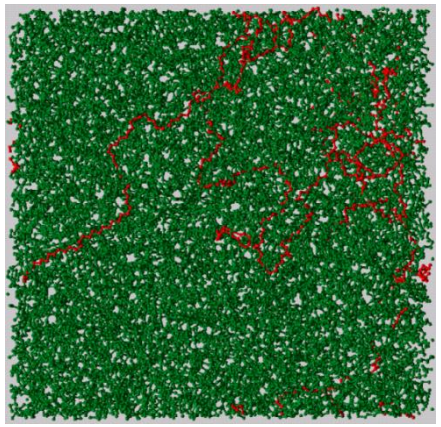

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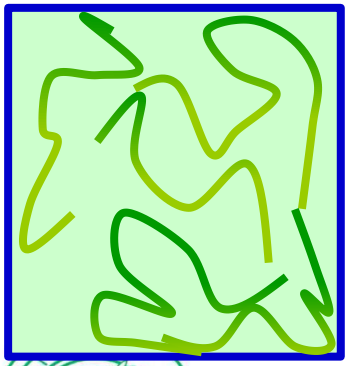

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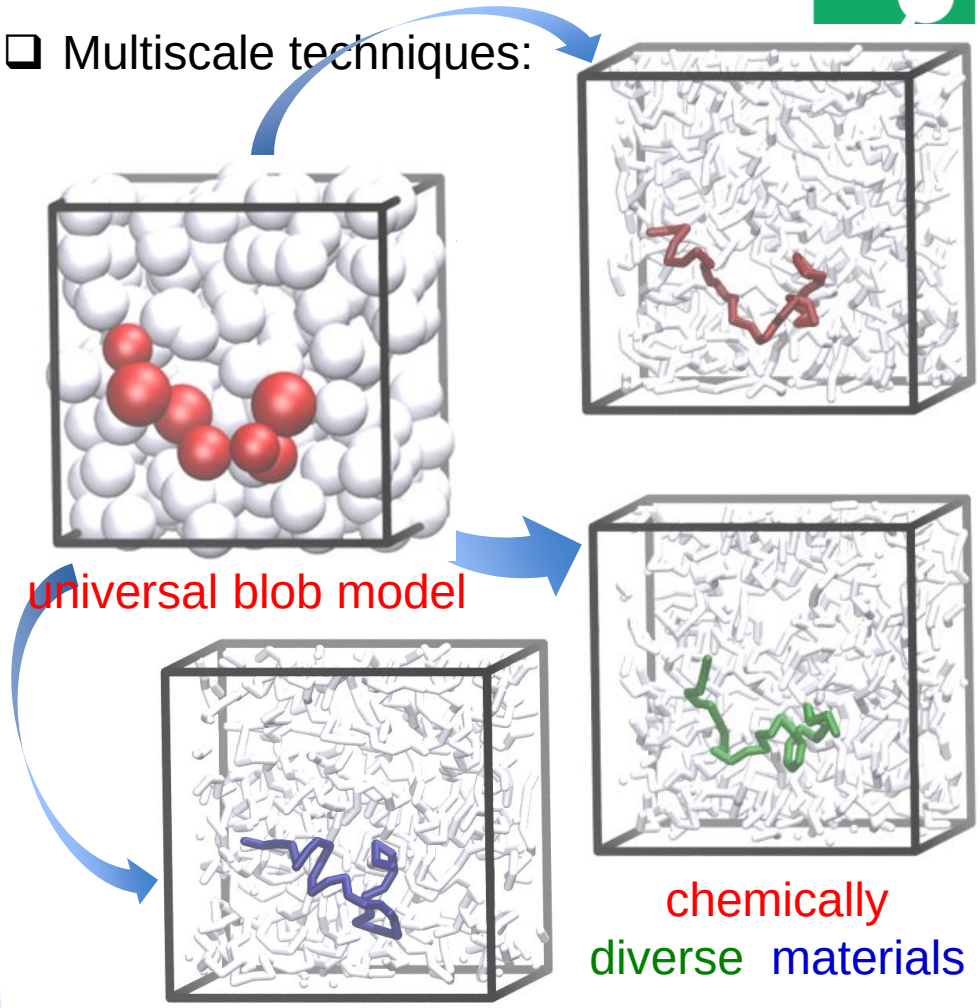
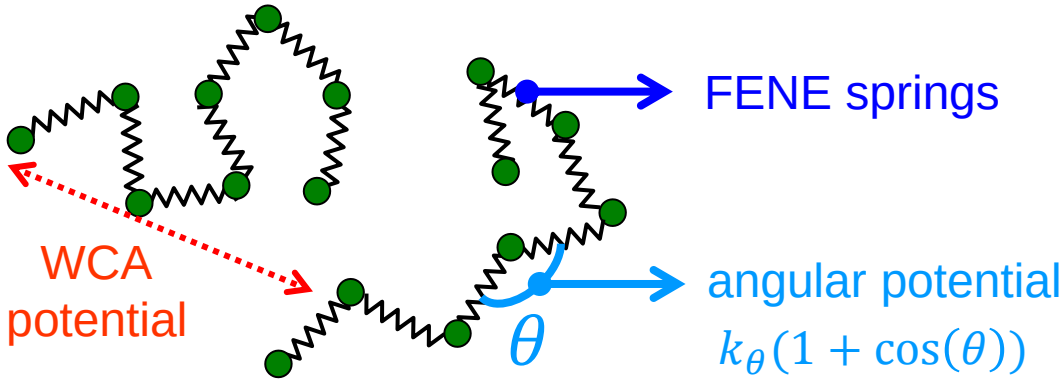
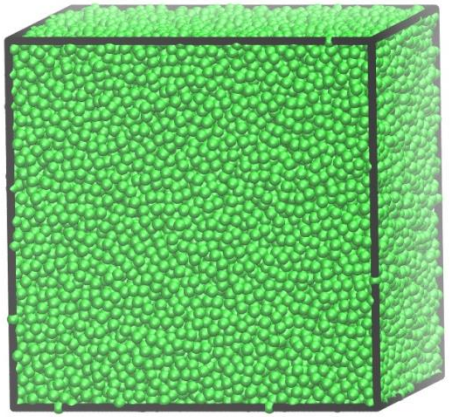


- Opportunities:
  - Equilibrate samples of unprecedented size / chain length
  - Benefit from universality: "materials genomic" strategies

MICROSCOPIC DESCRIPTIONS OF MELTS

❑ **Generic**:





standard monomer density

$\sigma_o{}^3\rho = 0.85$

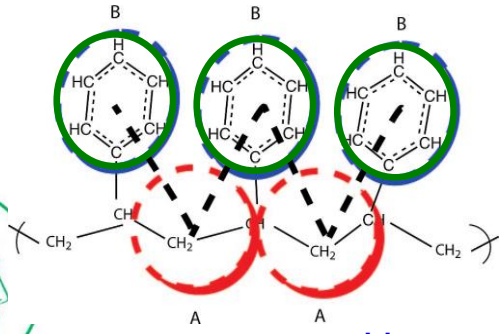
Kremer & Grest, *J. Chem. Phys.* 1990

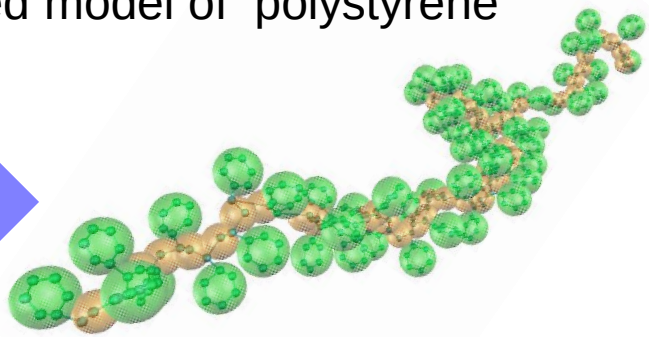
- Model represents key features of real melts:

  → Strong covalent bonds, hard excluded volume, high density

- Tool for understanding fundamentals of polymer physics, especially rheology

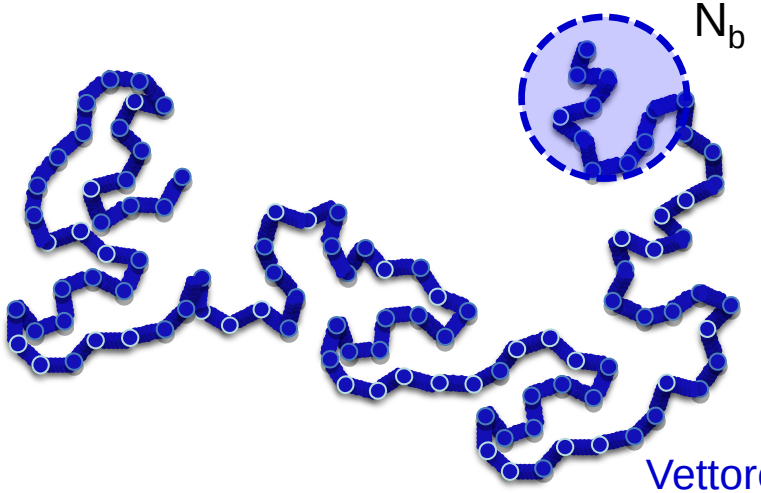
❑ **Chemistry specific:** moderately coarse-grained model of polystyrene



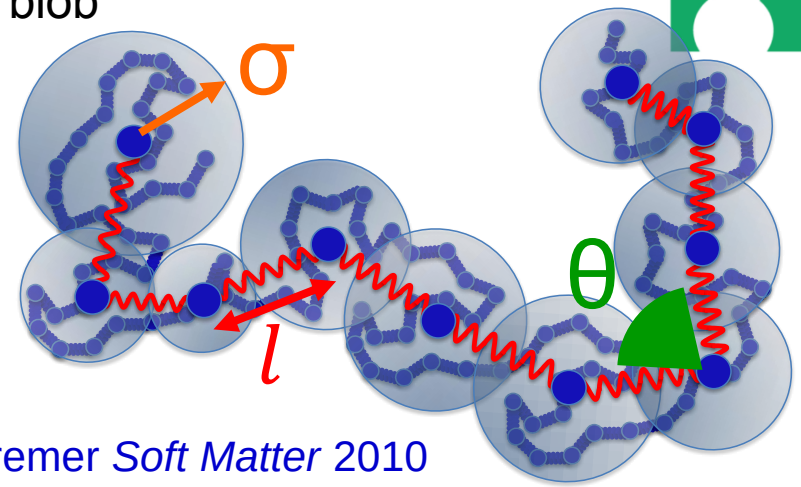


Harmandaris et al, *Macromol. Chem. Phys.* 2007; Macromolecules 2009

MAPPING MICROSCOPIC MODELS ON BLOB REPRESENTATIONS



N_b beads → one blob



Vettorel, Besold, & Kremer *Soft Matter* 2010

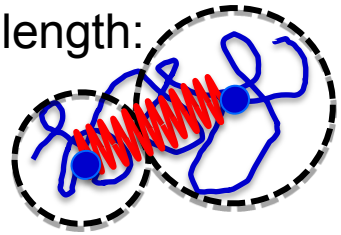
❑ Blob size:

$$U_{sp} = a_1 \frac{N_b}{\sigma^3}^2 + a_2 \frac{\sigma^2}{N_b}$$

$\left(\frac{N_b}{\sigma^3}\right)^2 \sigma^3$ repulsive excluded volume interaction

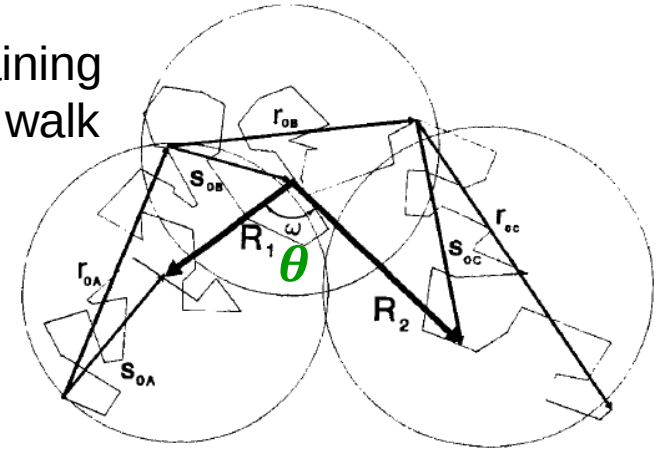
$\frac{\sigma^2}{N_b}$ entropic cost of stretching the sub-chain

❑ "Bond" length:

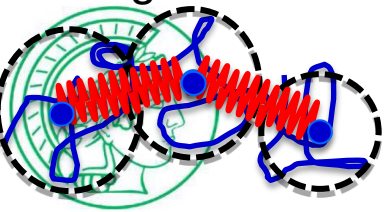


$$U_{bond} = \frac{k_{bond} l^2}{2}$$

coarse-graining a random walk



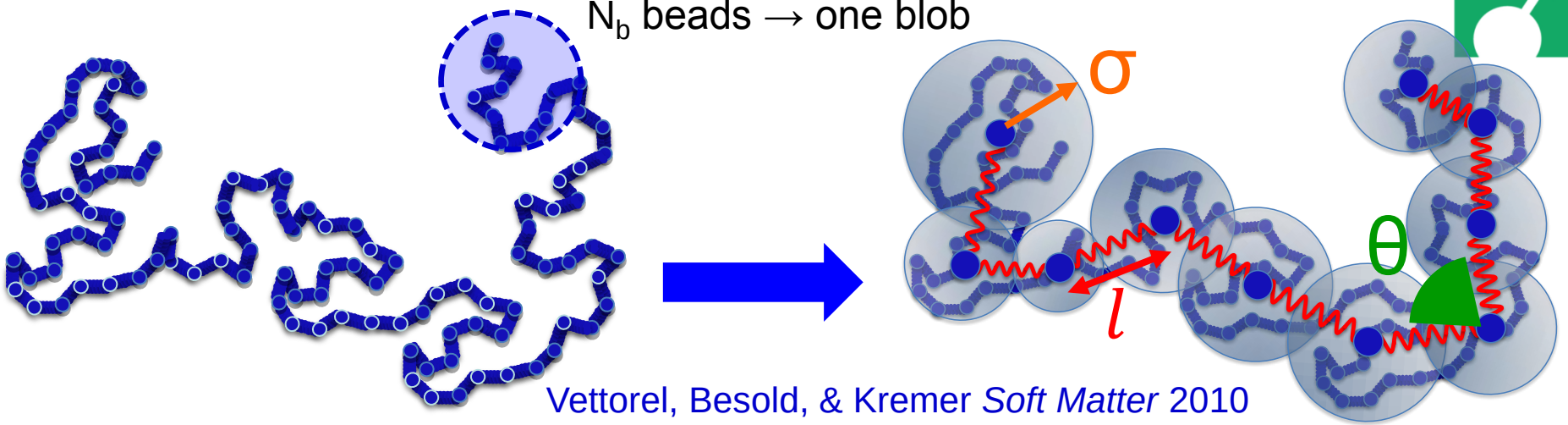
❑ Angular correlation:



$$U_{ang} = k_\theta(1 + \cos(\theta))$$

Laso et al, *J. Chem. Phys.* 1991

MAPPING MICROSCOPIC MODELS ON BLOB REPRESENTATIONS

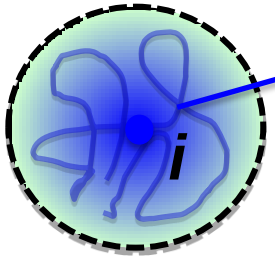


Vettorel, Besold, & Kremer *Soft Matter* 2010

❑ Blob size:

$$U_{sp} = a_1 \frac{N_b{}^2}{\sigma^3} + a_2 \frac{\sigma^2}{N_b}$$

❑ Each blob assigned:



Gaussian density cloud $\rho_i(\mathbf{r})$ of variance σ

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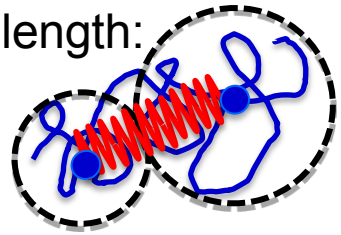
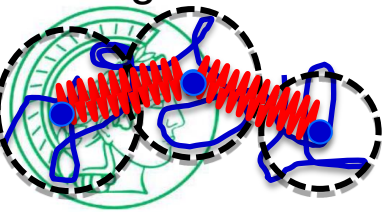


$$U_{bond} = \frac{k_{bond} l^2}{2}$$

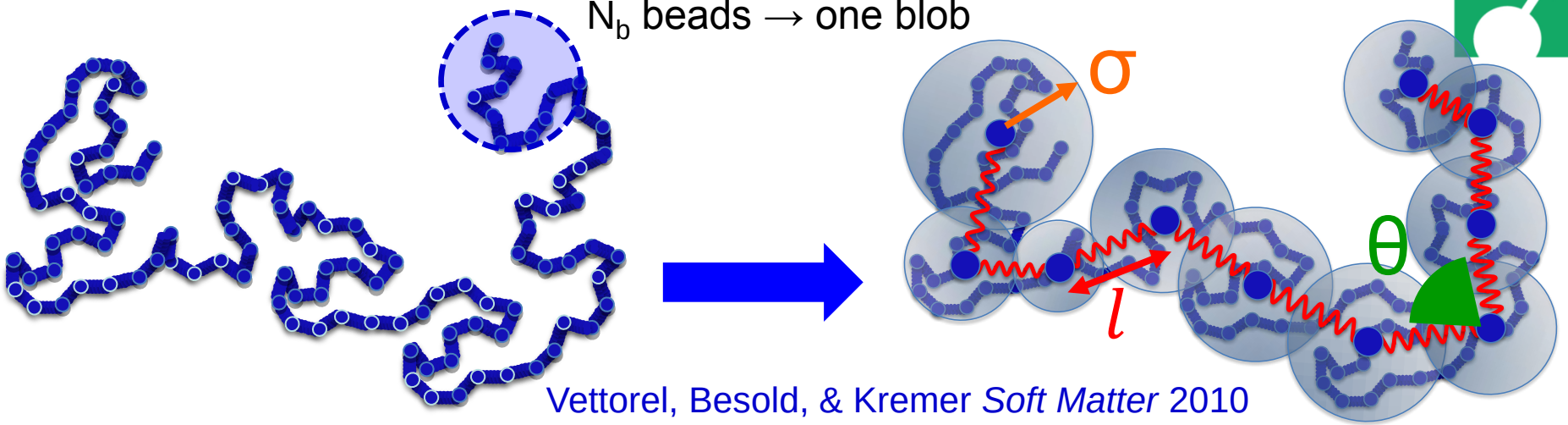
❑ Angular correlation:



$$U_{ang} = k_\theta (1 + \cos(\boldsymbol{\theta}))$$

Laso et al, *J. Chem. Phys.* 1991

MAPPING MICROSCOPIC MODELS ON BLOB REPRESENTATIONS

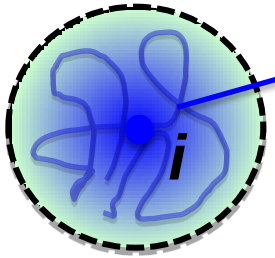


Vettorel, Besold, & Kremer *Soft Matter* 2010

❑ Blob size:

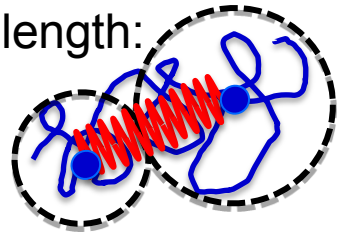
$$U_{sp} = a_1 \frac{N_b{}^2}{\sigma^3} + a_2 \frac{\sigma^2}{N_b}$$

❑ Each blob assigned:



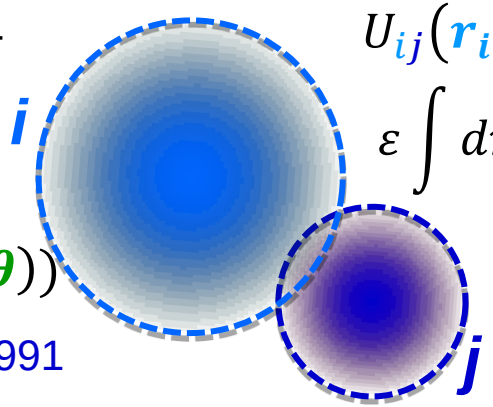
Gaussian density cloud $\rho_i(\mathbf{r})$ of variance σ

❑ "Bond" length:



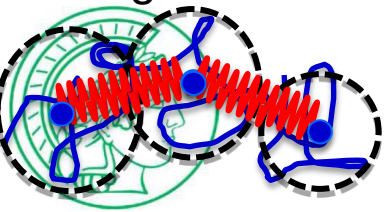
$$U_{bond} = \frac{k_{bond} l^2}{2}$$

❑ Repulsion of two blobs:



$$U_{ij}(\boldsymbol{r_i} - \boldsymbol{r_j}) = \varepsilon \int d\boldsymbol{r} \rho_i(\boldsymbol{r_i} - \boldsymbol{r}) \rho_j(\boldsymbol{r_j} - \boldsymbol{r})$$

❑ Angular correlation:



$$U_{ang} = k_\theta(1 + \cos(\boldsymbol{\theta}))$$

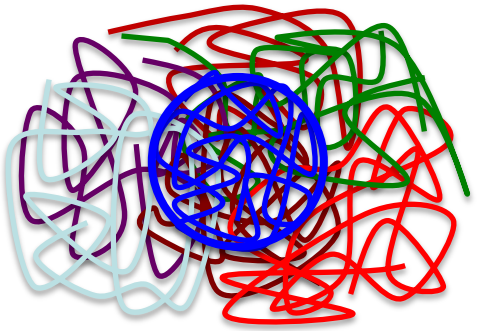
Laso et al, *J. Chem. Phys.* 1991

EFFICIENT MONTE CARLO METHOD FOR BLOB-BASED MODELS

❑ Blob-based models can be considered with standard techniques

- Monte Carlo using: U_{sp}, U_{bond}, U_{ang}, and U_{ij}

However: Higher molecular weights → more "drastic" coarse-graining → larger N_b



- Number of interacting soft spheres increases

$$\sqrt{\overline{N}} = \frac{n_{subchains}}{V} R^3_{\substack{sub \\ chains}} \sim \rho_o \sqrt{N_b}$$

→ more interacting neighbors → less efficiency !!!

❑ Rewriting non-bonded interactions as a functional of collective variables allows for an efficient simulation scheme without neighbor-lists

- Collective variables:

$$\hat{\varphi}(\mathbf{r}) = \sum_{i=1}^{all\ spheres} \rho_i(\mathbf{r})$$

$$\hat{\psi}(\mathbf{r}) = \sqrt{\sum_{i=1}^{all\ spheres} \rho_i^2(\mathbf{r})}$$

- Non-bonded interactions:

$$H_{nb} = \frac{1}{2} \sum_{i=1}^{\substack{all \\ spheres}} \sum_{j=1}^{\substack{all \\ spheres}} U_{ij}(\boldsymbol{r_i} - \boldsymbol{r_j})$$

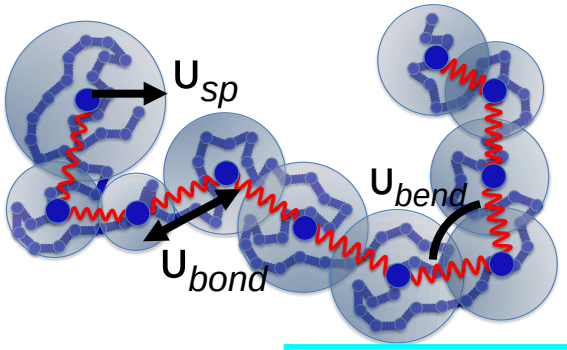
Equivalent to the functional:

$$H_{nb} = \frac{\varepsilon}{2} \int \left[\hat{\varphi}^2(\boldsymbol{r}) - \hat{\psi}^2(\boldsymbol{r})\right] d\boldsymbol{r}$$

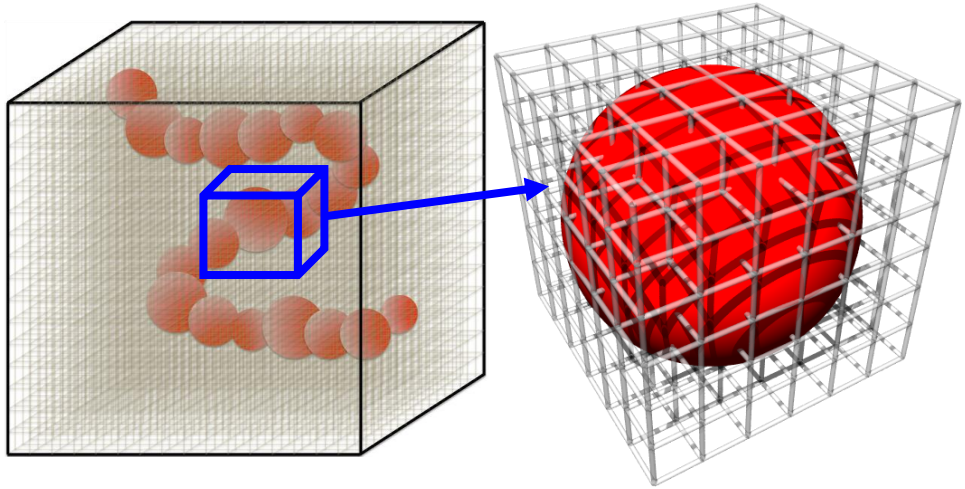
Zhang, Daoulas, & Kremer, *Macromol. Chem. Phys.* 2013

EFFICIENT MONTE CARLO METHOD FOR BLOB-BASED MODELS

- Bonded interactions: use explicit potentials



- Non-bonded interactions:
  - Introduce high-resolution mesh



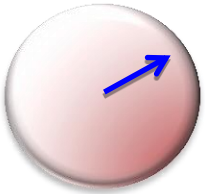
- Map the Gaussian density cloud of each sphere on the grid-nodes

- Density distribution of configuration calculated:

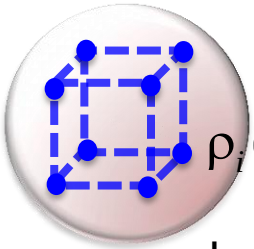
$$\hat{\varphi}(\mathbf{c}) = \sum_{i=1}^{all\ spheres} \rho_i(\mathbf{c})$$

$$\hat{\psi}(\mathbf{c}) = \sqrt{\sum_{i=1}^{all\ spheres} \rho_i^2(\mathbf{c})}$$

Our case:



density cloud

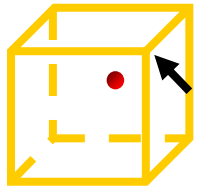


mapped on grid

Typical PM:

Hockney & Eastwood *Computer Simulation Using Particles* IOP 1988

point particle



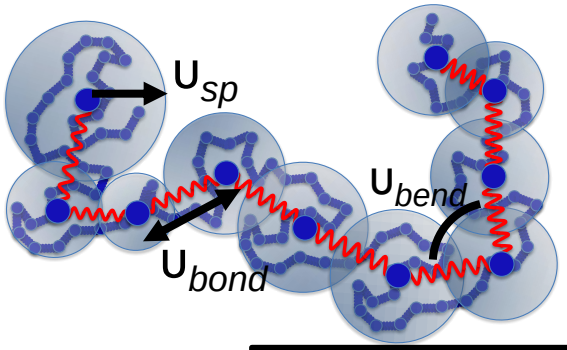
mapped on grid

- Non-bonded energy:

$$H_{nb} = \frac{\varepsilon}{2} \sum_{c=1}^{ncells} \left[\hat{\varphi}^2(\boldsymbol{c}) - \hat{\psi}^2(\boldsymbol{c})\right] \Delta L^3$$

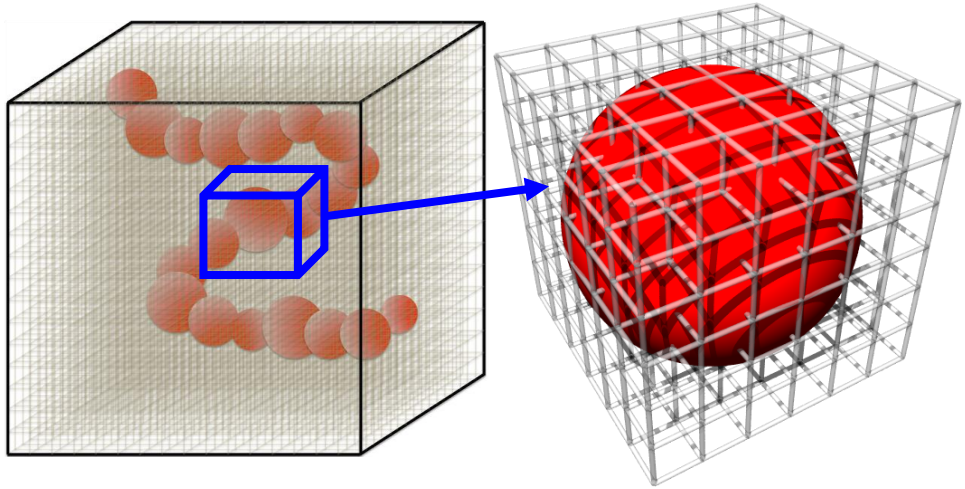
EFFICIENT MONTE CARLO METHOD FOR BLOB-BASED MODELS

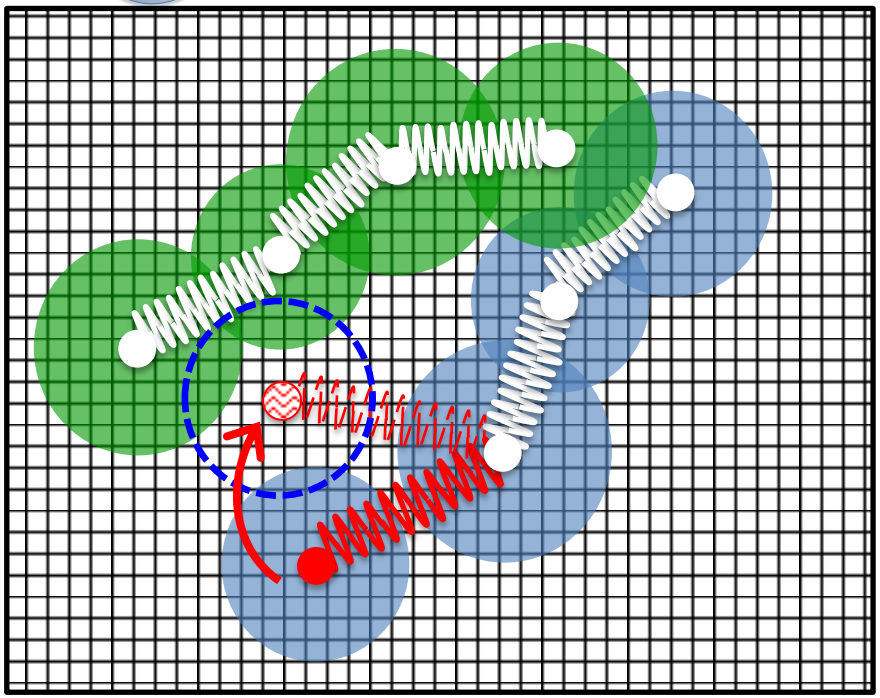
- Bonded interactions: use explicit potentials



- Non-bonded interactions:
  - Introduce high-resolution mesh

Energy changes obtained from density changes





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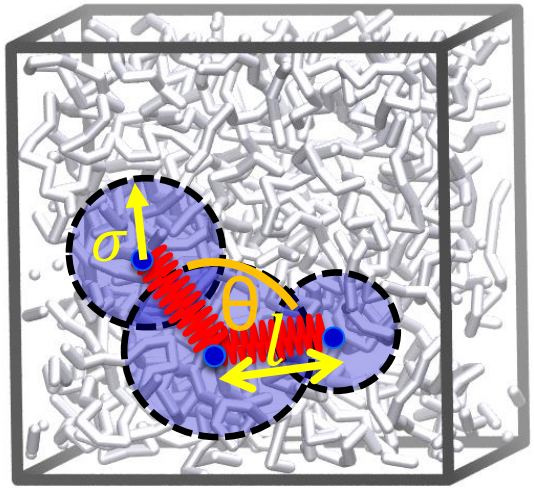
PARAMETERIZATION OF BLOB-BASED MODEL

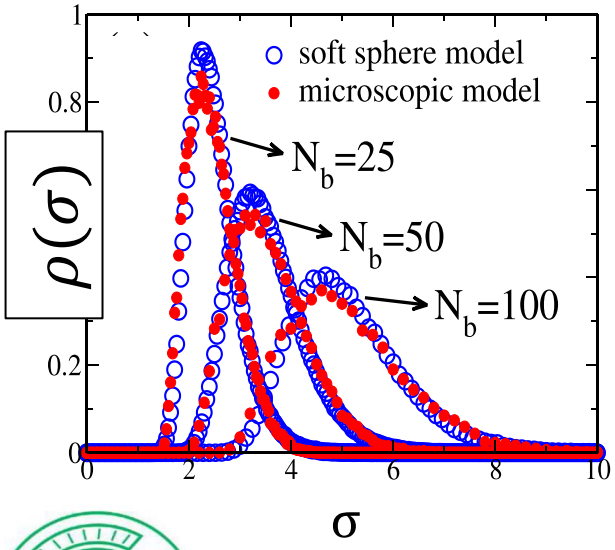


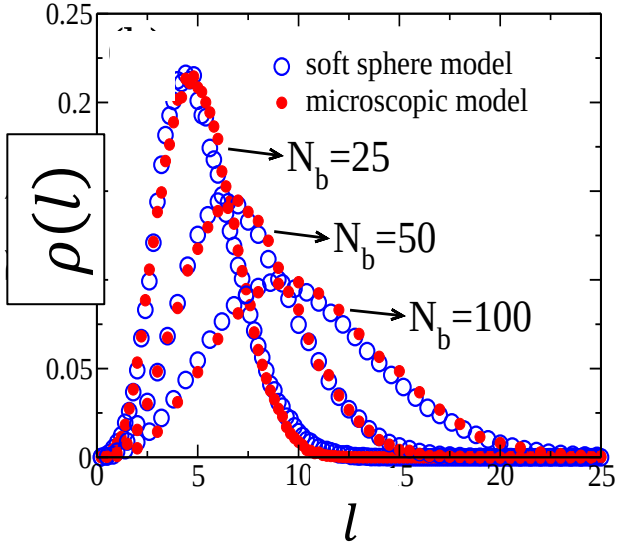
- Parameters tuned to reproduce local blob properties in reference samples described with the microscopic model
- Examples:

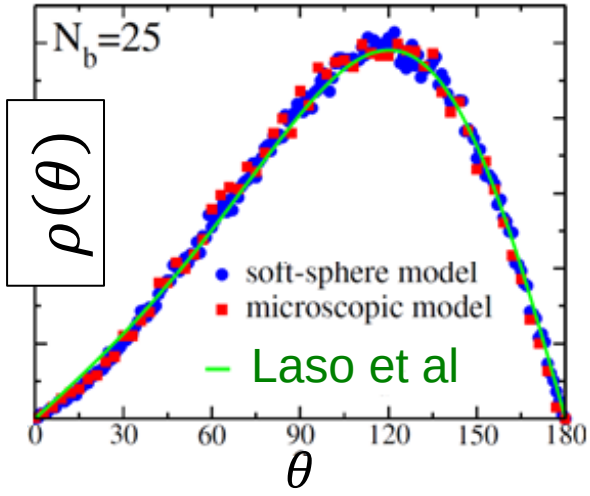
  Distributions: $\rho(\sigma),\ \rho(l), \rho(\theta)$

  Pair-correlation-function for blob centers, $g(r)$

- Performance of blob-based model for generic melt:



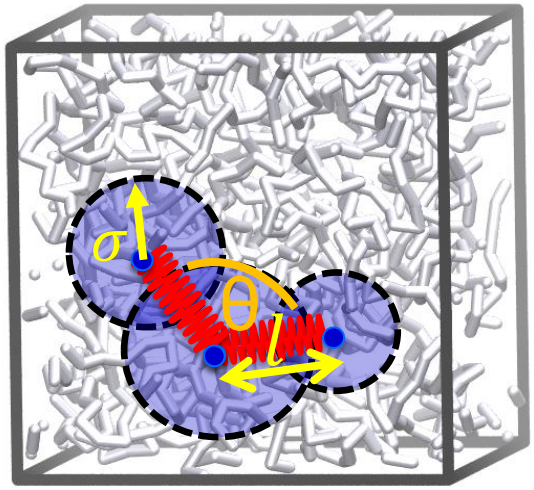




Zhang, Moreira, Stuehn, Daoulas, & Kremer *ACS Macro Lett.* 2014

Zhang, Stuehn, Daoulas, & Kremer *J. Chem. Phys.* 2015

PARAMETERIZATION OF BLOB-BASED MODEL



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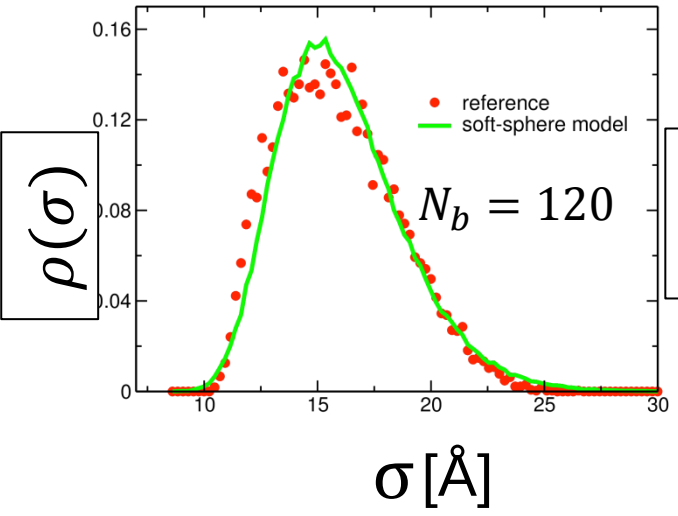
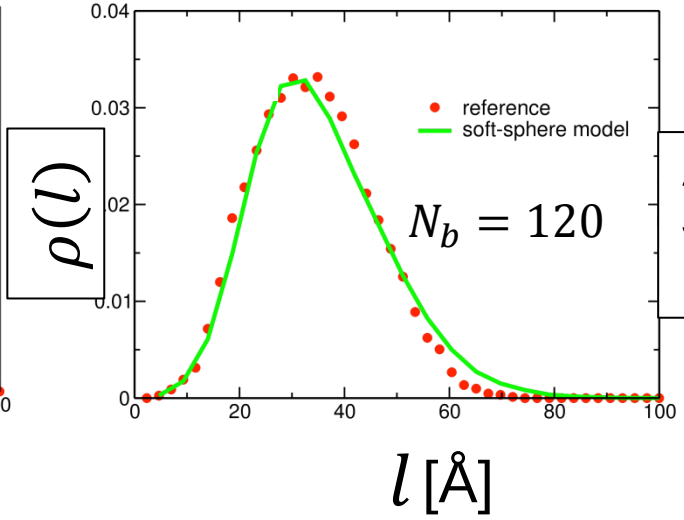
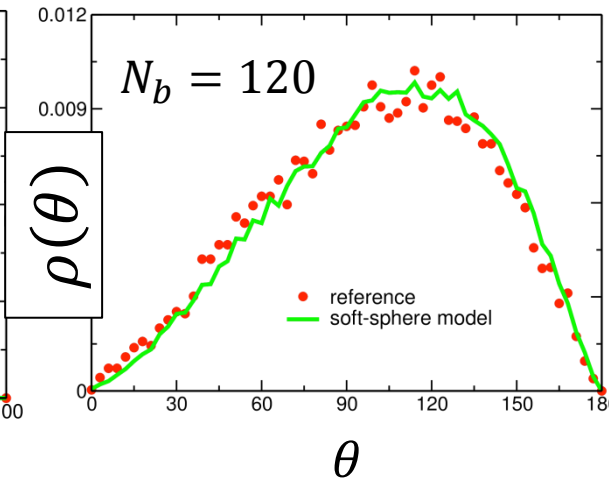
  Pair-correlation-function for blob centers, $g(r)$

- Performance of blob-based model for polystyrene melt:

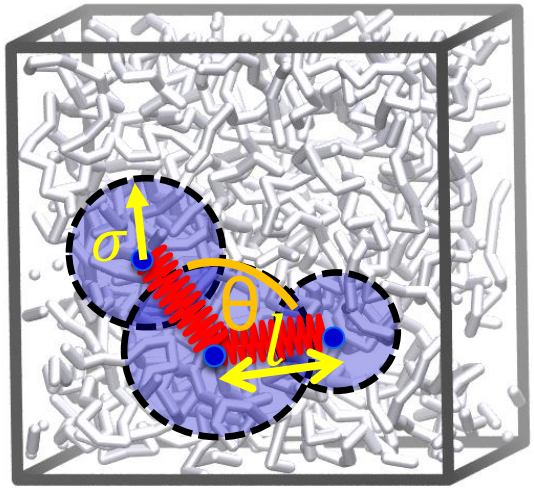






Zhang, Hazirakis, Stuehn, Harmandaris, Daoulas, & Kremer *manuscript in preparation*

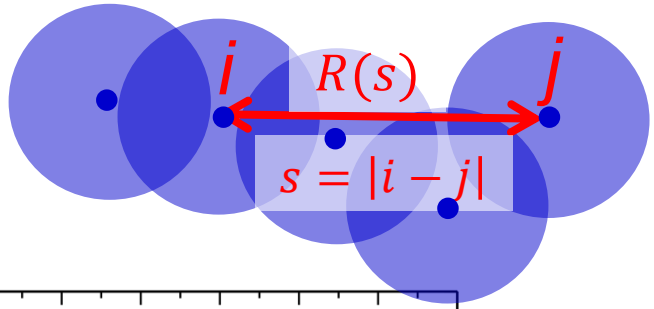
BOTTOM-UP PARAMETERIZATION OF BLOB-BASED MODEL



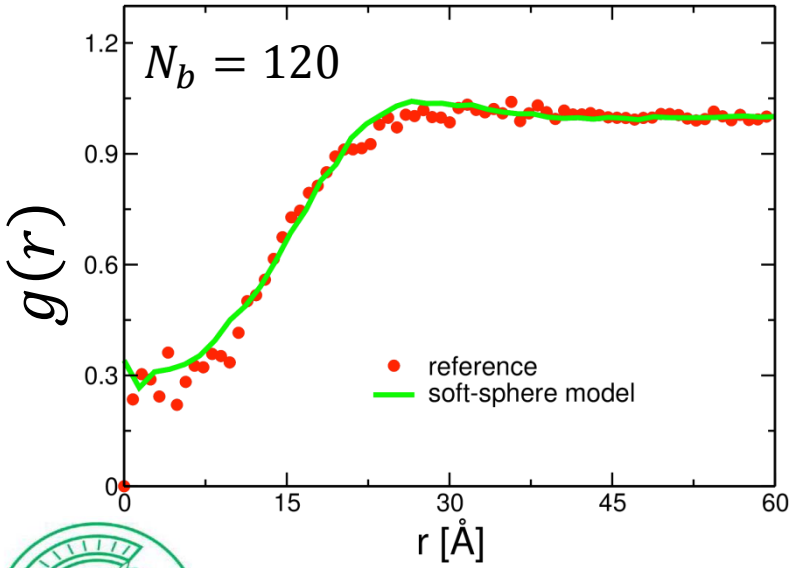
- Parameters tuned to reproduce local blob properties in reference samples described with the microscopic model
- Examples:

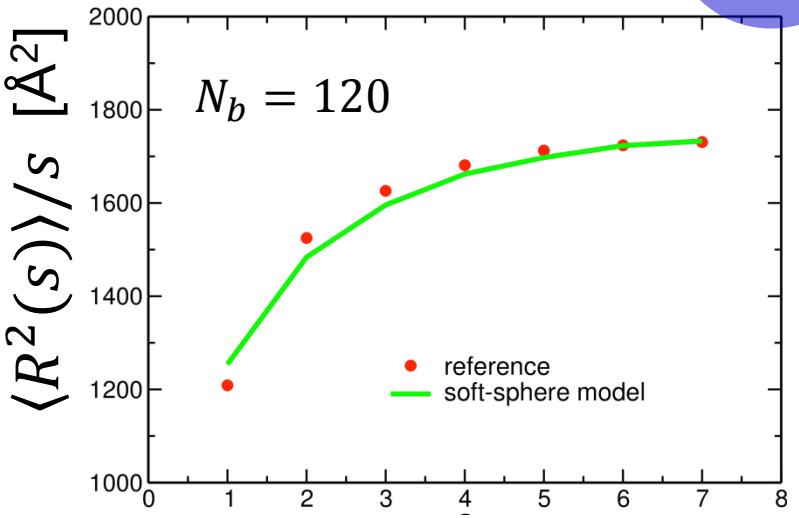
  Distributions: $\rho(\sigma),\ \rho(l), \rho(\theta)$

  Pair-correlation-function for blob centers, $g(r)$



- Performance of blob-based model for polystyrene melt:

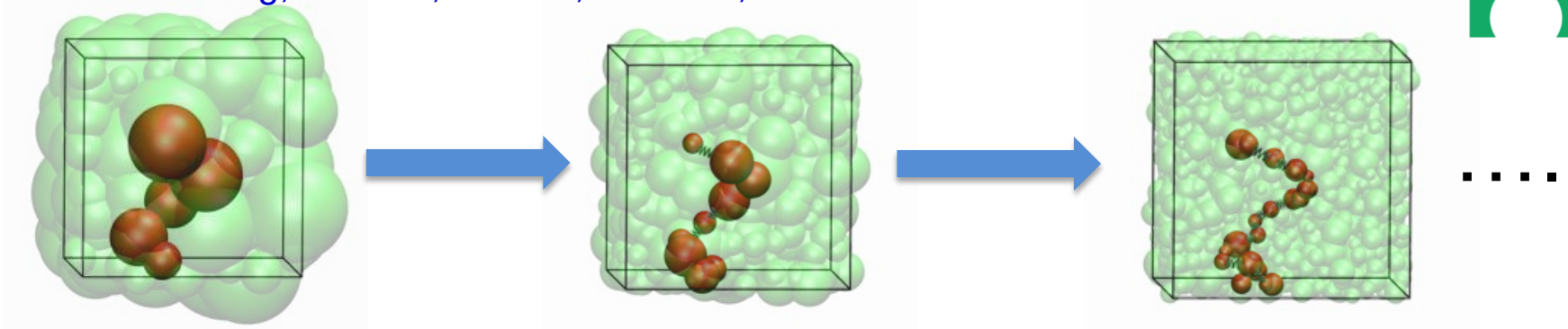




difference of blob ranking numbers → s

I. HIERARCHICAL BACK-MAPPING STRATEGY: FINE-GRAINING

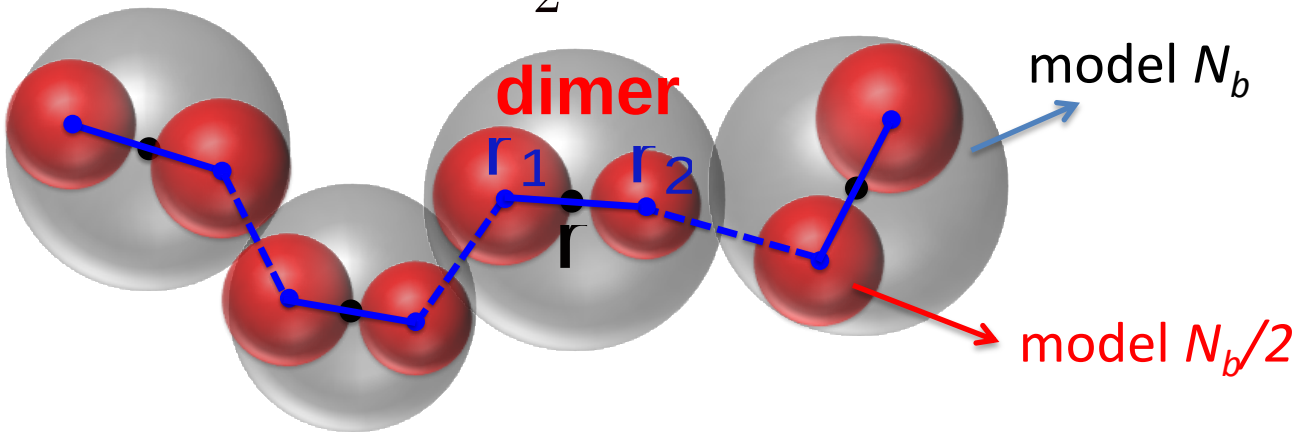
Zhang, Moreira, Stuehn, Daoulas, & Kremer *ACS Macro Lett.* 2014



- Starting configuration equilibrated "from scratch"
  1 blob → N_b beads
- Double resolution
  1 blob → $\frac{N_b}{2}$ beads
- Double resolution
  1 blob → $\frac{N_b}{4}$ beads

❑ Fine-graining concept:

$$\mathbf{r} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$$

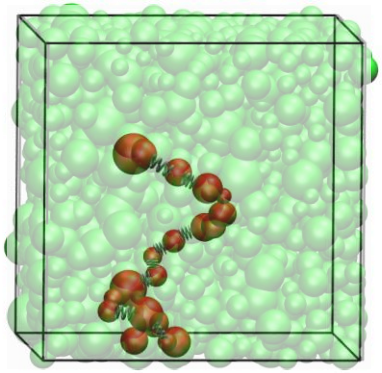


→ Relaxation time of smaller blobs is short ~ Rouse time of dimer

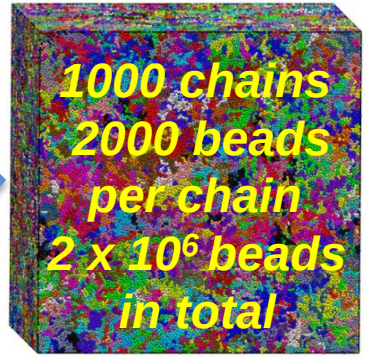
II. HIERARCHICAL BACK-MAPPING STRATEGY: REINSERTION

Zhang, Moreira, Stuehn, Daoulas, & Kremer *ACS Macro Lett.* 2014

small blobs,
e.g., 1 blob: 25 beads

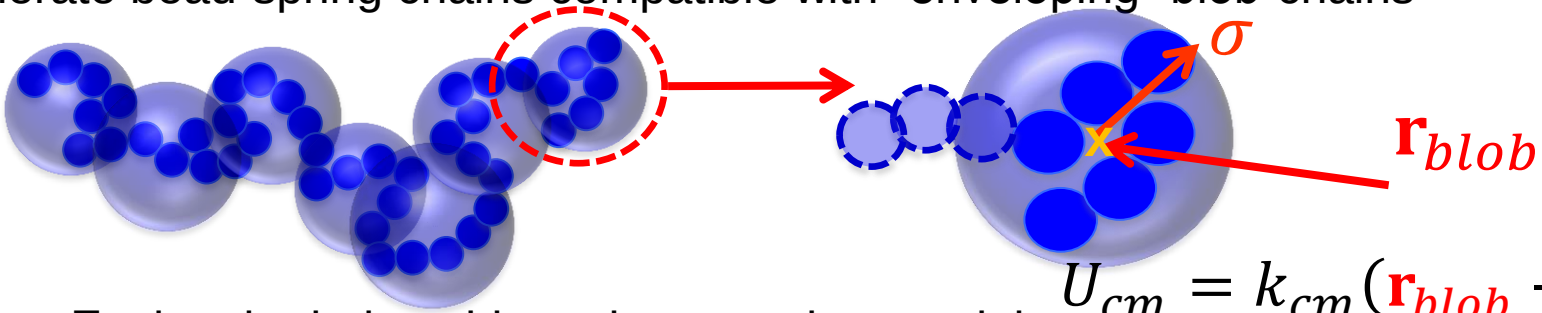


???



underlying
microscopic
configuration

❑ Generate bead-spring chains compatible with "enveloping" blob-chains



$$U_{cm} = k_{cm}(\mathbf{r}_{blob} - \mathbf{R}_{cm})^2$$

$$U_g = k_g(\sigma - R_g^2)^2$$

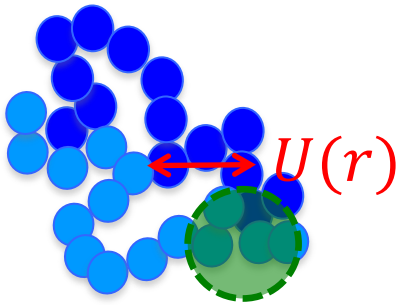
→ Each sub-chain subjected to pseudopotentials:

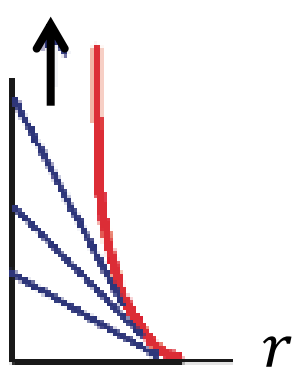
→ No intrachain correlations

→ No intermolecular correlations

❑ Introduce slowly excluded volume
removing monomer overlaps

Auhl el al. *J. Chem. Phys.* 2003

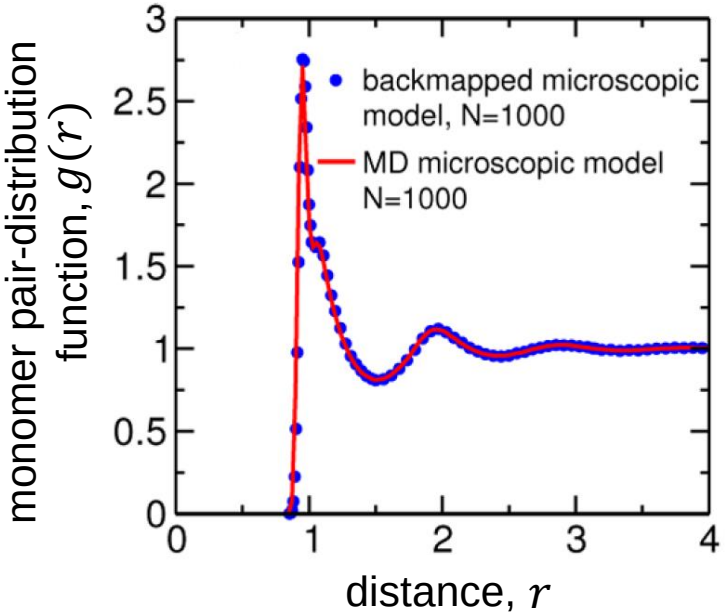




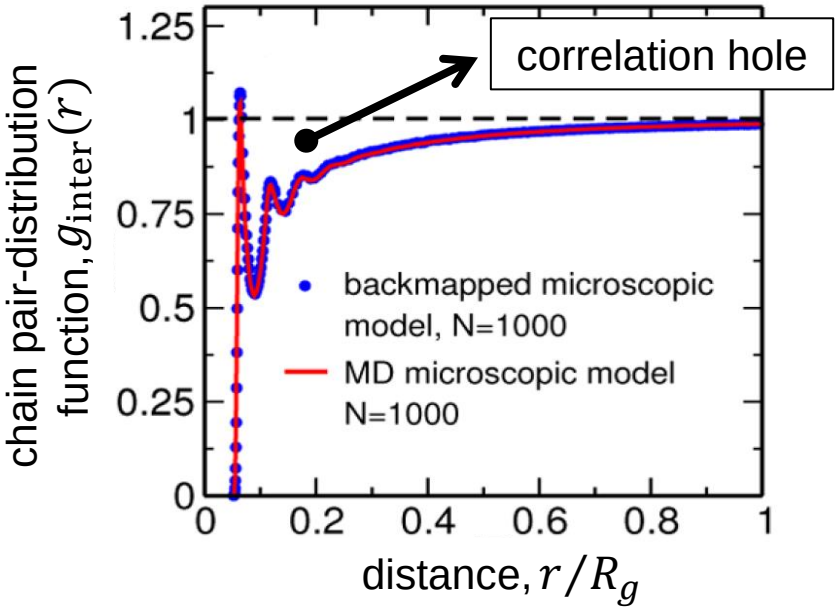
VERIFYING EQUILIBRATION OF MELTS OF LONG POLYMERS

❑ Local liquid structure:

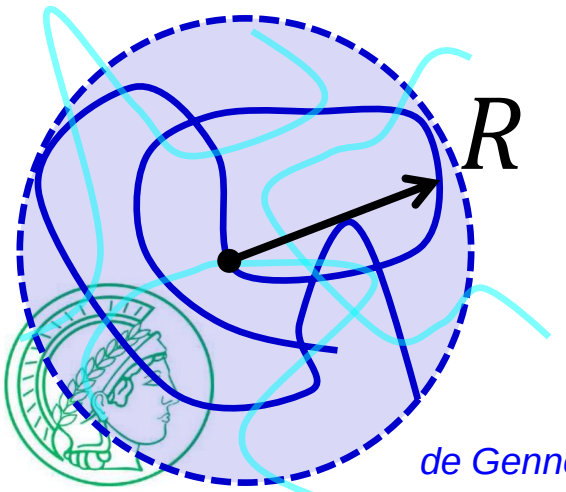
Generic melt:



❑ Long-wavelength liquid structure:



❑ Correlation hole → "packing" of polymer molecules



Due to connectivity monomers of same chain are close by →

Liquid has fixed density → monomers of other chains expelled

$$g_{inter}(small\ r) \sim \frac{(n-1)N}{R^3 bulk\ density} = 1 - \frac{N}{R^3 bulk\ density}$$

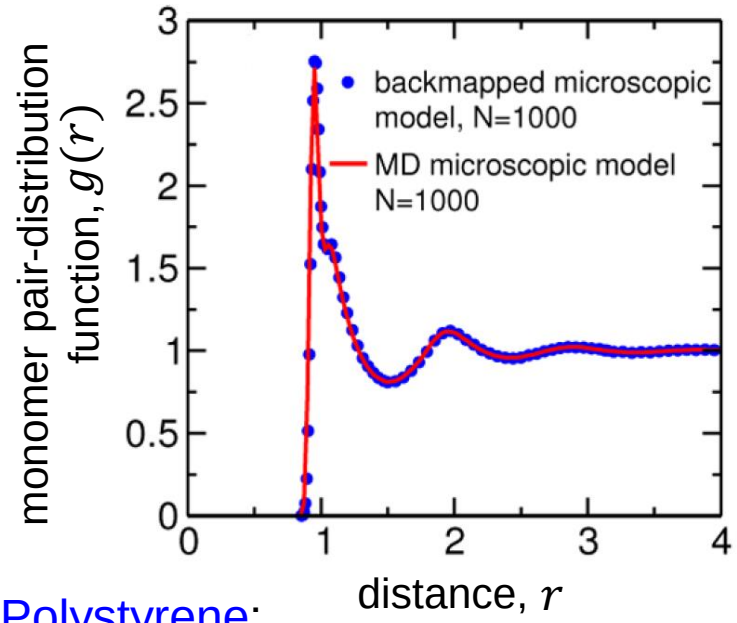
$$\frac{R^3\ bulk\ density}{N} \equiv \sqrt{N} \qquad g_{inter}(small\ r) \sim 1 - \frac{1}{\sqrt{N}}$$

de Gennes, Scaling Concepts in Polymer Physics 1979

VERIFYING EQUILIBRATION OF MELTS OF LONG POLYMERS

- Local liquid structure:

Generic melt:



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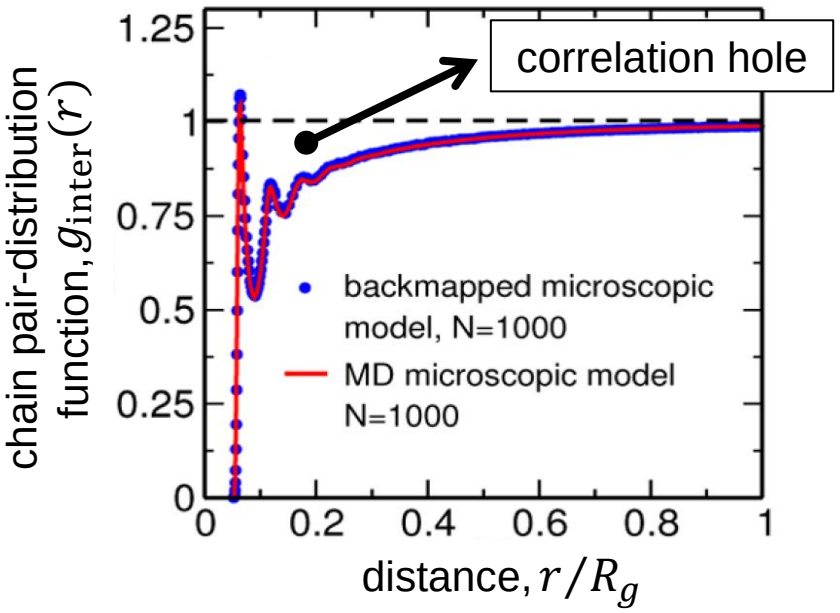
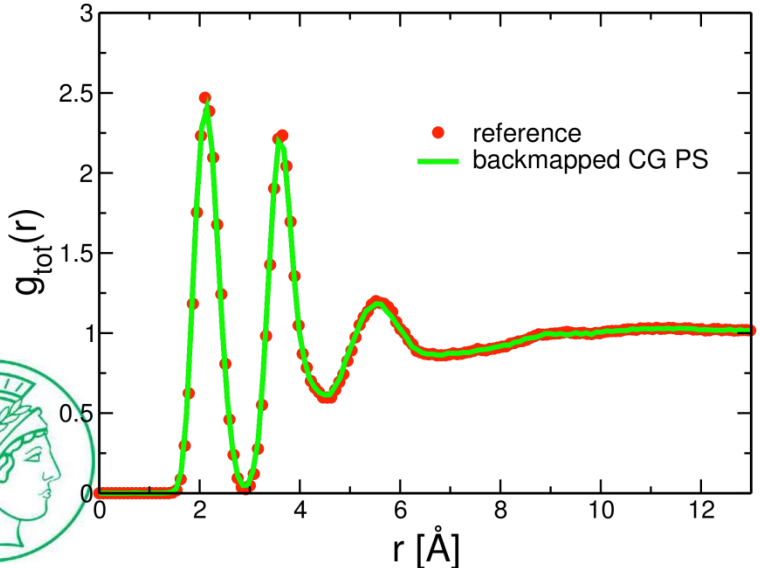
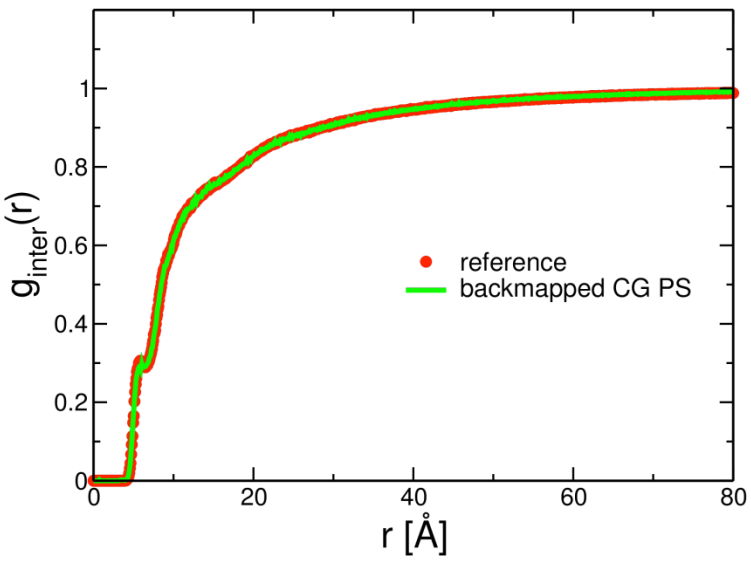


Polystyrene:

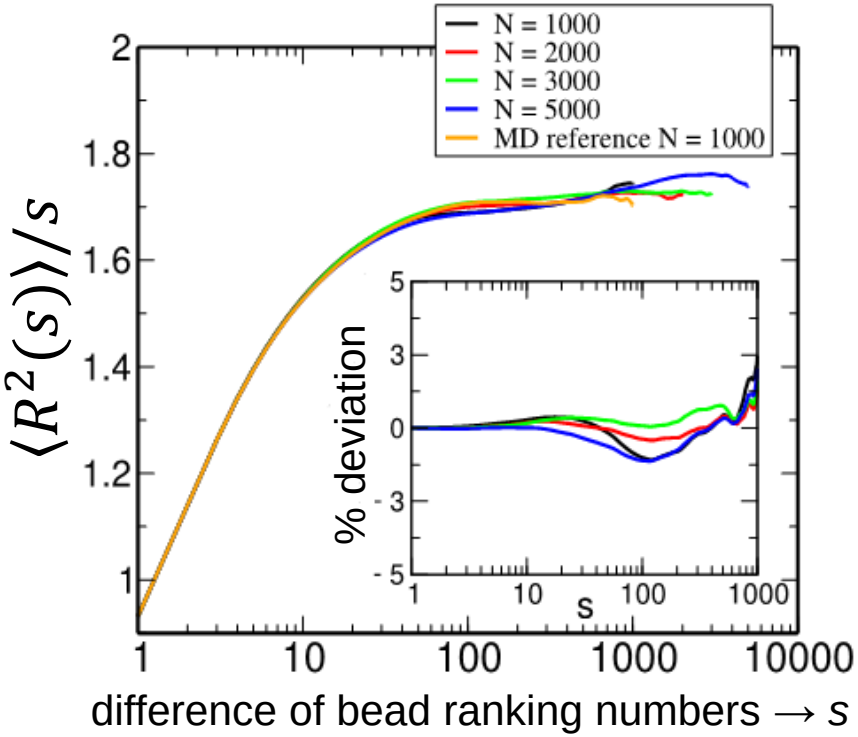




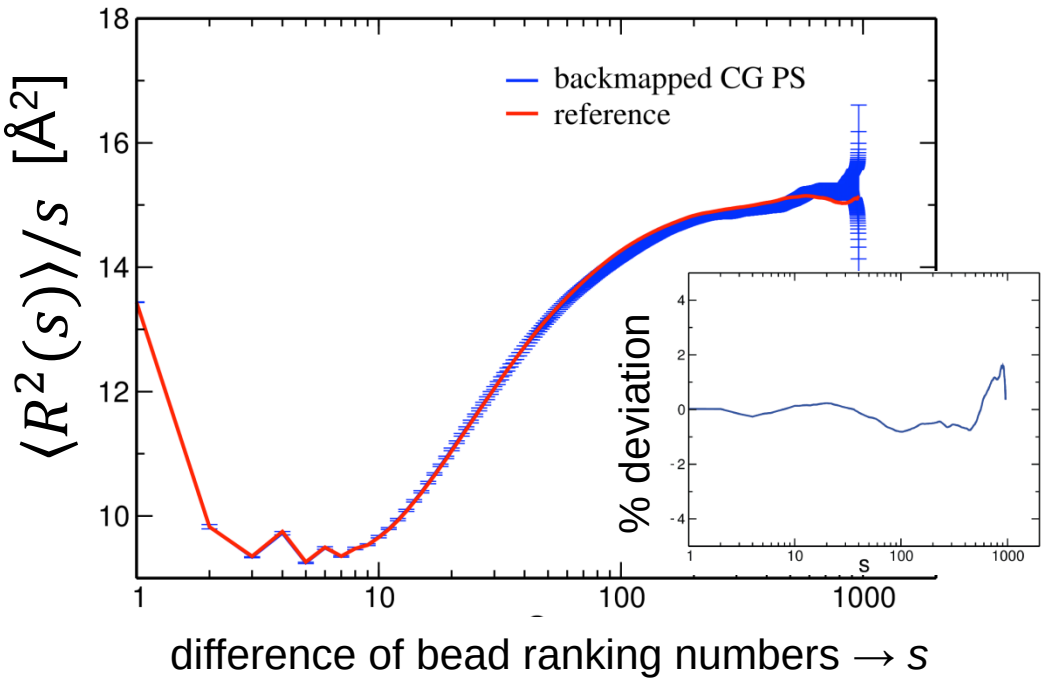
VERIFYING EQUILIBRATION OF MELTS OF LONG POLYMERS

- Chain conformations:

Generic melt:

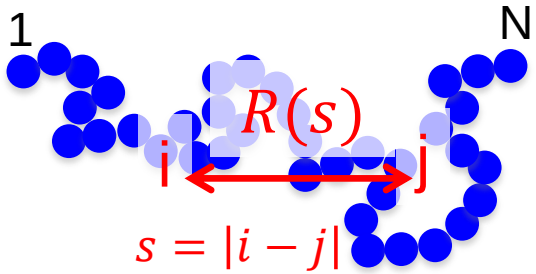


Polystyrene:



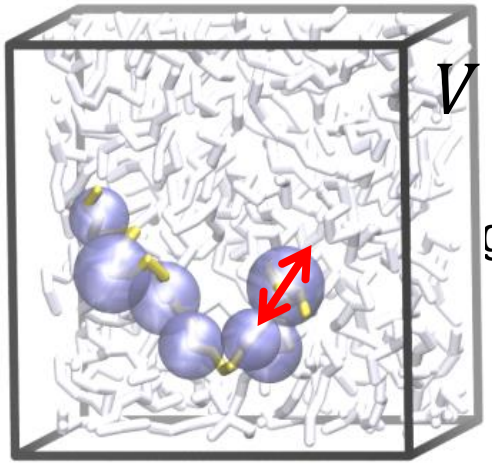
- Internal distance plots highlight excellent equilibration

- The method equilibrates samples with more than 1000 chains and N = 5000



For generic model representative computation time ~ 6 days on 32 processors
For polystyrene model, complexity raises computation time by an order of magnitude

UNIVERSAL BLOB-BASED REPRESENTATION OF MELTS

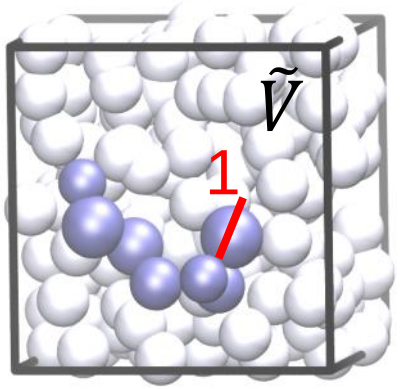


coarse graining scale ΔL

N_{CG} blobs in a chain

renormalization

$\mathbf{r}/\Delta L$



N_{CG} blobs in a chain

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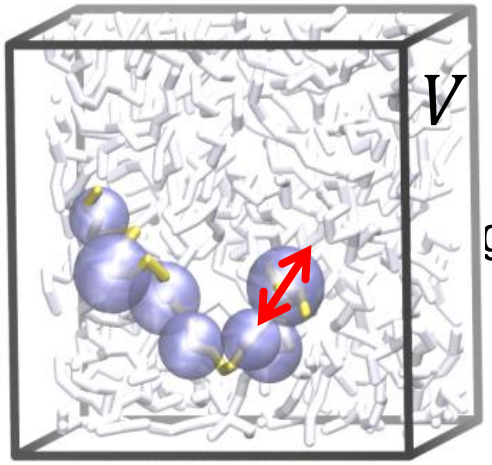
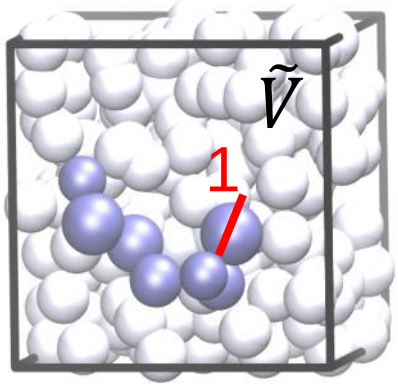


coarse graining scale ΔL

renormalization $\mathbf{r}/\Delta L$

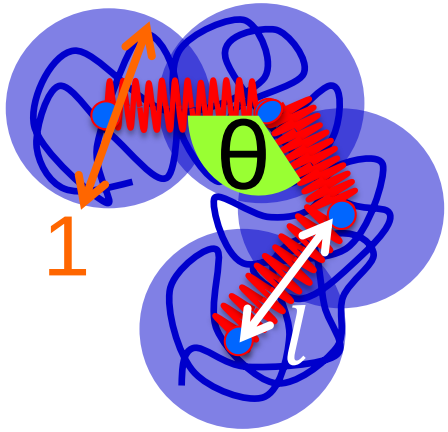


N_{CG} blobs in a chain

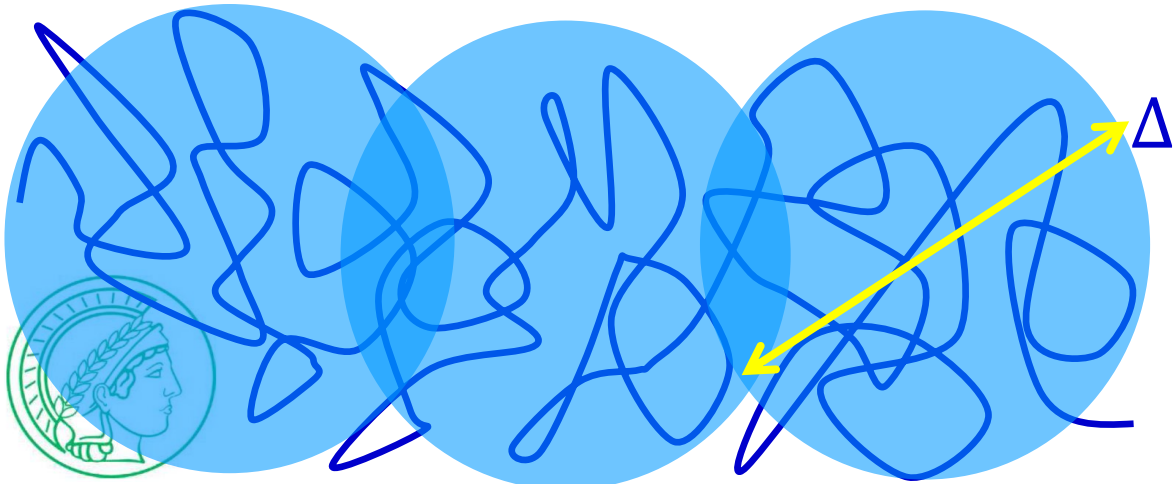
- Different melts map on the same renormalized blob representation when:

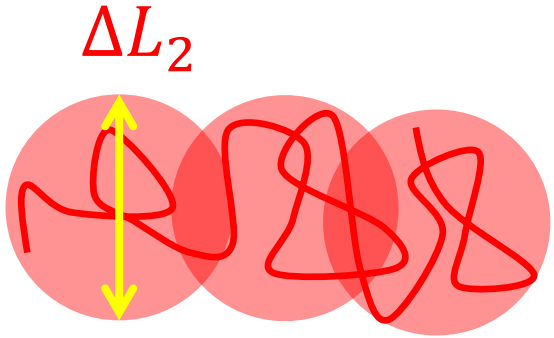
A) For each melt ΔL chosen so that chains have N_{CG} blobs

universal distributions $\rho(\theta)$ $\rho(l)$ + same N_{CG} = same conformations



Laso et al, *J. Chem. Phys.* 1991





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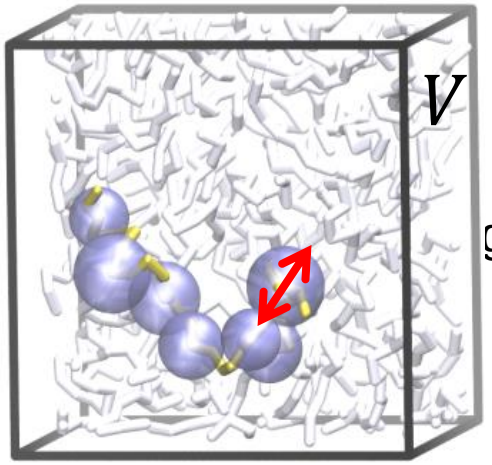
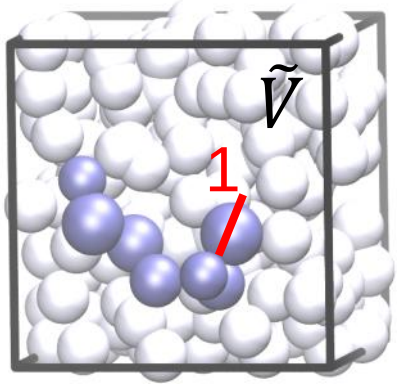


coarse graining scale ΔL

renormalization $\mathbf{r}/\Delta L$



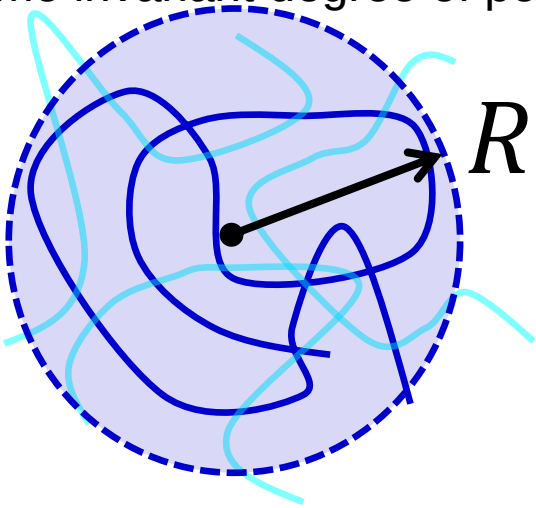
N_{CG} blobs in a chain

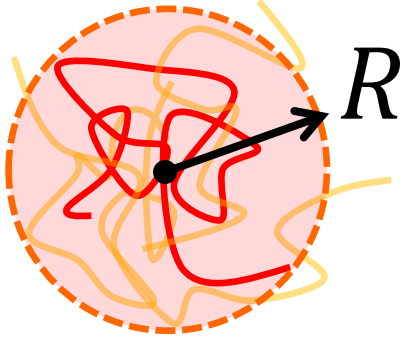
- Different melts map on the same renormalized blob representation when:

B) Melts have the same invariant degree of polymerization $\overline{N}$

$$\sqrt{\overline{N}} = nR^3/V$$

quantifies chain overlap



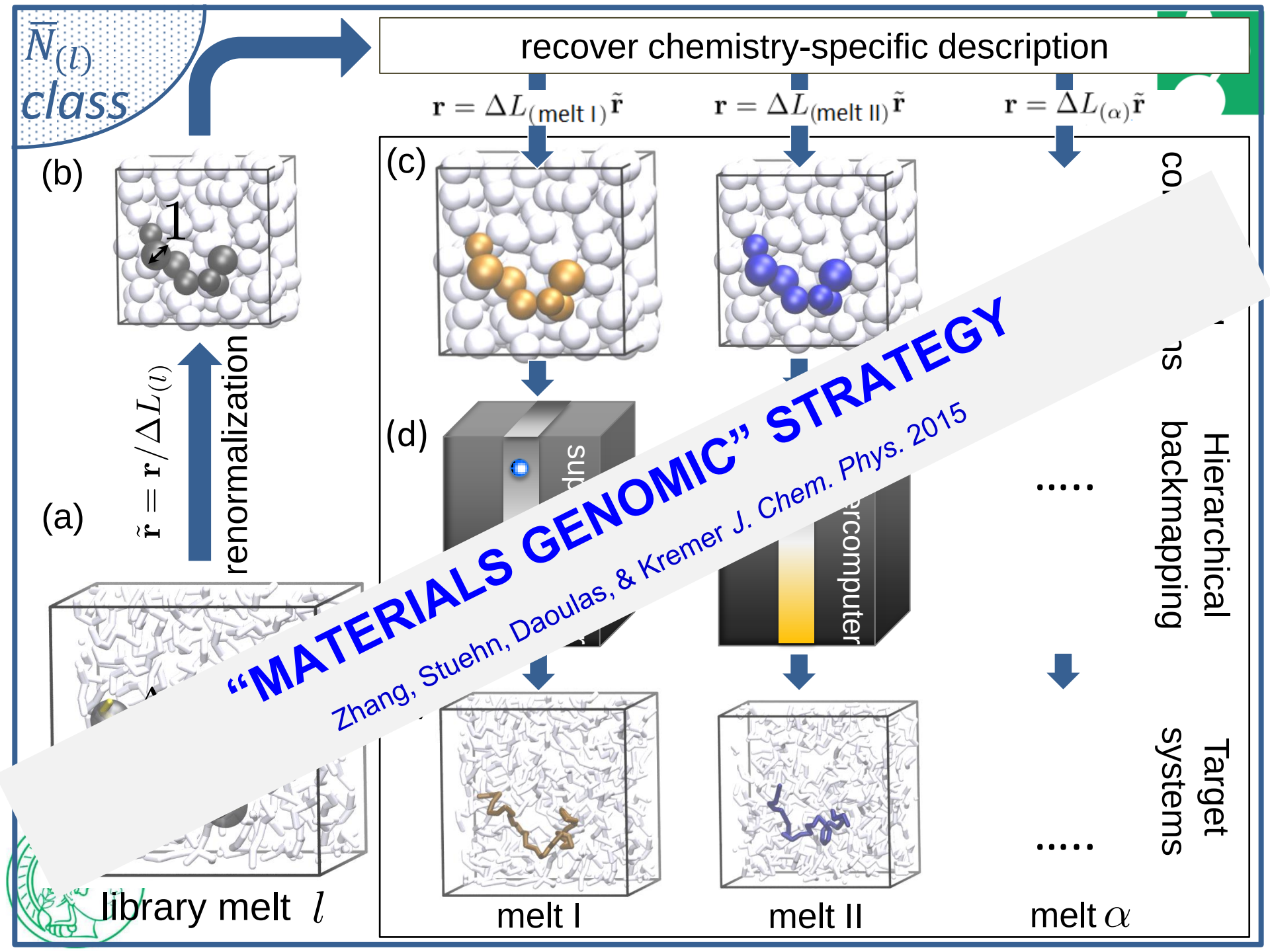


same liquid structure

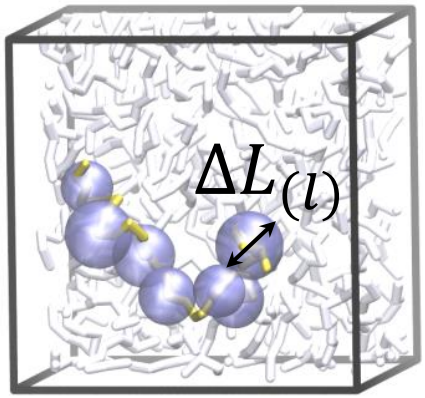
chains have the same $N_{CG} \Rightarrow$ blobs have the same $\overline{N}_b \Rightarrow$

$$g_{CG}(\tilde{r}) = 1 - \frac{1}{\sqrt{\overline{N}_b}} X_o(\tilde{r}, N_{CG})$$

Clark, McCarty, & Guenza *J. Chem. Phys.* 2013


$\bar{N}_{(l)}$ class
recover chemistry-specific description
$\mathbf{r} = \Delta L_{(\text{melt I})}\tilde{\mathbf{r}}$
$\mathbf{r} = \Delta L_{(\text{melt II})}\tilde{\mathbf{r}}$
$\mathbf{r} = \Delta L_{(\alpha)}\tilde{\mathbf{r}}$
(b)
(c)
(d)
(a)
1
$\tilde{\mathbf{r}} = \mathbf{r}/\Delta L_{(l)}$
renormalization
supercomputer
supercomputer
.....
.....
Hierarchical backmapping
Target systems
library melt l
melt I
melt II
melt α
"MATERIALS GENOMIC" STRATEGY
Zhang, Stuehn, Daoulas, & Kremer J. Chem. Phys. 2015

PROOF-OF-PRINCIPLE

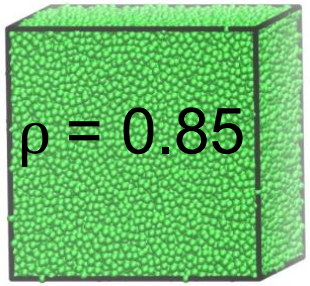


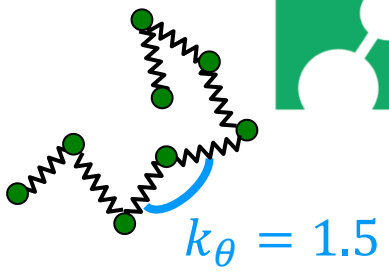
- All library melts →

  Same "chemical" substance

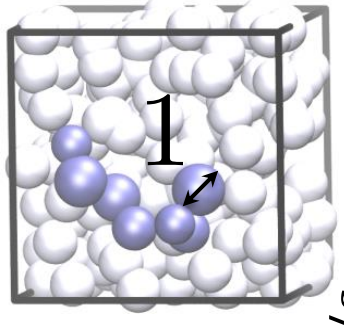
$\bar{N} = 7.5 \times 10^3$

$\bar{N} = 15 \times 10^3$

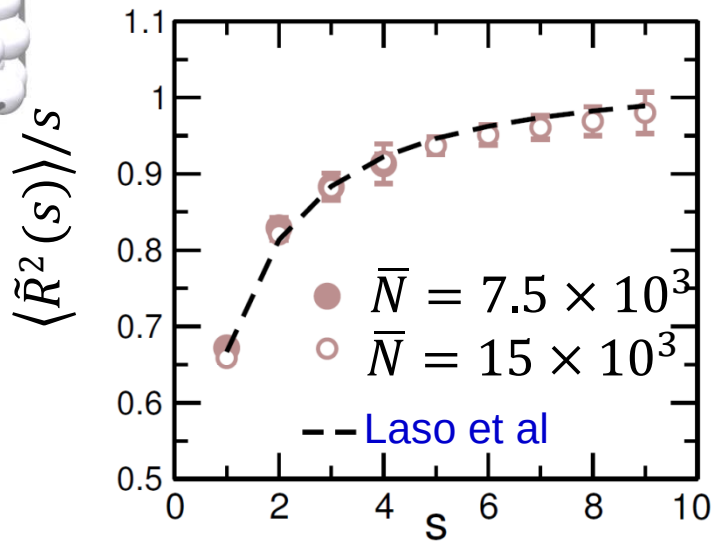




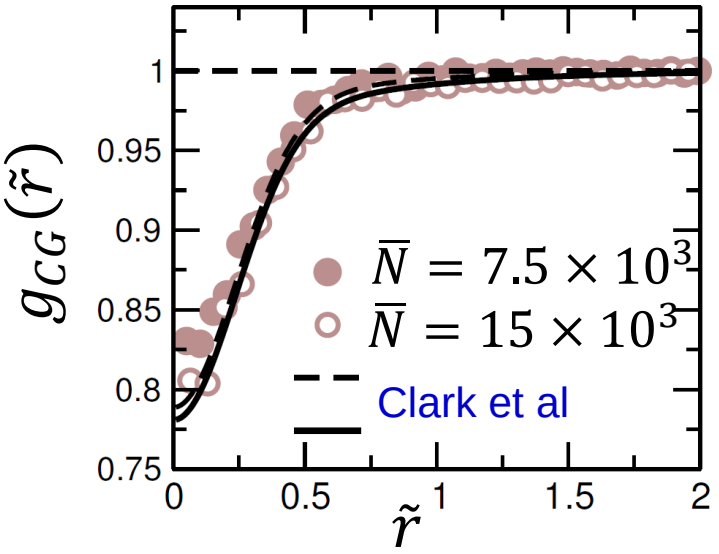
- Universal blob-based description exists:



- Universality of conformations

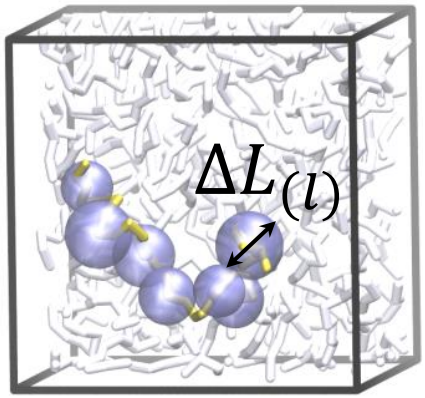


- Universality of blob-packing



Zhang, Stuehn, Daoulas, & Kremer *J. Chem. Phys.* 2015

PROOF-OF-PRINCIPLE



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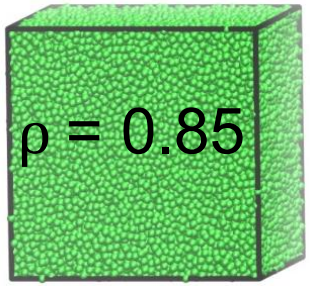
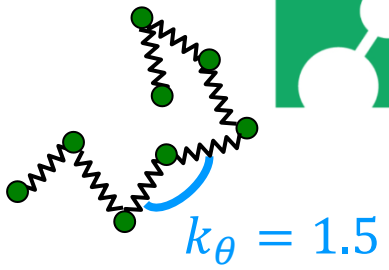
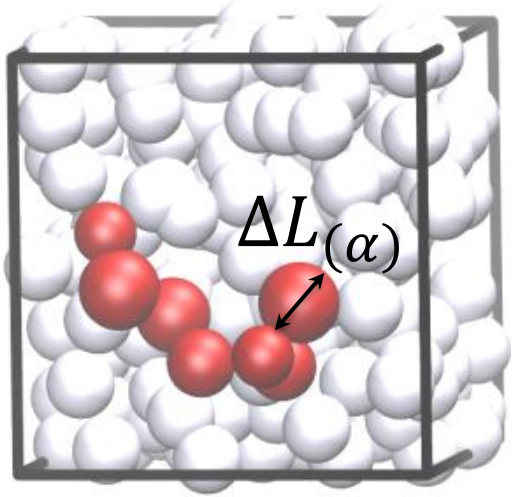
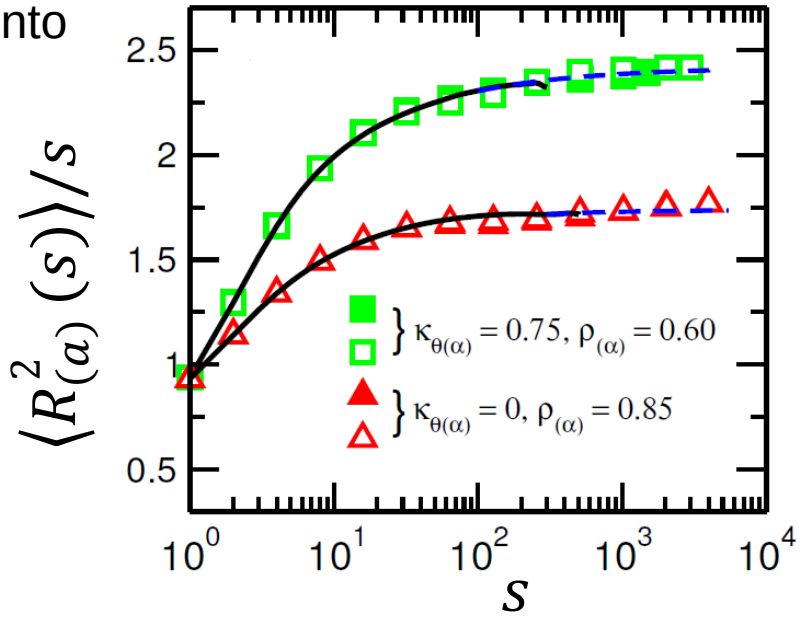






- Convert library melts into "different" materials:



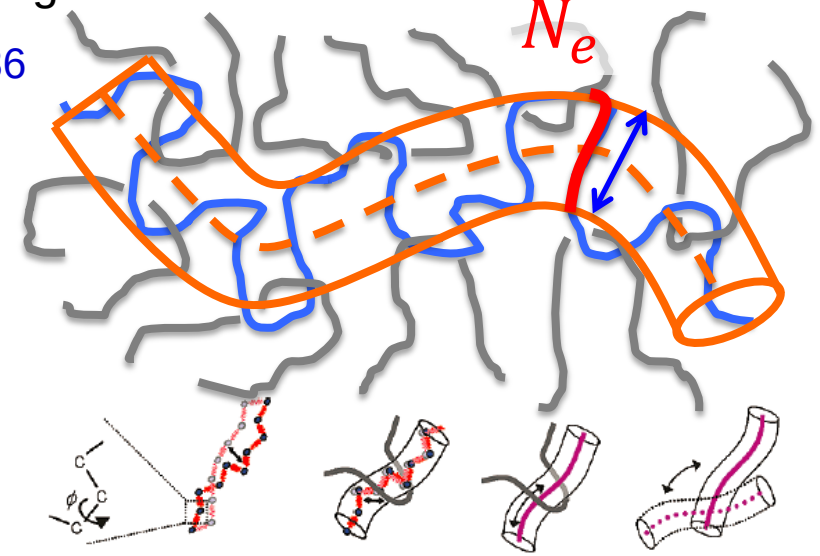
Zhang, Stuehn, Daoulas, & Kremer *J. Chem. Phys.* 2015

EQUILIBRATED SAMPLES ARE STARTING-POINT FOR COMPUTATIONAL RHEOLOGICAL "EXPERIMENTS"

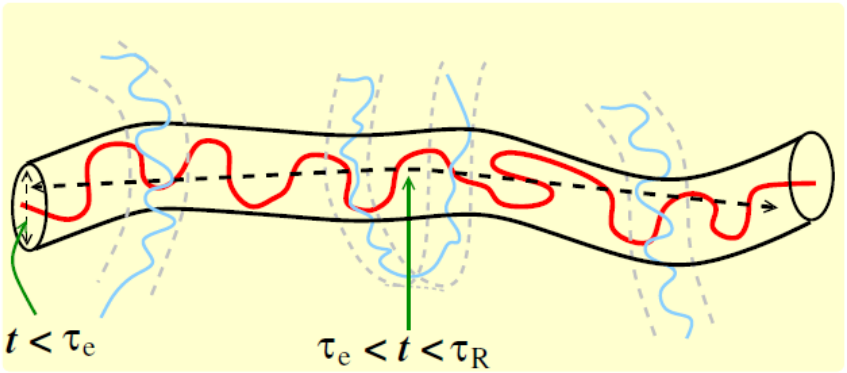
- Simple illustration:
  Equilibrium chain dynamics in highly entangled regime

  Doi & Edwards, *The Theory of Polymer Dynamics* 1986

tube-model

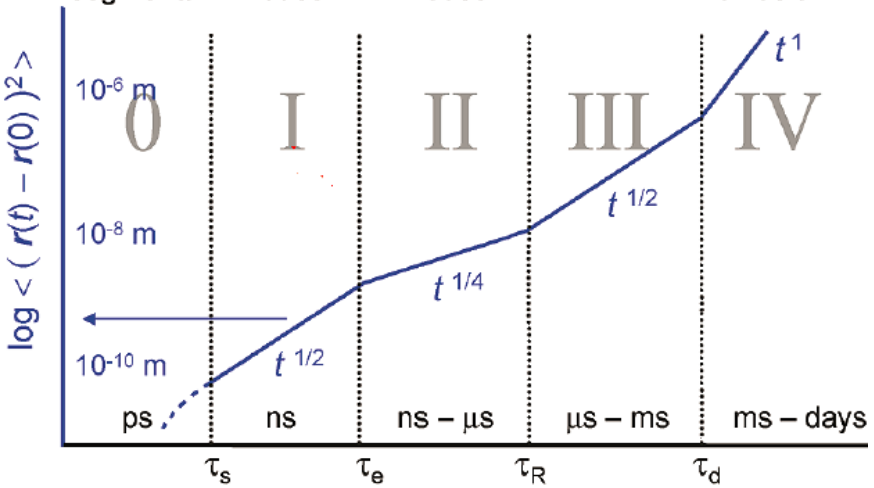


Example: mean square monomer displacement



$$g_1(t) \sim \begin{cases} t^{1/2} & \text{for} \quad t \le \tau_e \\ t^{1/4} & \text{for} \quad \tau_e \le t \le \tau_R \\ t^{1/2} & \text{for} \quad \tau_R \le t \le \tau_d \\ t & \text{for} \quad \tau_d \le t \end{cases}$$

Rubinstein & Colby, *Polymer Physics 2003*



Adapted from: Chávez & Saalwächer *Macromolecules* 2011

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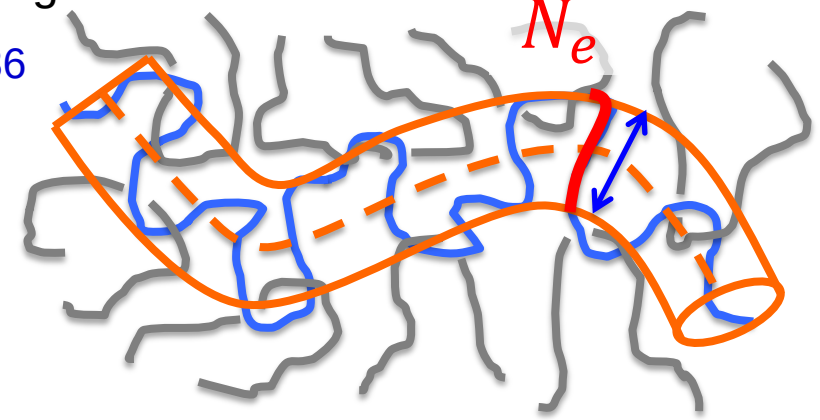

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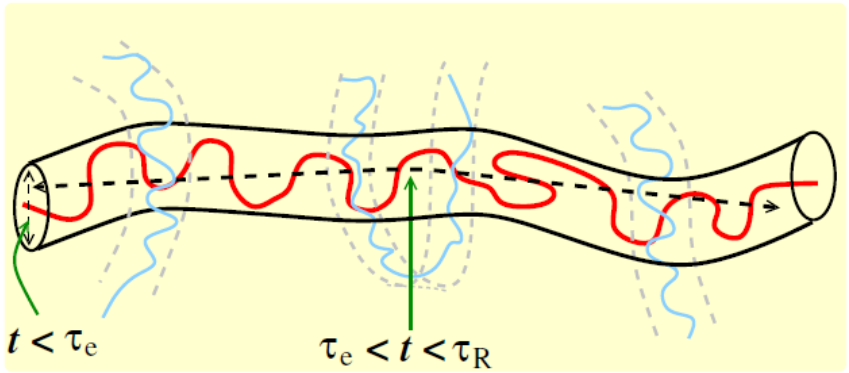

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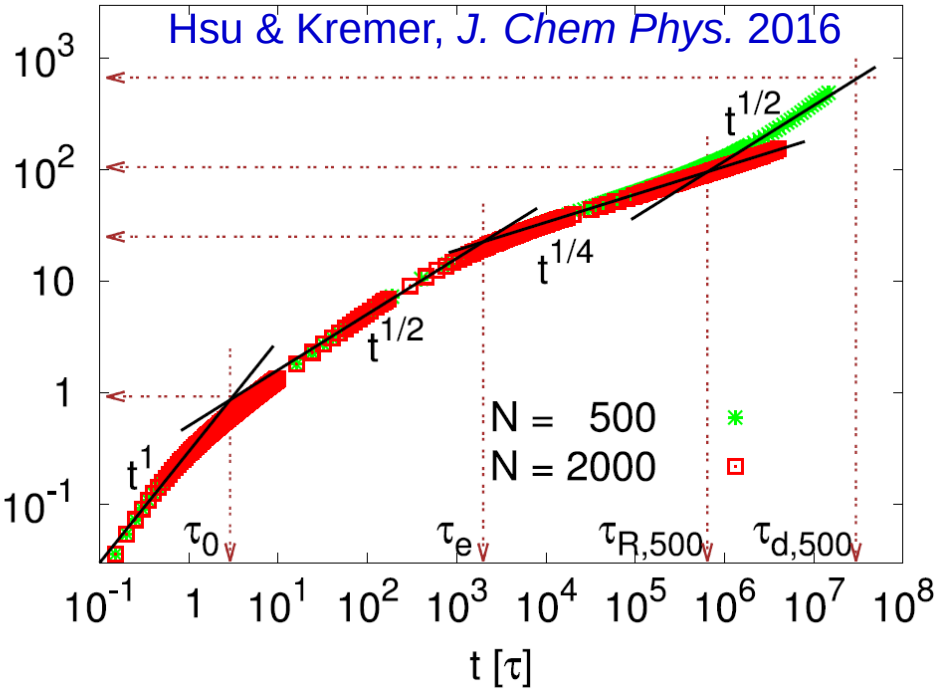
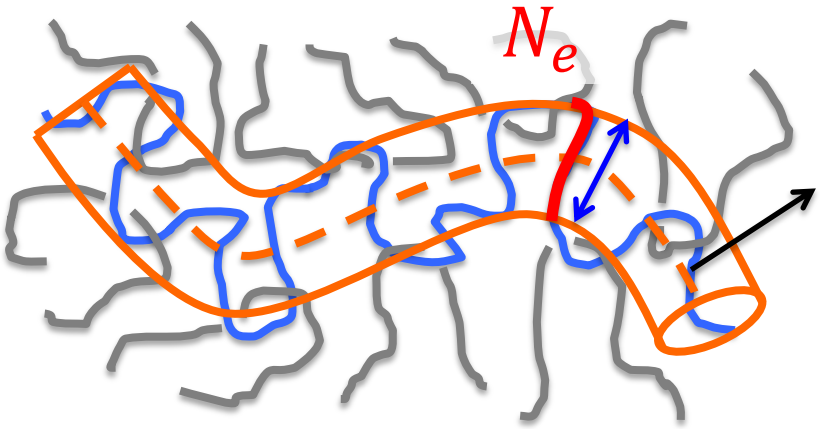


Rubinstein & Colby, Polymer Physics 2003

TOPOLOGICAL ANALYSIS: PRIMITIVE PATH



Primitive path (PP)

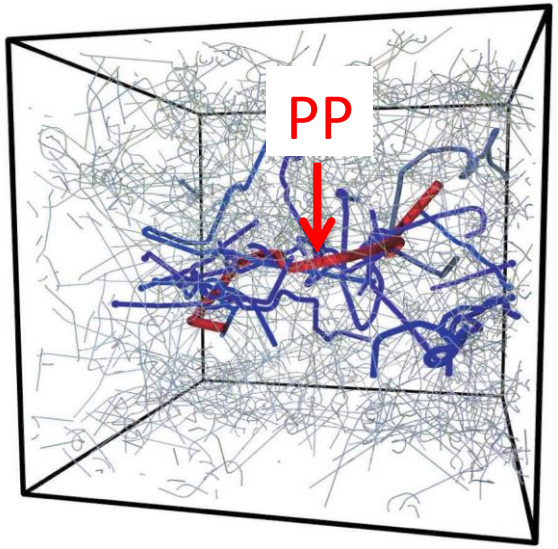
Shortest path between endpoints of original chain into which its contour can be contracted without crossing any obstacle

N_e is defined as the number of monomers in a Kuhn segment of Primitive Path.

$$N_e = a_{pp}/b_{pp}$$

$$a_{pp} = \langle R^2 \rangle / L_{pp} \qquad b_{pp} = L_{pp}/N$$

Kuhn length of PP bond length of PP



bead-spring model, k_θ=1.5

N	1000	2000	3000
$N_{e,PPA}$	29 ± 2	28 ± 1	29 ± 1

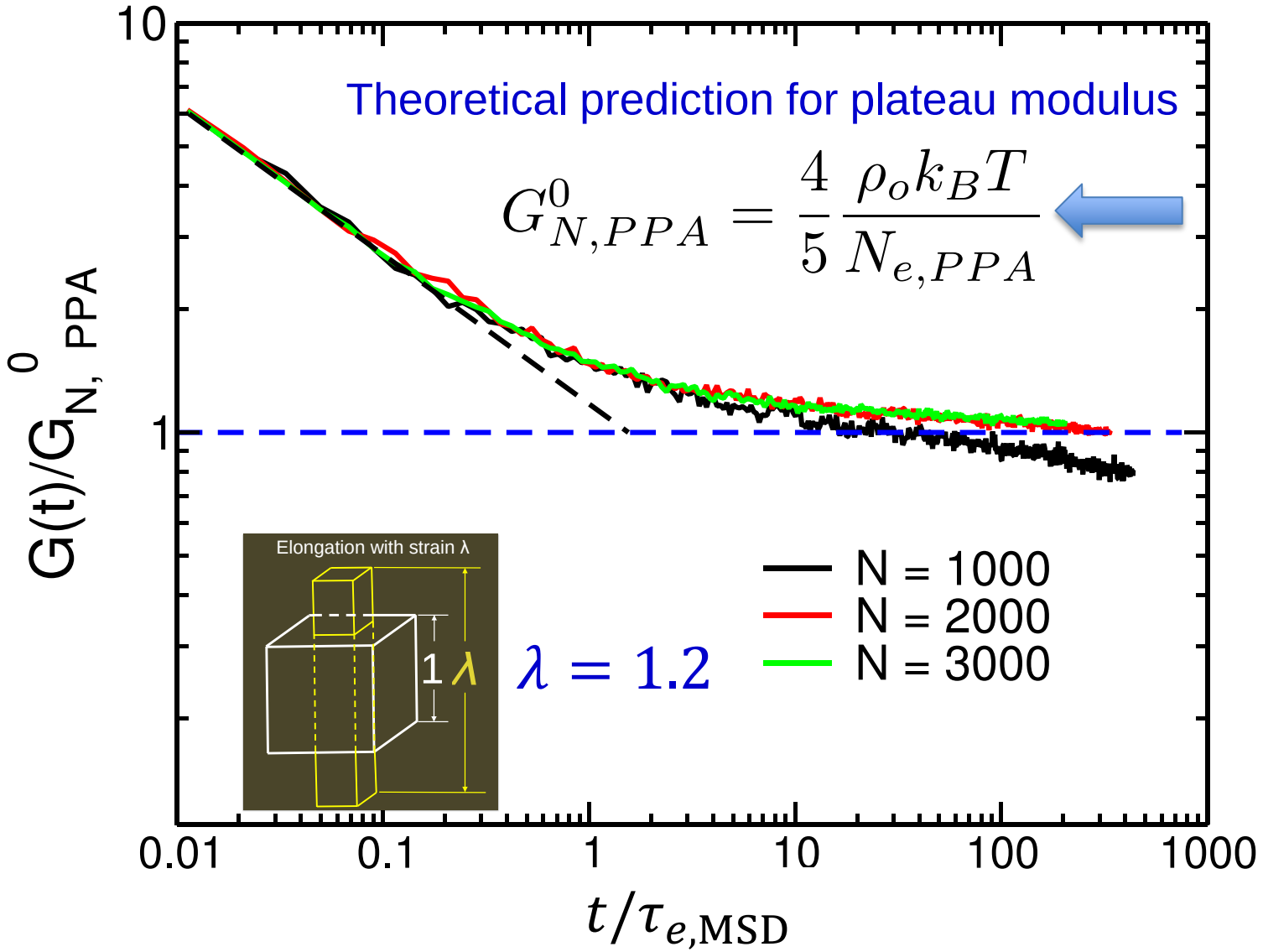
- Fixing the chain ends, pull all chains till they are taut
- Inter-chain excluded-volume interactions are retained, while intrachain excluded-volume interactions are disabled

Everaers, Sukumaran, Grest, Svaneborg, Sivasubramanian, & Kremer, Science, 2004

PREDICTING THE PLATEAU MODULUS

- Rheological experiments

  Example: stress relaxation modulus after step elongation



SUMMARY

- A hierarchical scheme for equilibrating high molecular weight polymer melts was presented. Creating very large samples with chains ~ 100 N_e long is now feasible
- The scheme is applicable to generic and chemically specific microscopic models
- Hierarchical modeling was combined with universality concepts:
  - → Long-wavelength structure of a single melt can be back-mapped onto "chemically" different homopolymer melts with the same $\overline{N}$
  - → Perspectives for materials genomic libraries: for different classes long-wavelength structure can be stored in a few configurations of a single material
  - → Modelling blends
- Parameterization of blob models requires medium-sized "brute force" MD simulations
  - → Can one benefit from other strategies, e.g. integral-equation-state theories?

CPU time:

John von Neumann - Institut für Computing
NIC