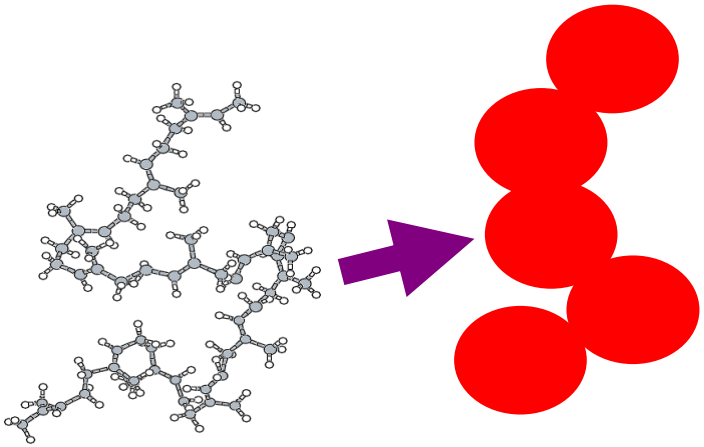


Self Consistent Multiscale Modeling of Polymers

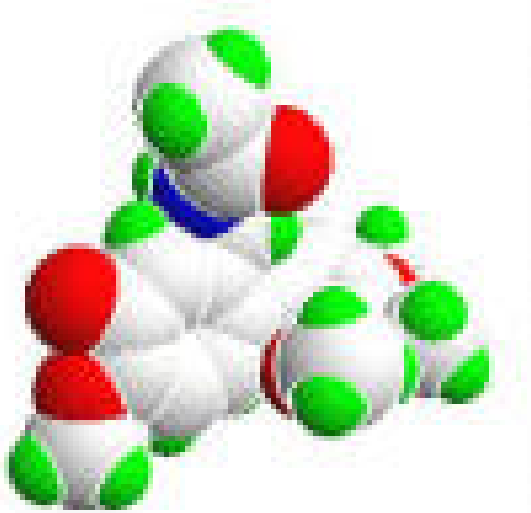
Roland Faller

Department of Chemical Engineering & Materials Science

UC Davis

NanoFocUL: Integrated Multiscale Modeling for the NanoSciences,
Oak Ridge, August 30, 2006

The Challenge of Length Scales



1 nm

Direct atomistic simulation

All information accessible

Coarse

Graining

0.5 m

Interesting properties

No direct accessible information

Multiscale Modeling

Multiscale Modeling means different things to different people

1. Using multiple connected models to represent different aspects of the same system

2. Modeling different aspects of one system

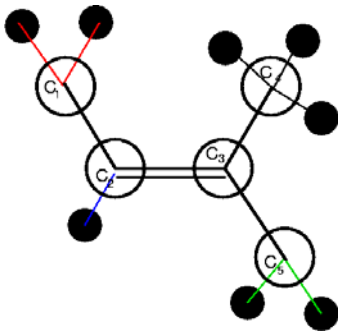
3. Simple large scale modeling with ad-hoc mapping

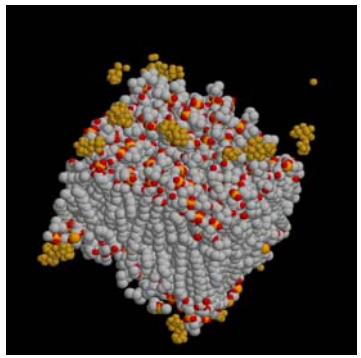
Overview

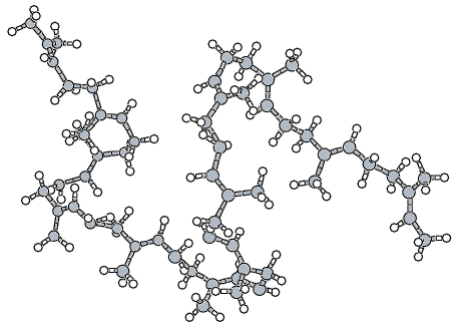
1. Molecular Dynamics using force fields
2. Optimization of Force Fields
3. Self Consistent Polymer Coarse Graining
4. Large Scale Polymer Simulations

Atomistic MD Simulations

- Every individual atom is represented in the simulation.







- Force-fields by optimization to reproduce density enthalpy of vaporization of small molecules; quantum-chemistry for the torsions; fixed bond lengths (SHAKE,LINCS)
- The simulation models are verified against experiments.
- Only short time and length scales are accessible (< 100ns, < 20nm).
- Constant temperature and pressure
- Experiments to directly compare with: NMR, ESR, neutron scattering

How to get the models for atomistic MD

1. Just take them off the shelf

2. Tune them by hand to your specific problem

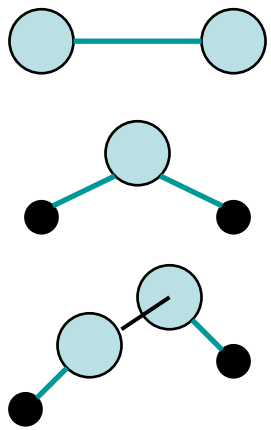
3. Automatically tune them against experimental data

Atomistic MD: Intramolecular Forces

- Total pair energy breaks into a sum of terms

$$U(\mathbf{r}^N) = \underbrace{U_{str} + U_{bend} + U_{tors}}_{\textit{Intramolecular only}} + U_{cross}$$

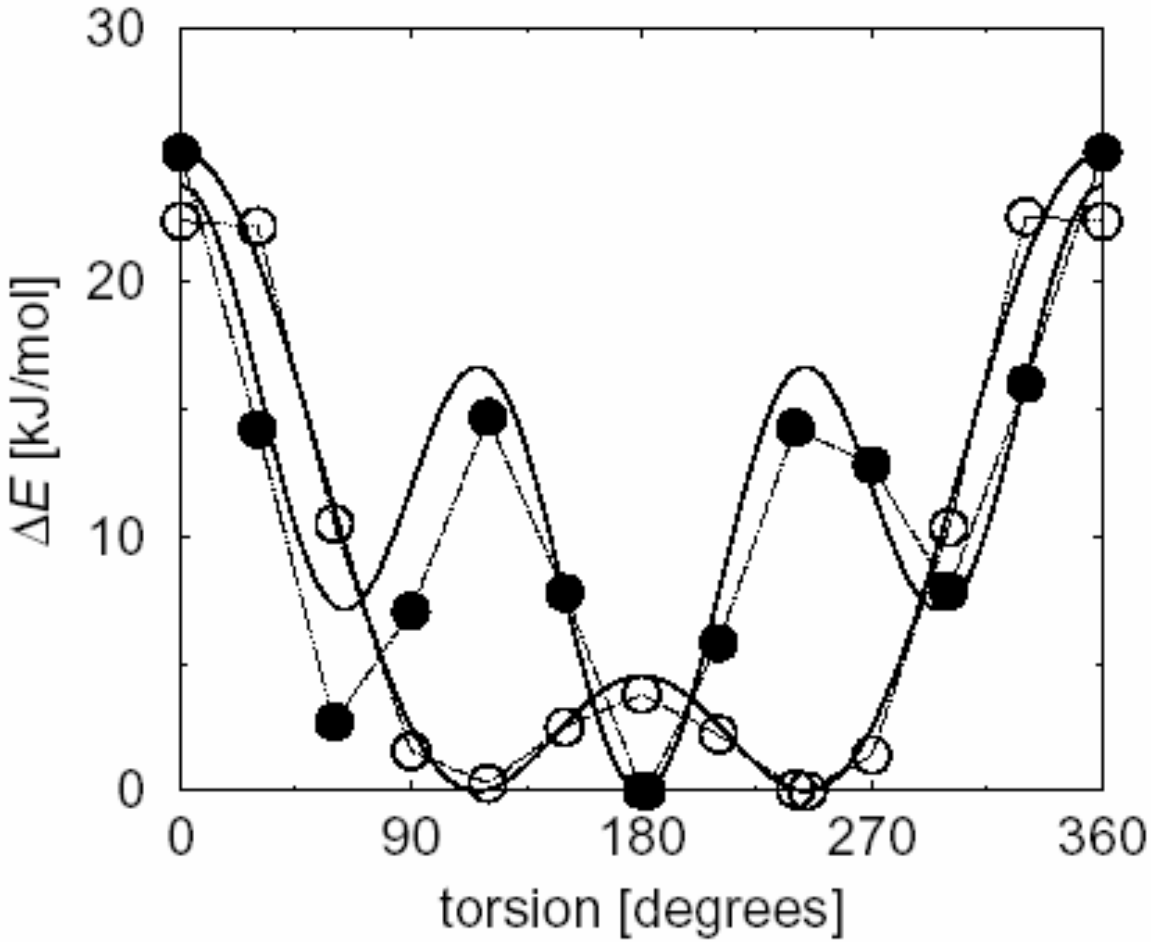
- U_{str} stretch
- U_{bend} bend
- U_{tors} torsion
- U_{cross} cross



Quantum Chemistry for Torsions

Torsion energies are calculated using quantum chemistry.

Fourier series is fitted to the results and used in atomistic simulations



Non-bonded Terms

- Electrostatic interactions (Coulomb's Law)

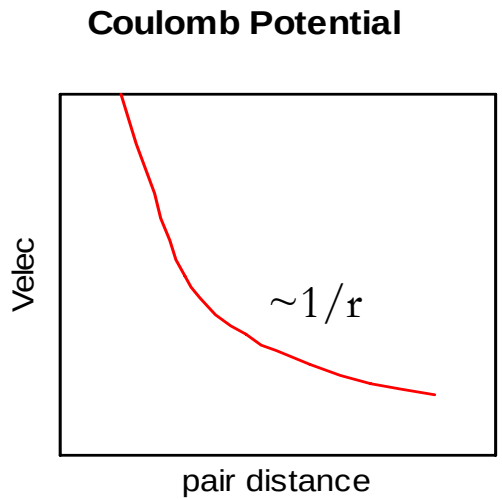
$$V_{elec} = \frac{1}{4\pi\varepsilon}\sum_{i<j}\frac{q_i q_j}{r_{ij}}$$

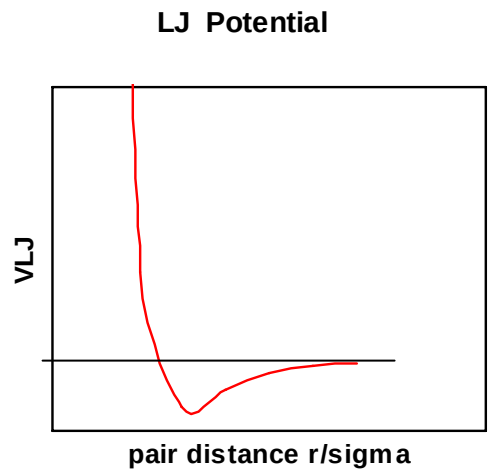
- Lennard-Jones interactions

$$V_{LJ} = \sum_{i<j} 4\varepsilon_{ij}\left[\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^{6}}{r_{ij}^{6}}\right]$$

- Combination Rules for LJ

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$$





Optimization Preliminaries: I Discrete Target Observables

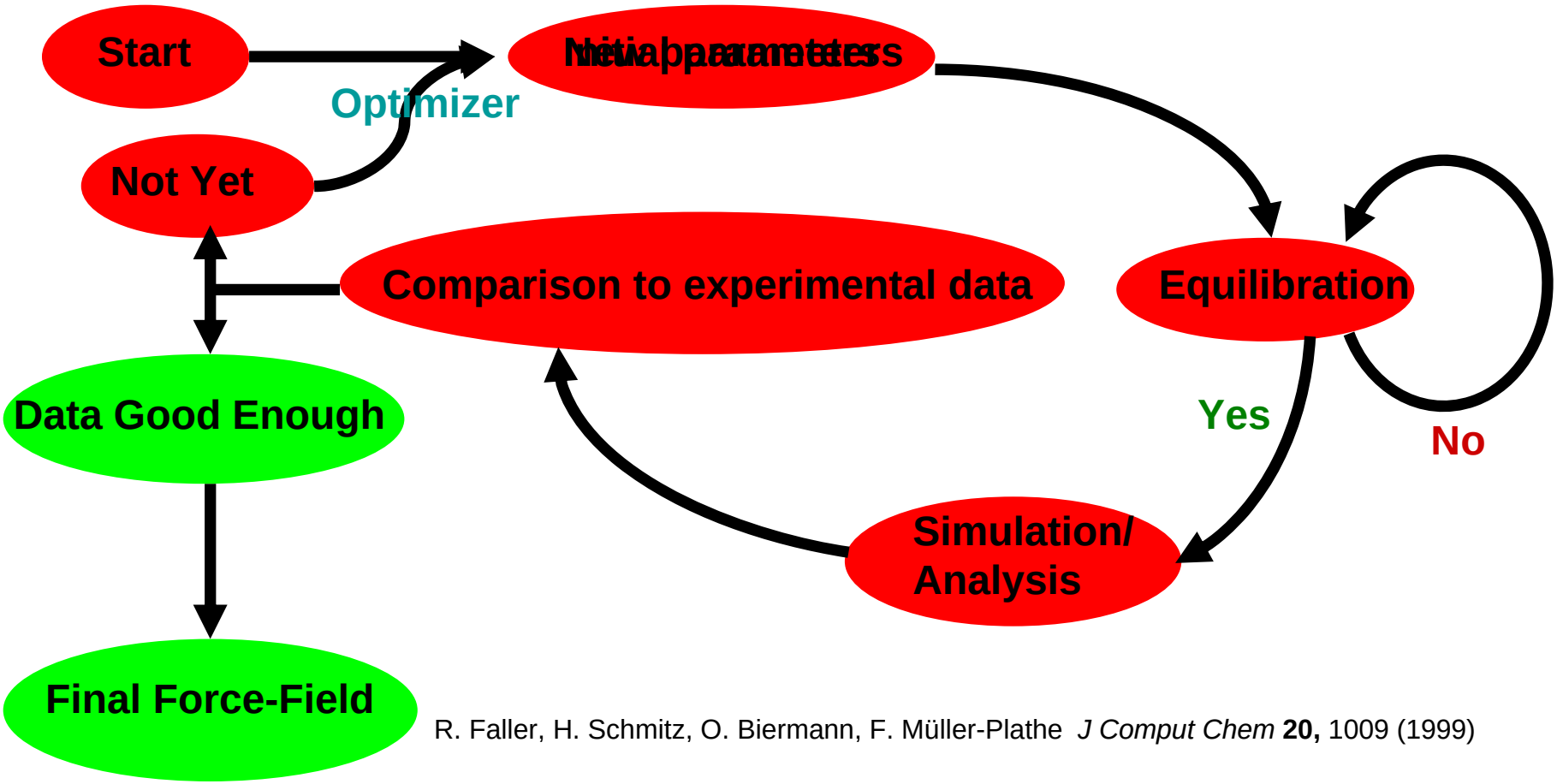
Define a *single valued* penalty function

$$f(\mathbf{p}) = \left[\sum_i w_i \left(1 - \frac{A_i(\mathbf{p})}{A_{i,\text{target}}} \right)^2 \right]^{1/2}$$

$\mathbf{p} = \{p_k\}$	set of force field parameters, e.g. ε, σ
A_i	observable, e.g. ρ, H_{vap}
w_i	weighting factor

Every evaluation of the penalty function $f(\mathbf{p})$ is a *whole MD* equilibration and simulation *cycle*

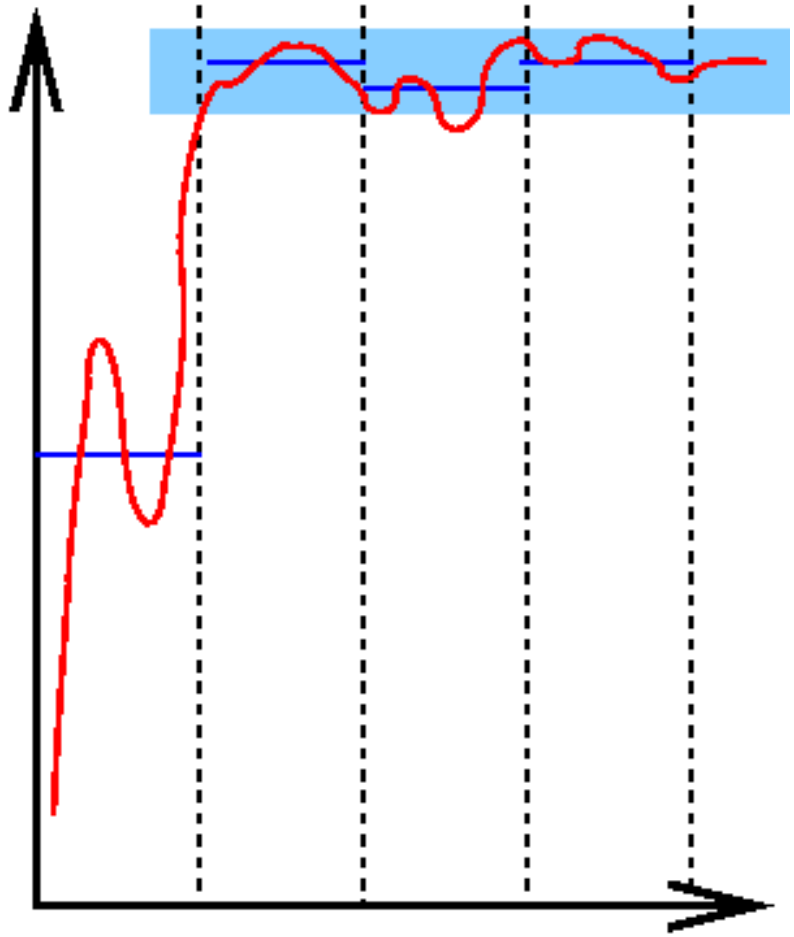
Automatic force-field development for small molecules



R. Faller, H. Schmitz, O. Biermann, F. Müller-Plathe *J Comput Chem* **20,** 1009 (1999)

Automatic Equilibration Detection

Only monitor density, automatically cut in pieces and sub averages compared



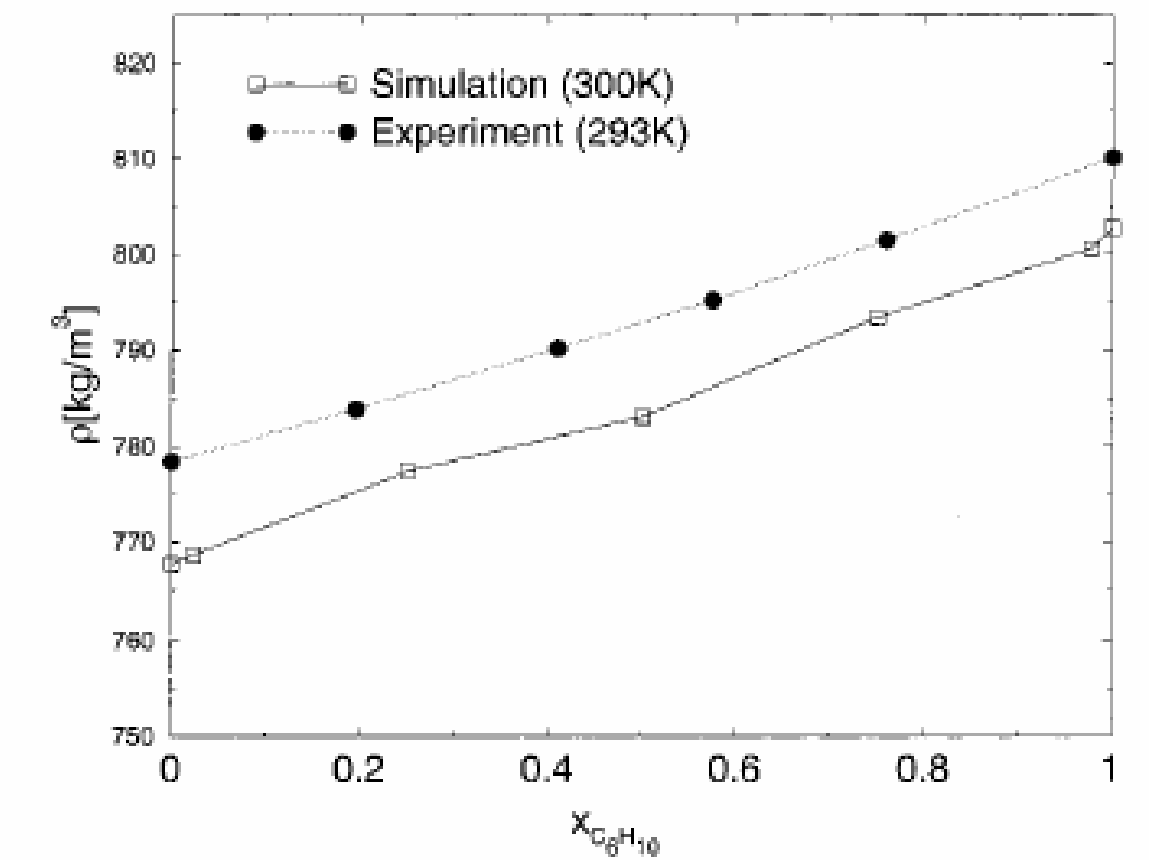
Implementation as a Shell Script

- A tcsh script runs the MD program
- small helper programs process the in and output files (written in C/C++)
- script evaluates target function and performs simplex
- can use any MD program which starts from a UNIX shell (YASP, GROMACS, DL_POLY etc)

Sample Files processed by script

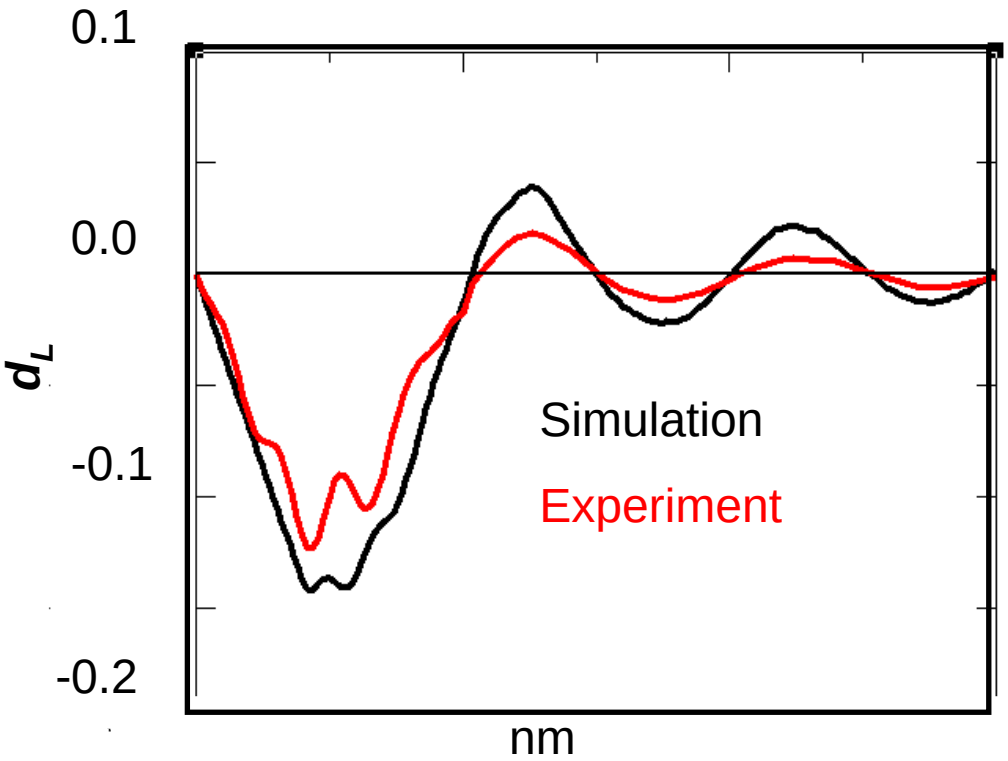
##	ϵ_C	σ_C	ϵ_H	σ_H	f_{target}	ΔH_{vap}	ρ
4							
0.291643	0.339215	0.154545	0.258859	0.030287	29.42	636.1	
0.290554	0.340351	0.151371	0.260571	0.052871	28.88	626.5	
0.290167	0.340656	0.151116	0.260825	0.057492	28.81	623.8	
0.290545	0.341183	0.149968	0.260762	0.043120	29.18	629.6	
0.290421	0.341161	0.150191	0.260763	0.051831	28.94	626.2	

Thermodynamics: Density

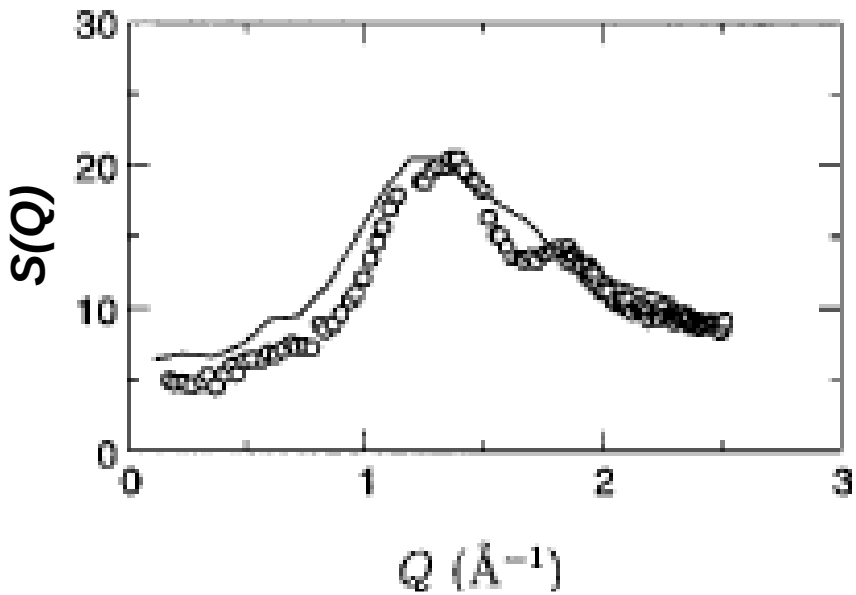


H. Schmitz, R. Faller, F. Müller-Plathe *J Phys Chem* **B** 103, 9731 (1999)

Atomistic Statics: Comparison to Neutron Scattering



Solvent Cyclohexane

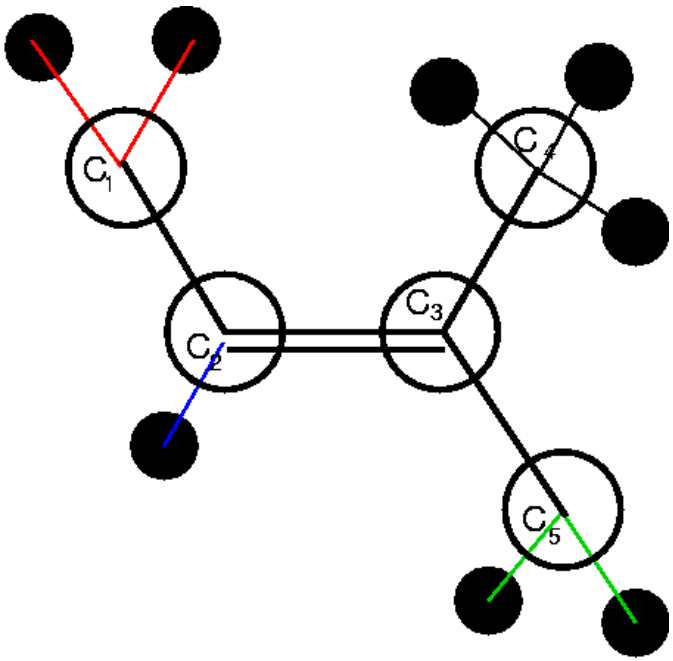


Polycarbonate melt

J. Eilhard *et al*. *J Chem Phys* **110**, 1819 (1999)

H. Schmitz, R. Faller, F. Müller-Plathe *J Phys Chem B* **103**, 9731 (1999)

Atomistic Dynamics: Comparison to NMR experiments



Reorientation Times

	Simulation	Experiment
C_1-H	0.42 ps	0.40 ps
C_2-H	0.16 ps	0.17 ps
C_5-H	0.18 ps	0.48 ps

NMR measures the reorientation of bond vectors.

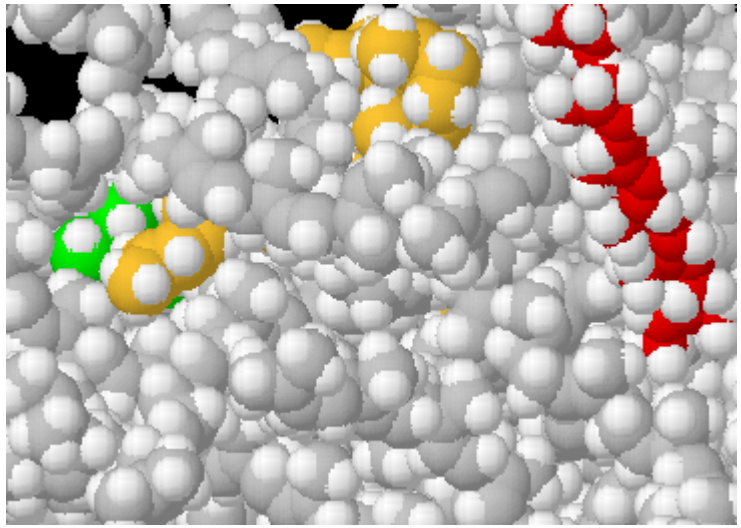
Simulations reproduce data reliably.

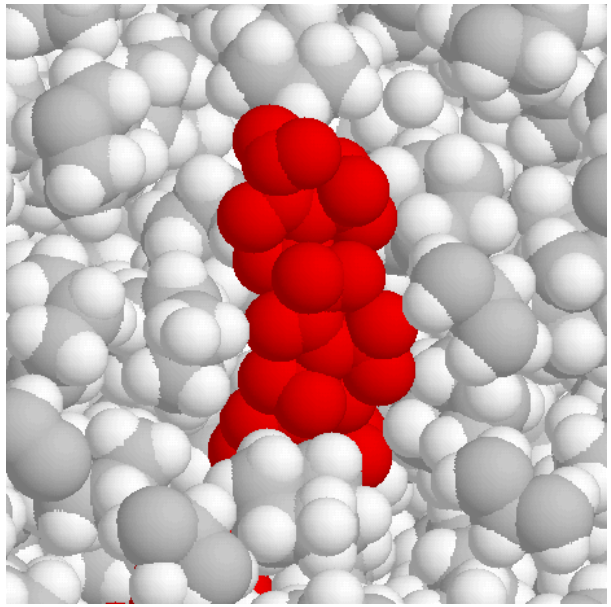
D. de la Batie *et al. Macromolecules* **22**, 122 (1989)

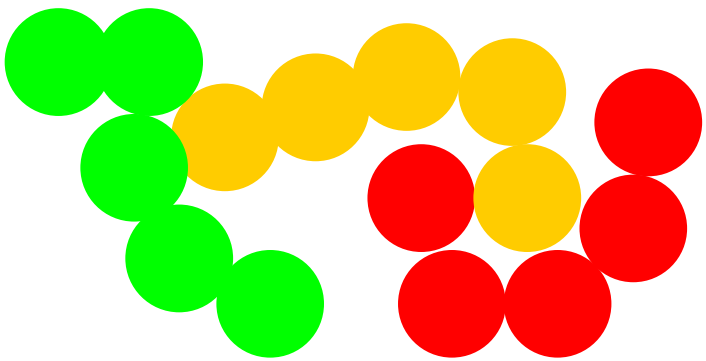
R. Faller *et al. Macromolecules* **34**, 1436 (2001)

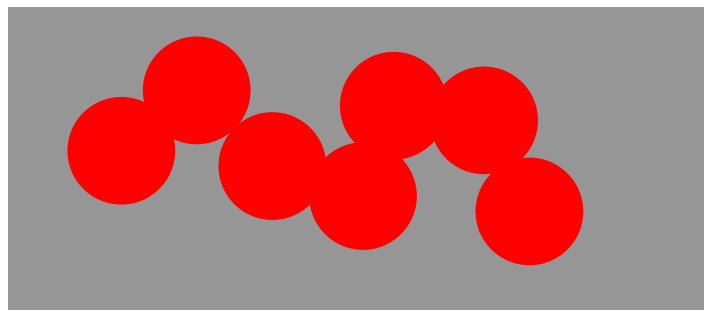
M. Doxastakis et al. *J Chem Phys* **119**, 6883 (2003)

Simulation of Large Scale Melts and Solutions









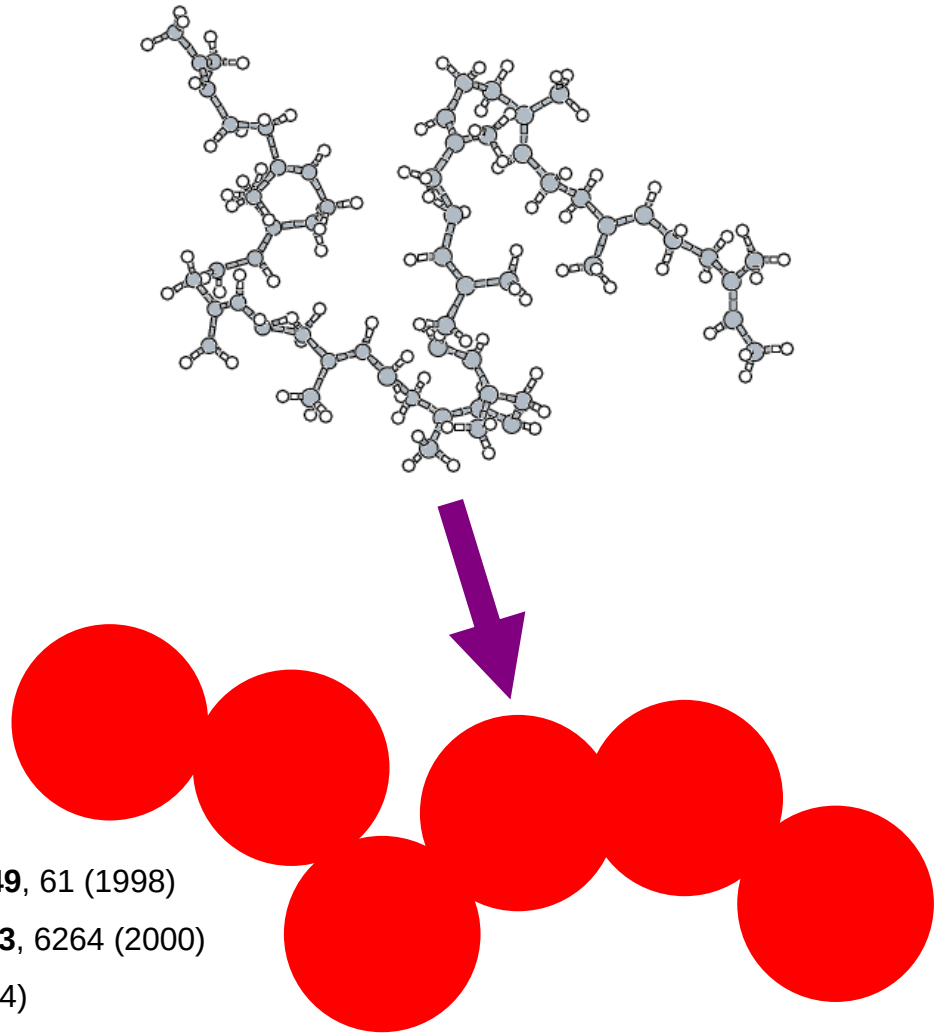
We want to simulate big melts and solutions of polymers without losing their chemical identity. We have to get rid off a number of interactions.

Mapping of Different Models

Two models represent the same system if they yield the same properties on the large scale.

Atomistic model defined “correct”, coarse-grained model optimized against properties of atomistic model.

Typical properties: radial distribution function, structure factor and bond angle distribution on the meso-scale



W. Tschöp et al. *Acta Polymer* **49**, 61 (1998)

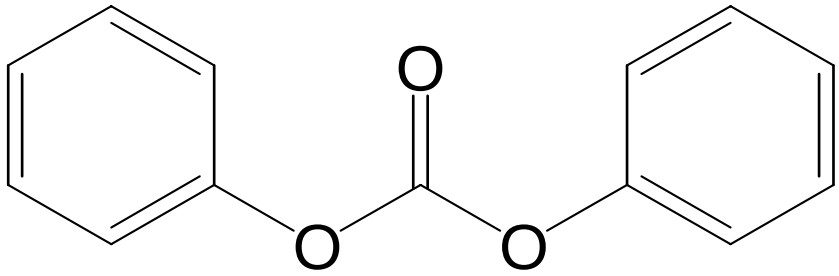
H. Meyer et al. *J Chem Phys* **113**, 6264 (2000)

R. Faller *Polymer* **45**, 3869 (2004)

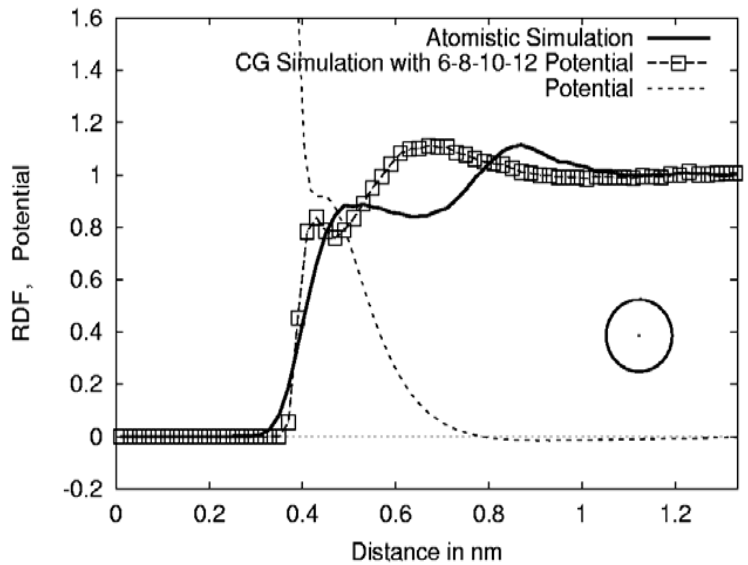
R. Faller *Rev Comp Chem* **23** in press (2007)

How many (isotropic) mapping points?

Diphenylcarbonate



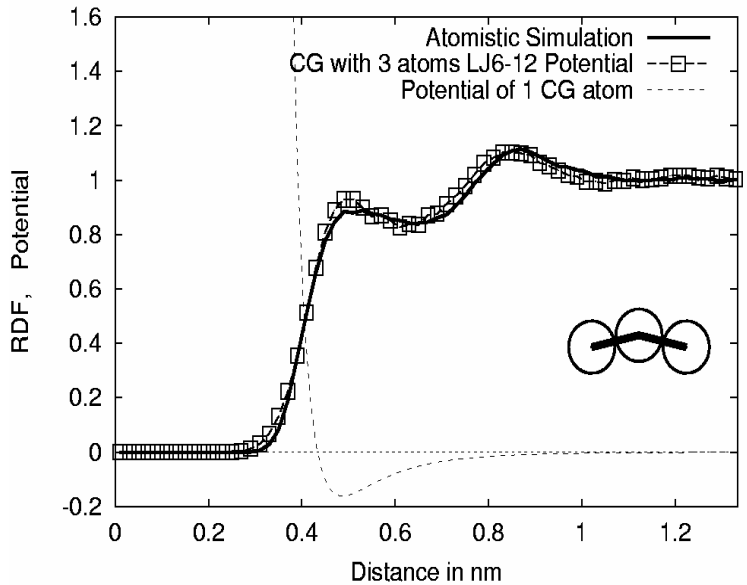
1:1 Mapping



$$V(r) = \frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} + \frac{C_{12}}{r^{12}}$$

Does not work!

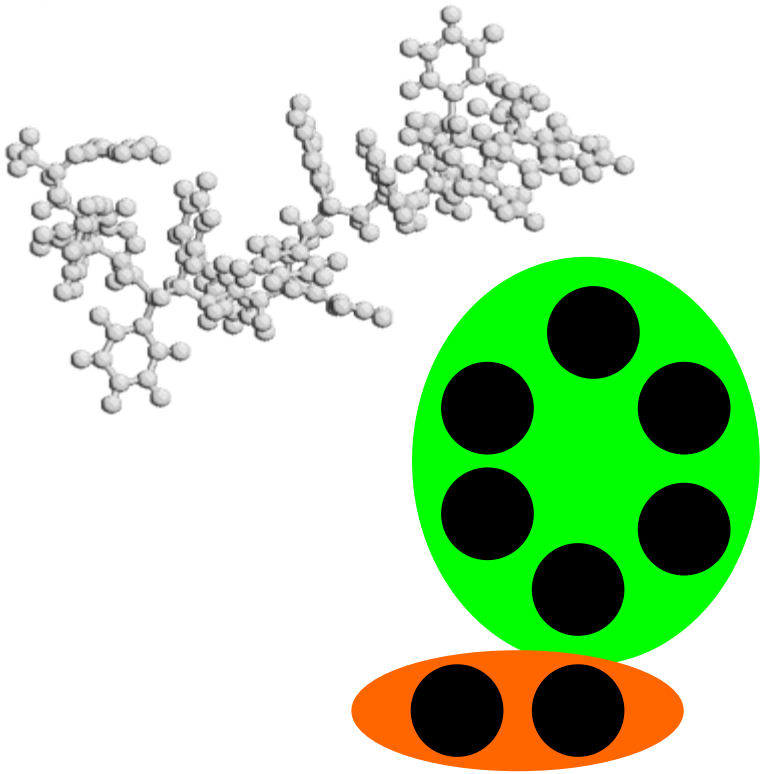
1:3 Mapping



$$3\times \quad V(r) = \frac{C_6}{r^6} + \frac{C_{12}}{r^{12}}$$ Works!

H. Meyer *et al. J Chem Phys* **113**, 6264 (2000)

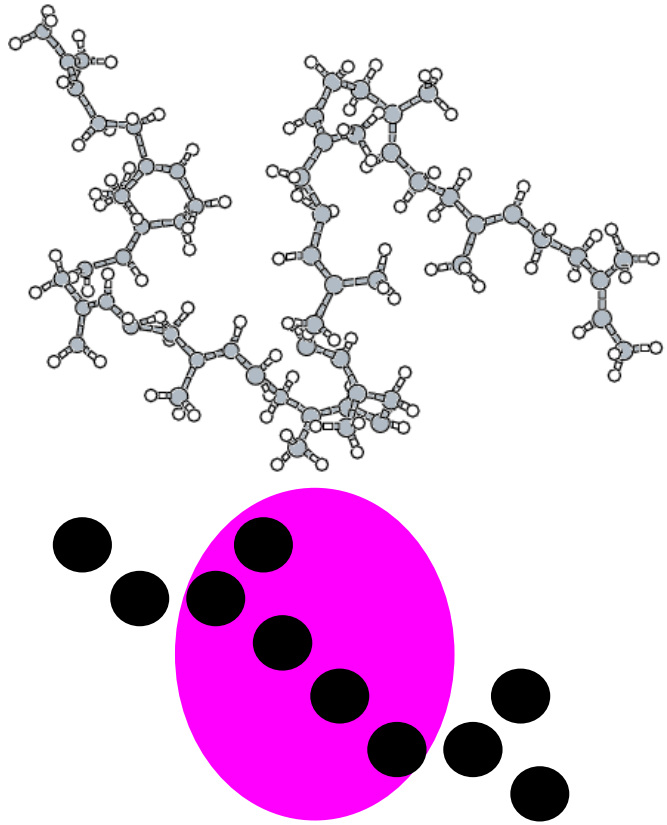
How many mapping points for polymers?



Polystyrene

one or two interaction centers per monomer,

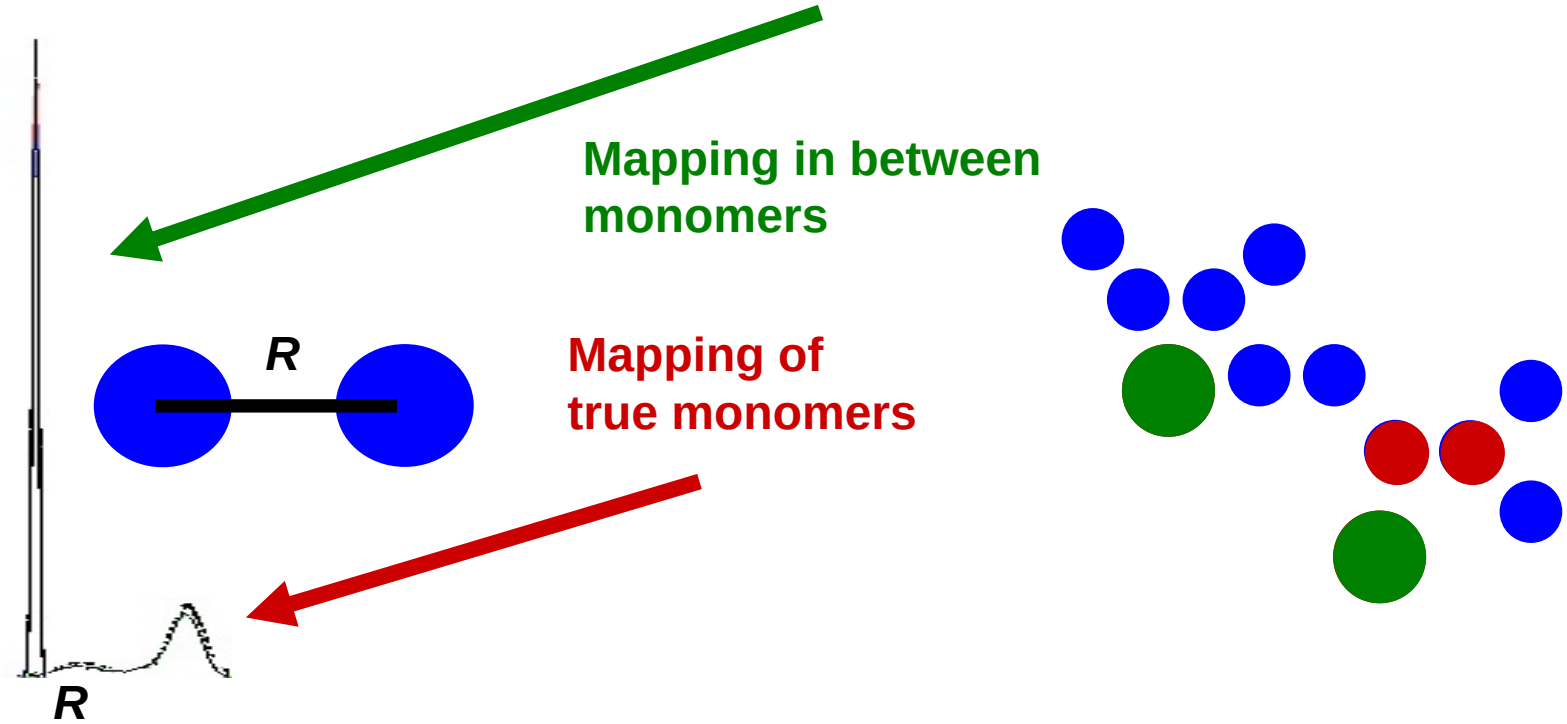
backbone and/or sidegroup



Polyisoprene

one interaction center per monomer

Location of mapping points

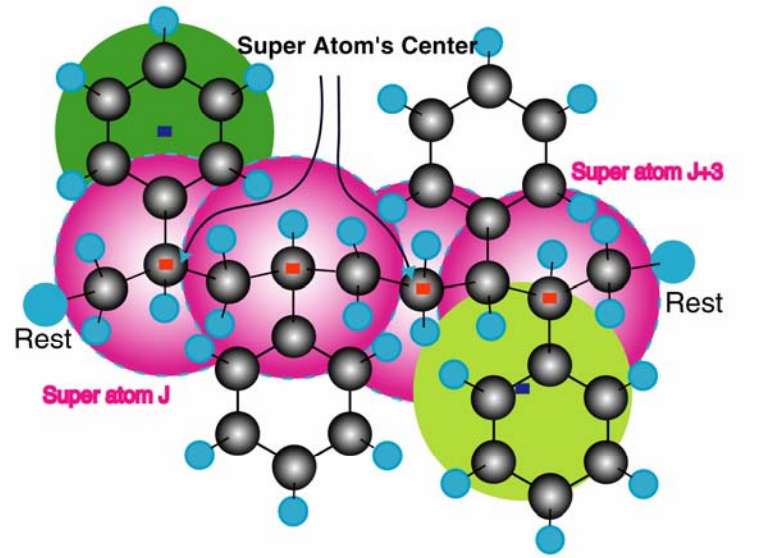


Good mapping means that bond and angle distributions (on the coarse-grained level) are narrow and have single maxima. Bonds can almost always be achieved to be very well harmonic.

Additionally spherical units have the advantage of isotropic potentials.

R. Faller, *Polymer* **45**, 3869 (2004)

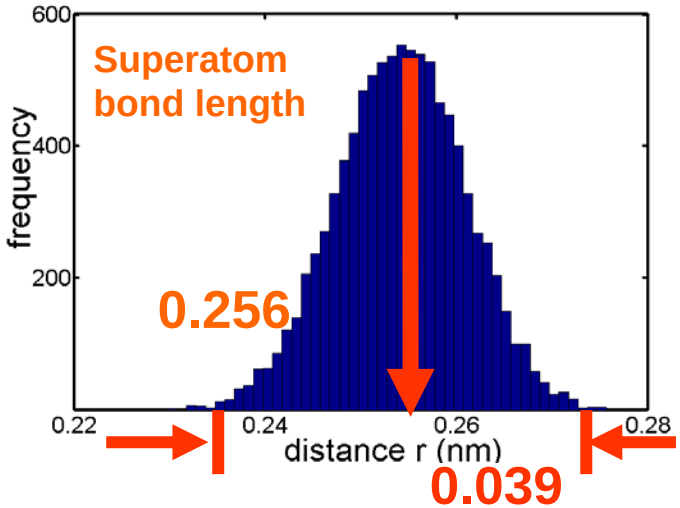
Superatom Centers

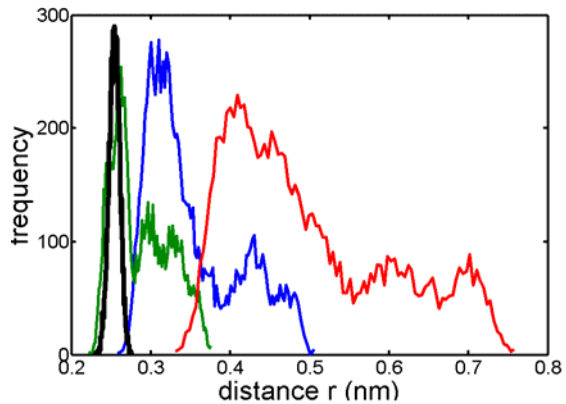


PS superatom centers

Good mapping means that bond and angle distributions are narrow and have single maxima. Bonds can almost always be achieved to be very well harmonic.

PS Superatom





Q. Sun, R. Faller *Comp & Chem Eng* **29**, 2380 (2005)

Q. Sun, R. Faller *Macromolecules* **39**, 812 (2006)

Optimization Preliminaries
Target Functions

Define penalty function as integral over target function

$$f\{V(\mathbf{r})\} = \int w(\mathbf{r})[X(\mathbf{r}) - X_{\text{target}}(\mathbf{r})]^2 \, \mathrm{d}\mathbf{r}$$

V(r) Interaction Potential

X(r) Distribution function, e.g. *g(r), H(ϕ)*

w(r) Weighting function, typically $w(r) \propto e^{-r}$

The Structure Difference Method

1. Simulate a starting model (guessed from similar problems or potential of mean force)

2. Analyze the observables (typically radial distribution function and bond angle distribution) and determine the discrepancy

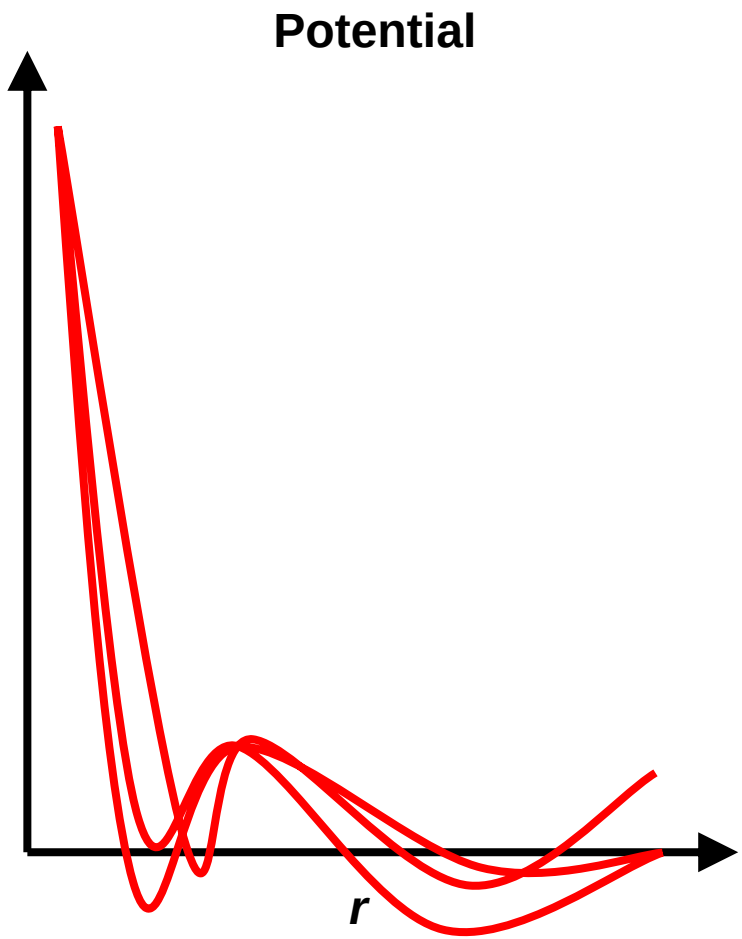
3. Boltzmann invert the difference of the radial distribution functions (Determine the relative free energies)

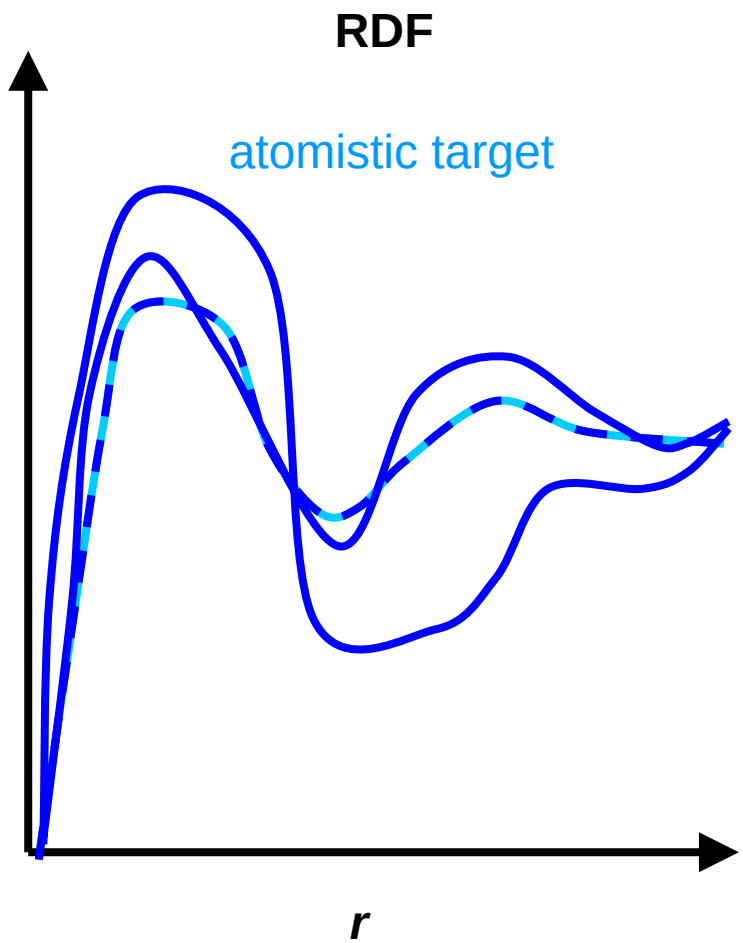
4. Add the difference in free energy to the potential and repeat.

➔ Model on the meso-scale (between monomers):

Harmonic bonds (by choice of mapping points), numerical potential for bond angles and non-bonded interactions; no coarse-grained torsion potential

The Structure Difference Method

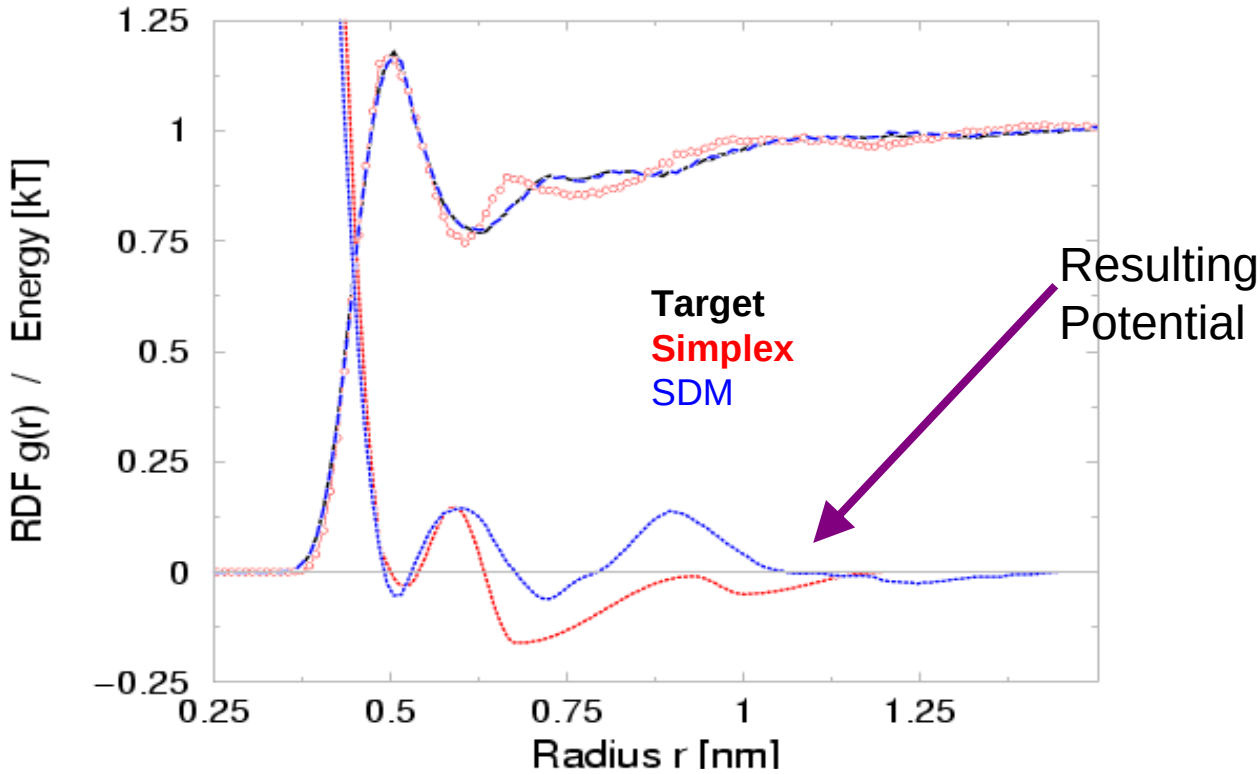




R. Faller, D. Reith *Macromolecules* **36**, 5406 (2003)

R. Faller *Polymer* **45**, 3869 (2004)

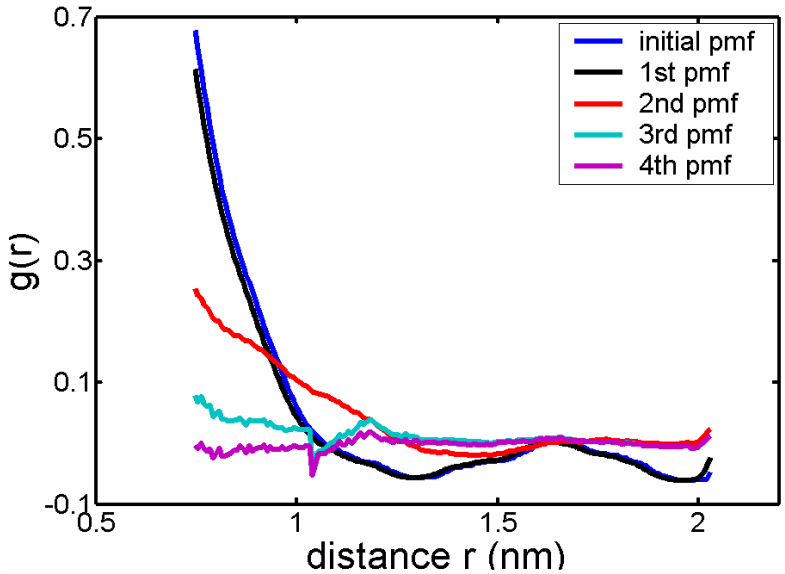
Example: Polyisoprene Homopolymers



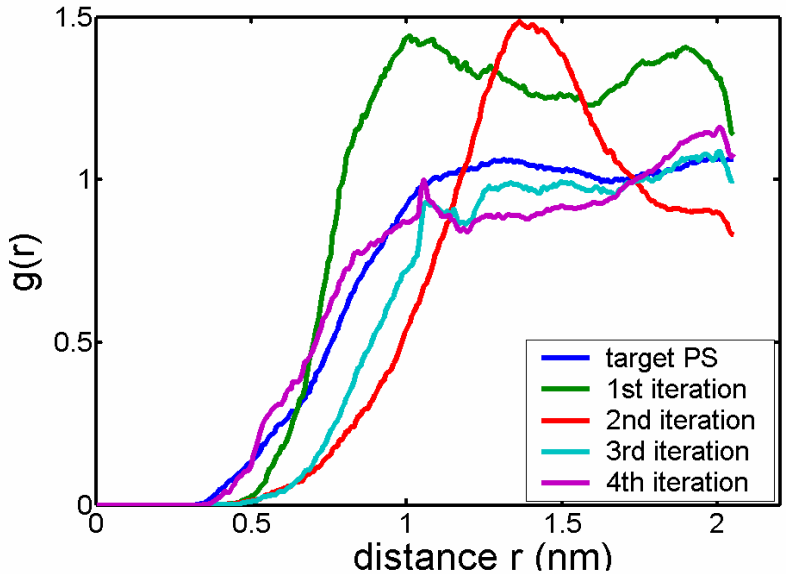
We are able to completely reproduce the radial distribution function of the atomistic model on the large scale by the structure difference method.

SDM for Pure Polystyrene

Potential of mean force of PS



g(r) of PS

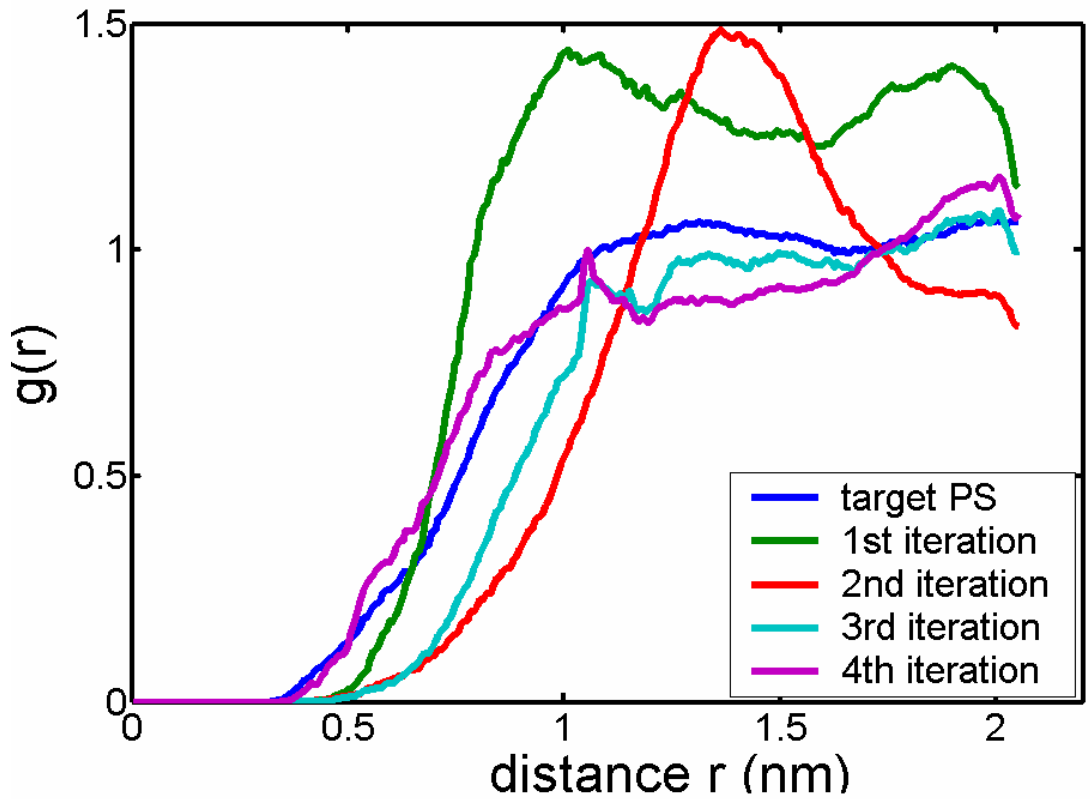


Weighting function: $\omega(r) = \exp(-r)$

is used to penalize deviations at small distances.

Q. Sun, R. Faller *Comp & Chem Eng* **29**, 2380 (2005)

Polystyrene in a 1:1 mixture

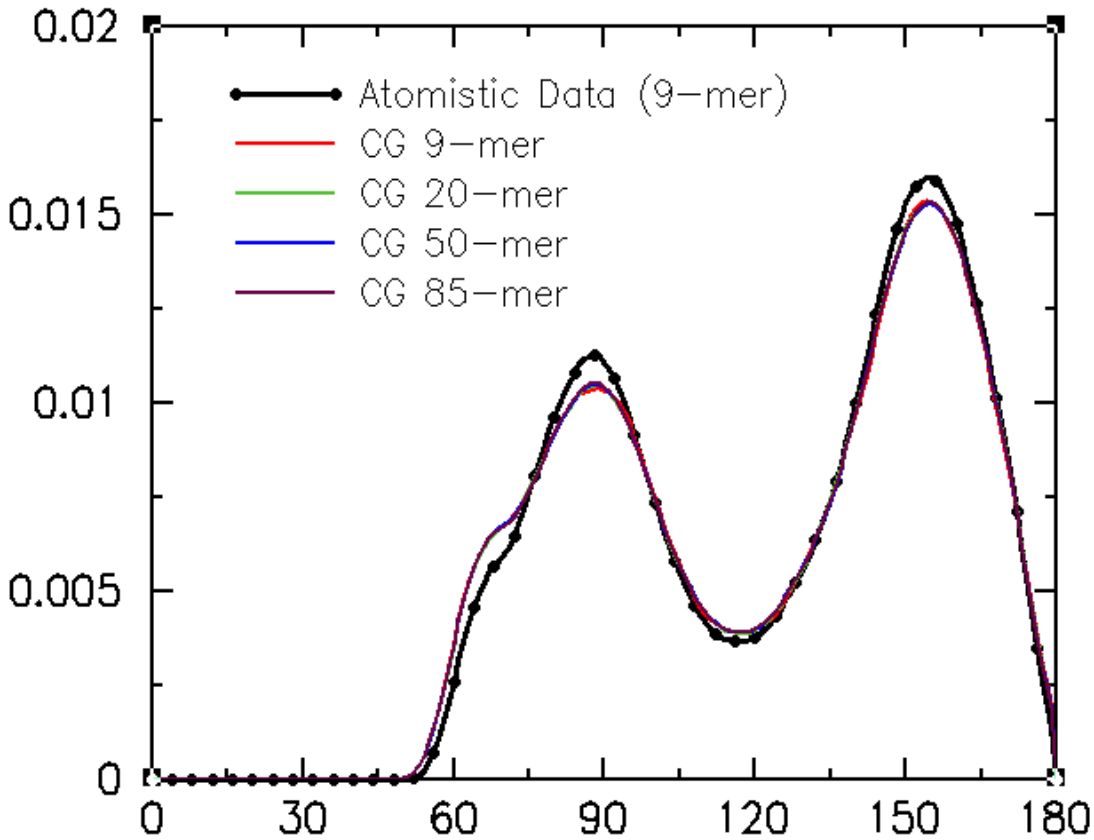


Radial distribution function of PS

Weighting function: $\omega(r) = \exp(-r)$

is used to penalize deviations at small distances.

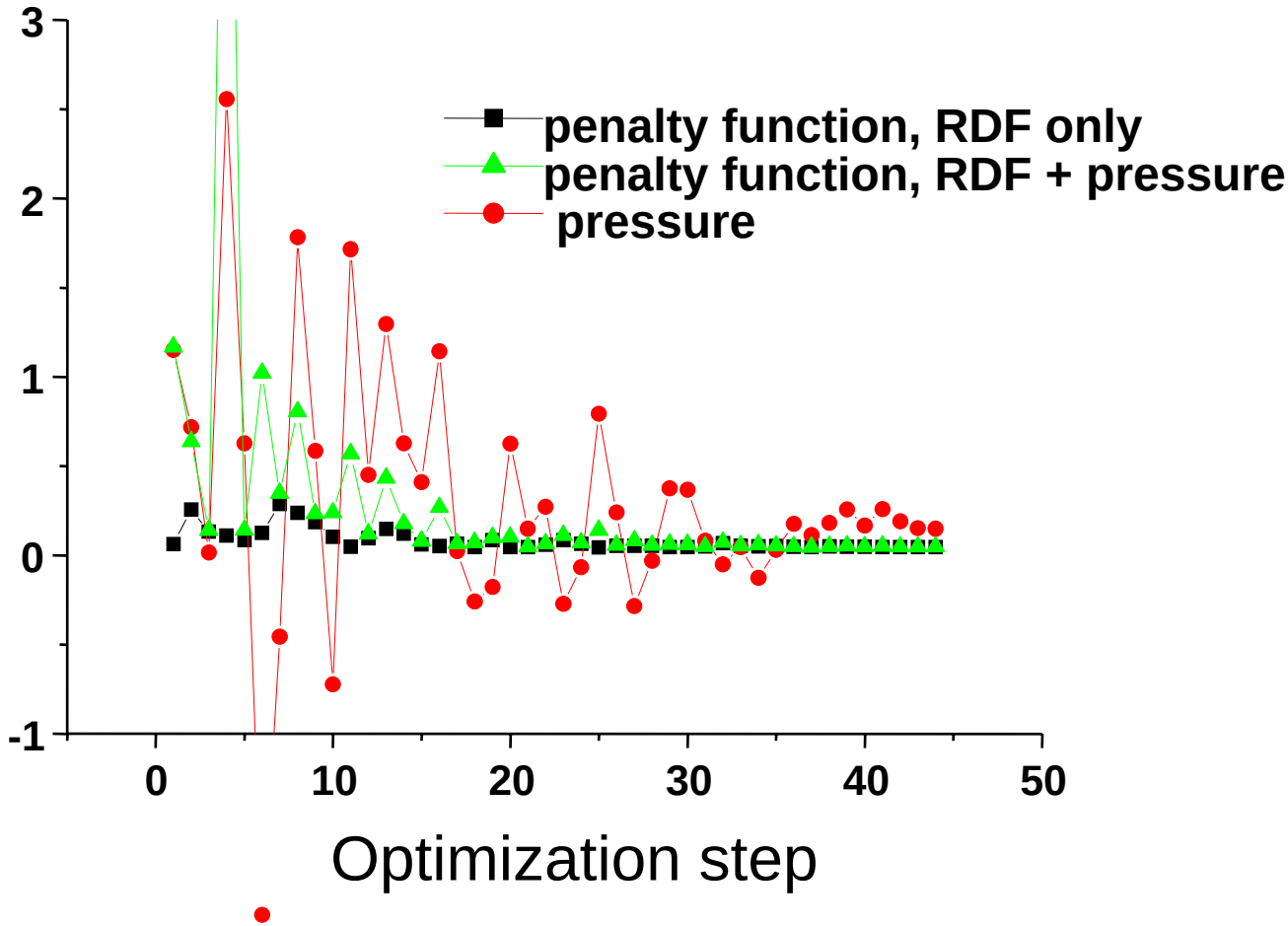
Scaling up the Chain Length



The bond angle distribution remains correct for different chain lengths ***N***.

Combining Penalty Functions for Structure and Thermodynamics

Polyvinylalcohol



D. Reith *et al J. Comput Chem*. **24**, 1624 (2003).

Implementation as a Shell Script

- A tcsh script runs the MD program
- small helper programs process the in and output files (written in C/C++)
- script evaluates rdf and target function and performs inversion
- can use any MD program which starts from a UNIX shell (here we use md_spherical, fully numerical)

Behavior of Long Polymer Chains

Melt

Random walk

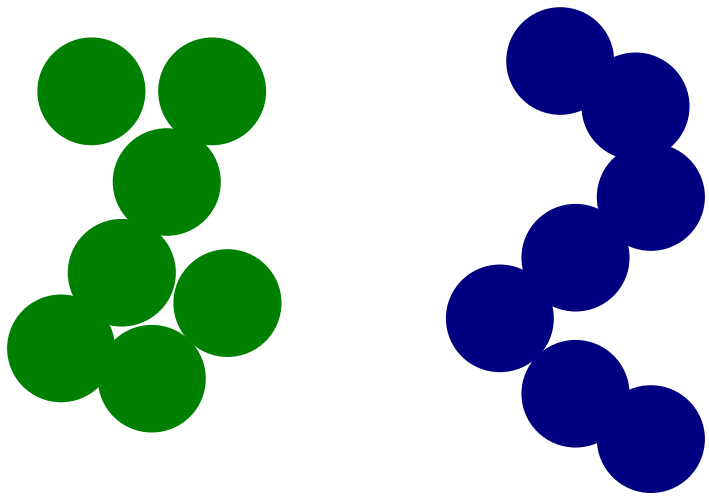
$$R_g \propto N^{1/2}$$

Good Solution

Self avoiding walk

$$R_g \propto N^{0.588}$$

On large scales chain can fold back onto itself.

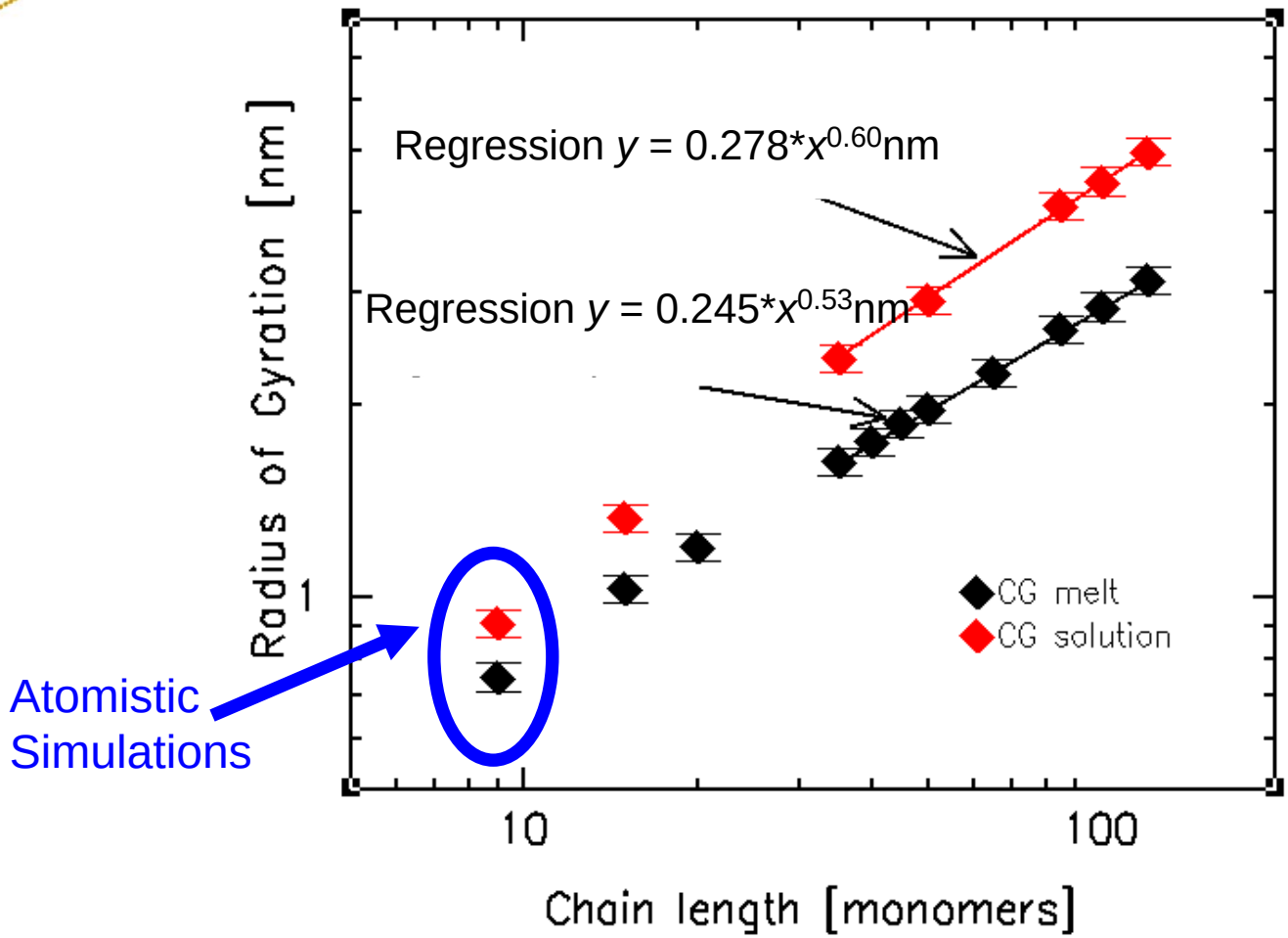


Chain avoids itself leading to a **global** directional bias.

Exponent can be measured by investigating different chain lengths and by static neutron scattering of long chains.

Need for independent models in melt and solution.

Simulated Static Behavior in Melt and Solution



Single chain structure in melt and solution comes out to obey correct scaling for long chains although optimized against short chains, extrapolation about 30% to long against experiments.

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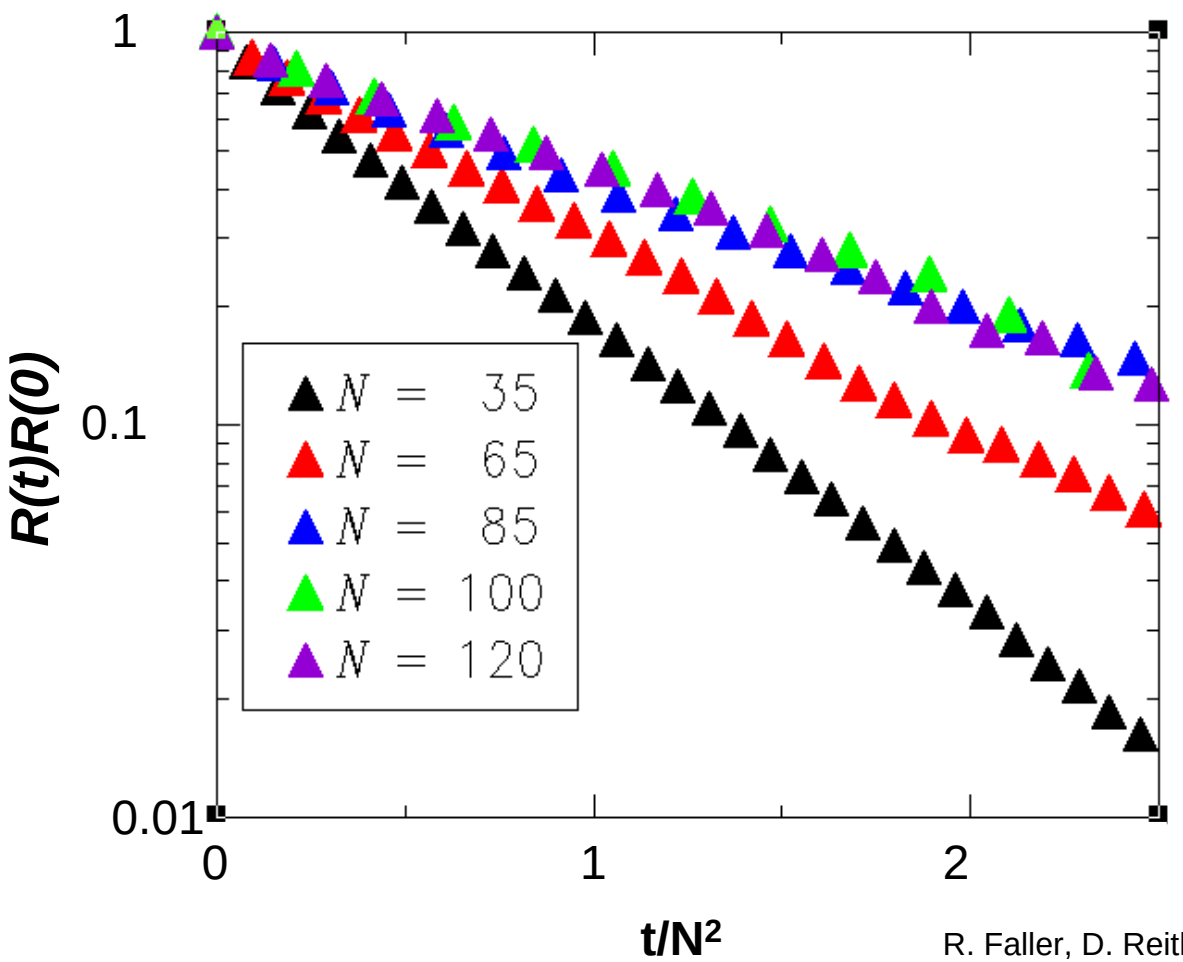
Rouse Behavior of Coarse-Grained Polyisoprene



Dynamic Investigations, Brownian Dynamics on coarse grained scale (using numerical potrtential).

Rouse behavior well obeyed above ***N***=85 for systematically coarse-grained model. The entanglement length is not yet reached.

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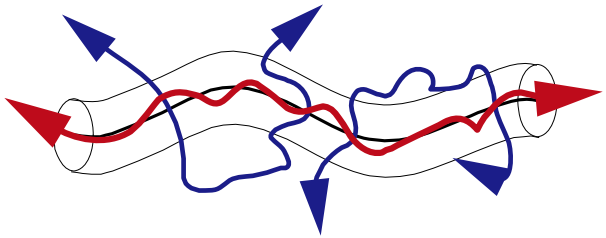
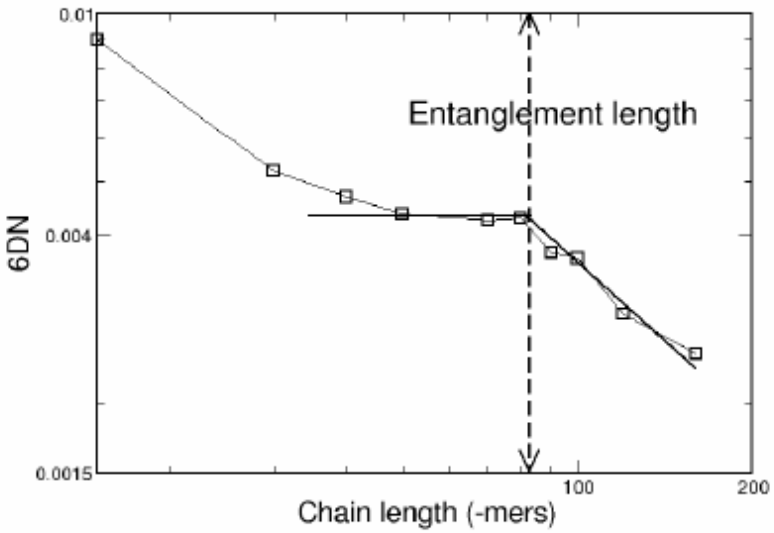
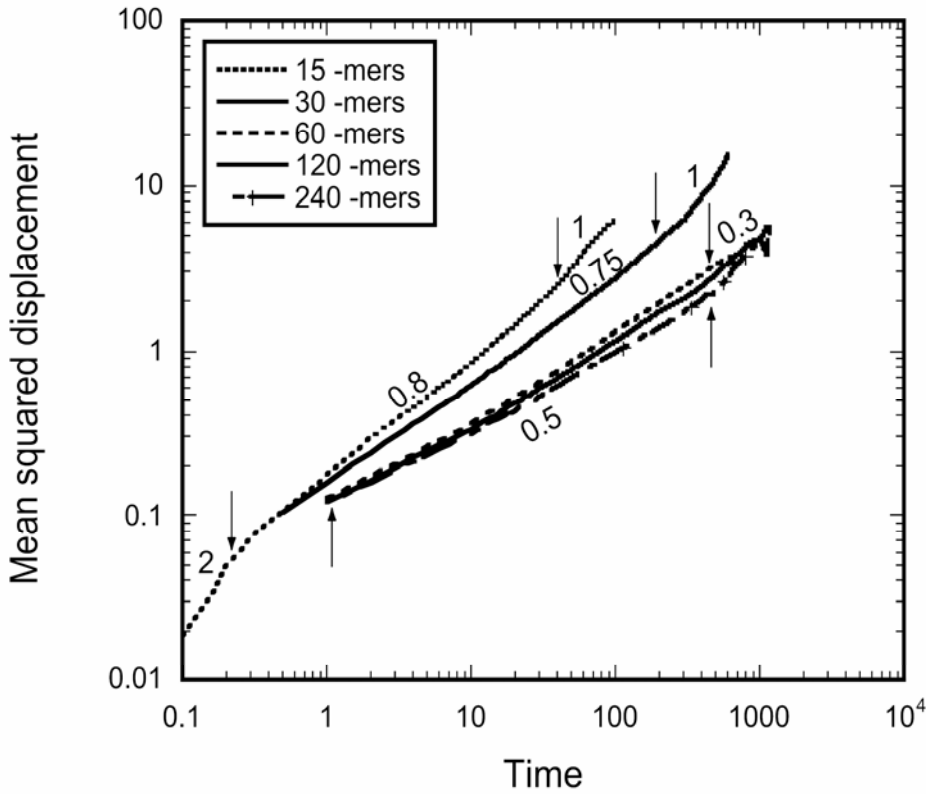
Application of the mesoscale model

Entanglement length of PS:







We see with the 240mers onset of reptation behavior, Entanglement length underestimated by a factor of 2

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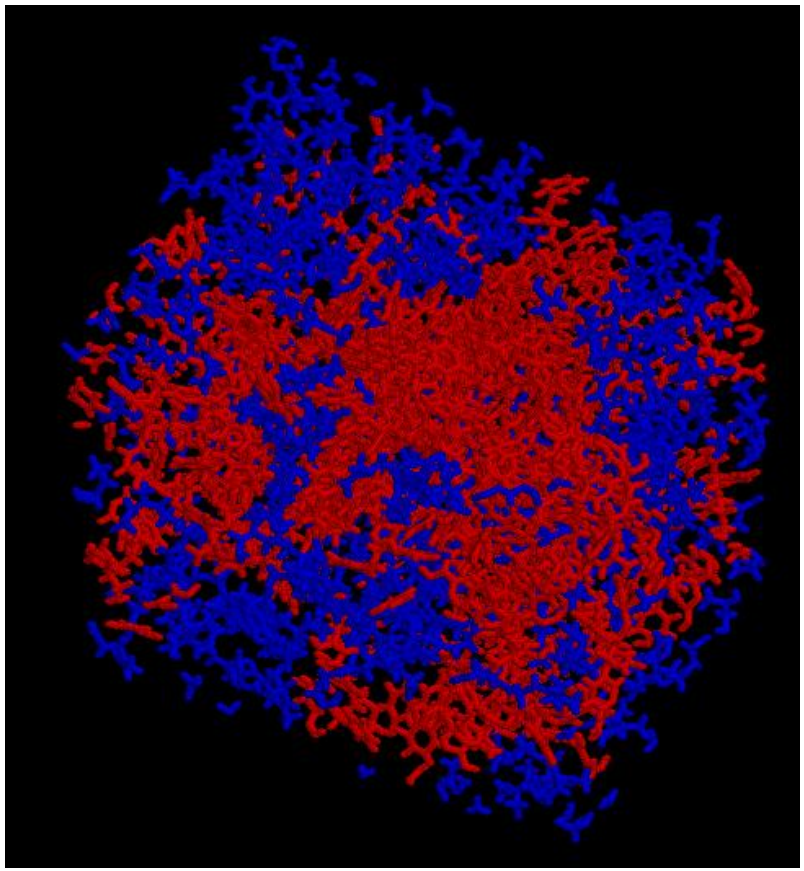
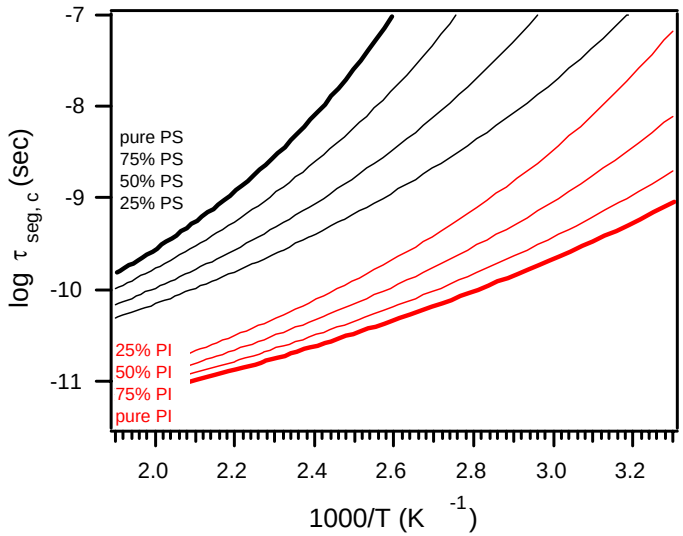
Mixtures of Polymers



Atomistic Simulations of PI-PS mixtures

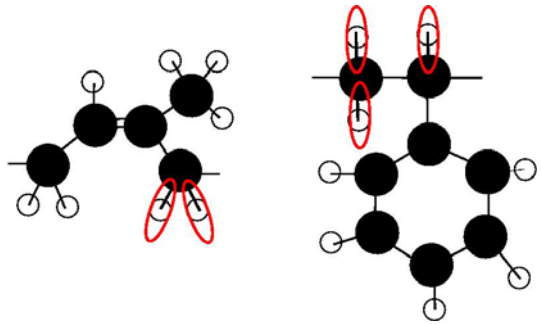
PS red, PI blue

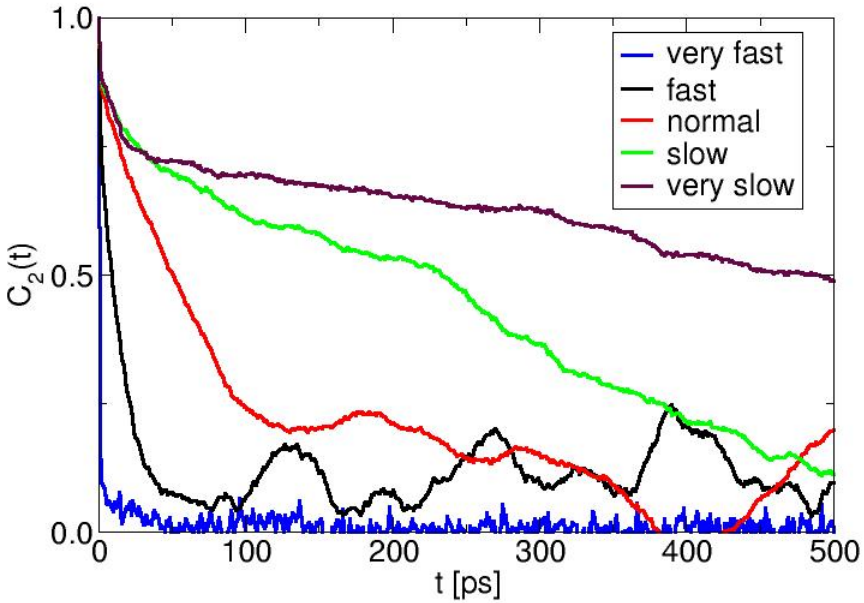
PS is a good glass former, whereas PI is mostly in the melt, wide difference in glass transition temperature

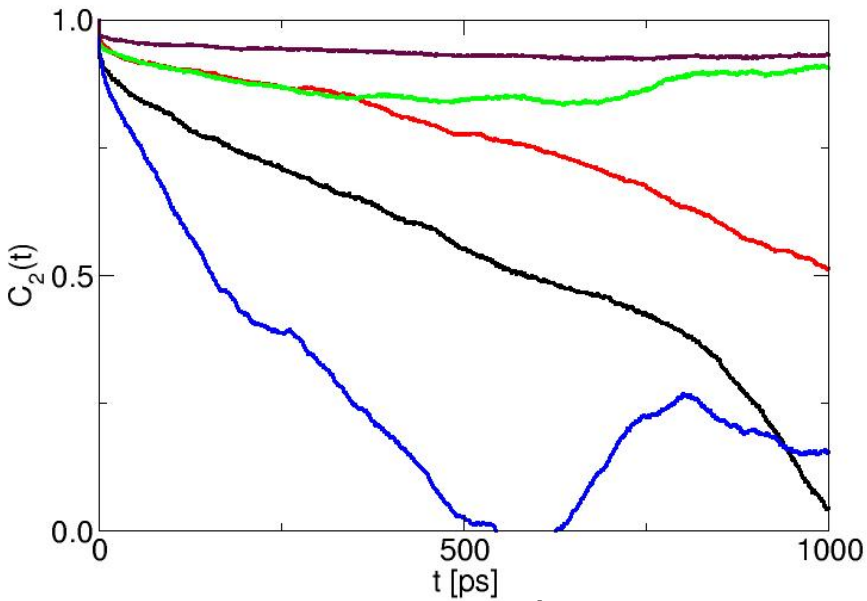


Correlation times, courtesy M. D. Ediger, Univ. of Wisconsin

Dynamic Heterogeneity in Mixtures







Dynamics of segments of the same type can vary over 2 order of magnitude

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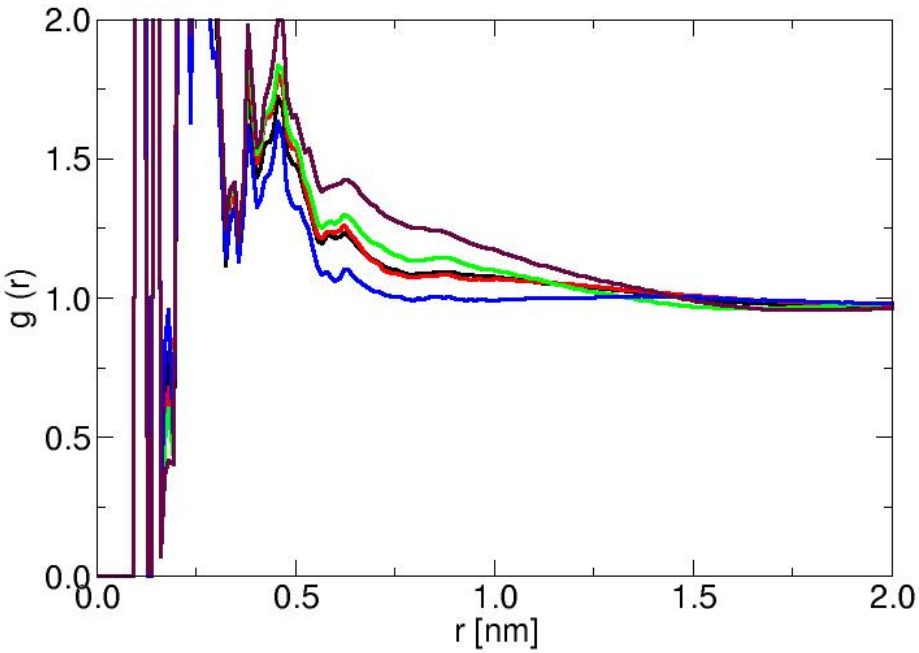
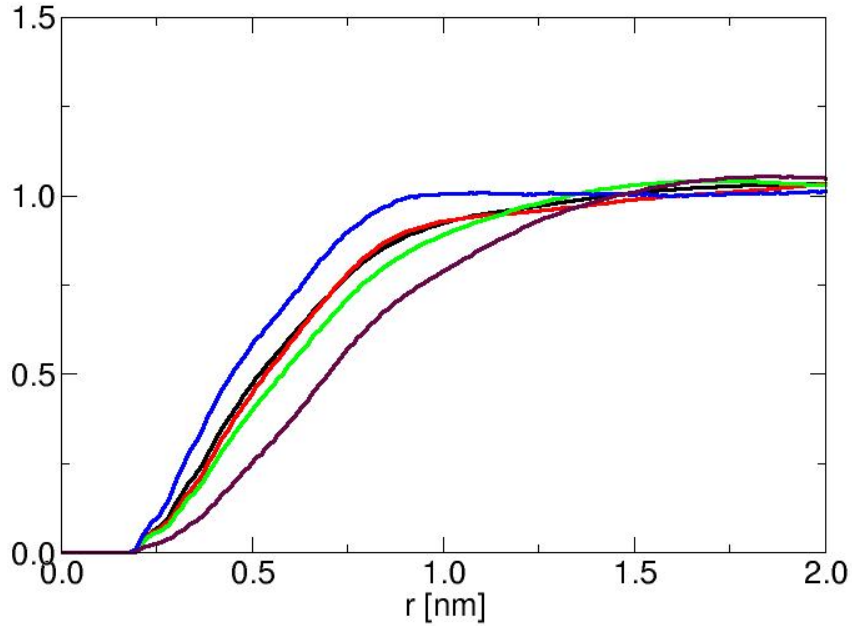
Correlation Statics – Dynamics PS





PS-PS

PS-PI

very fast
fast
normal
slow
very slow

Fast (PI) neighborhood leads to fast segments

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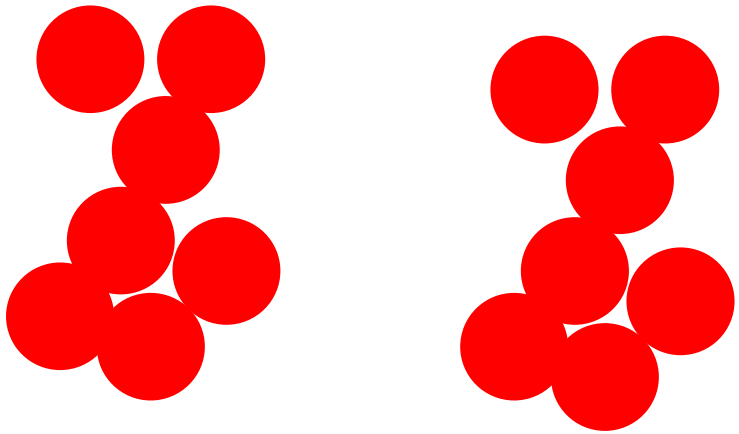
Technical Points Mixtures

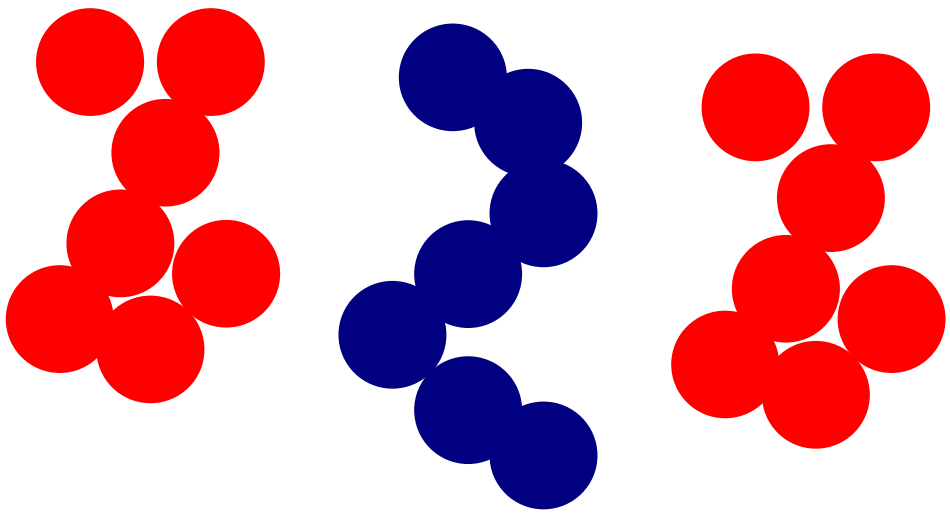
- Binary Mixture: 3 Target Functions
- Two possible strategies: Parallel, Serial
- Serial more efficient as self RDFs (and self potentials similar to homo) -> focus first on hetero

Mixtures

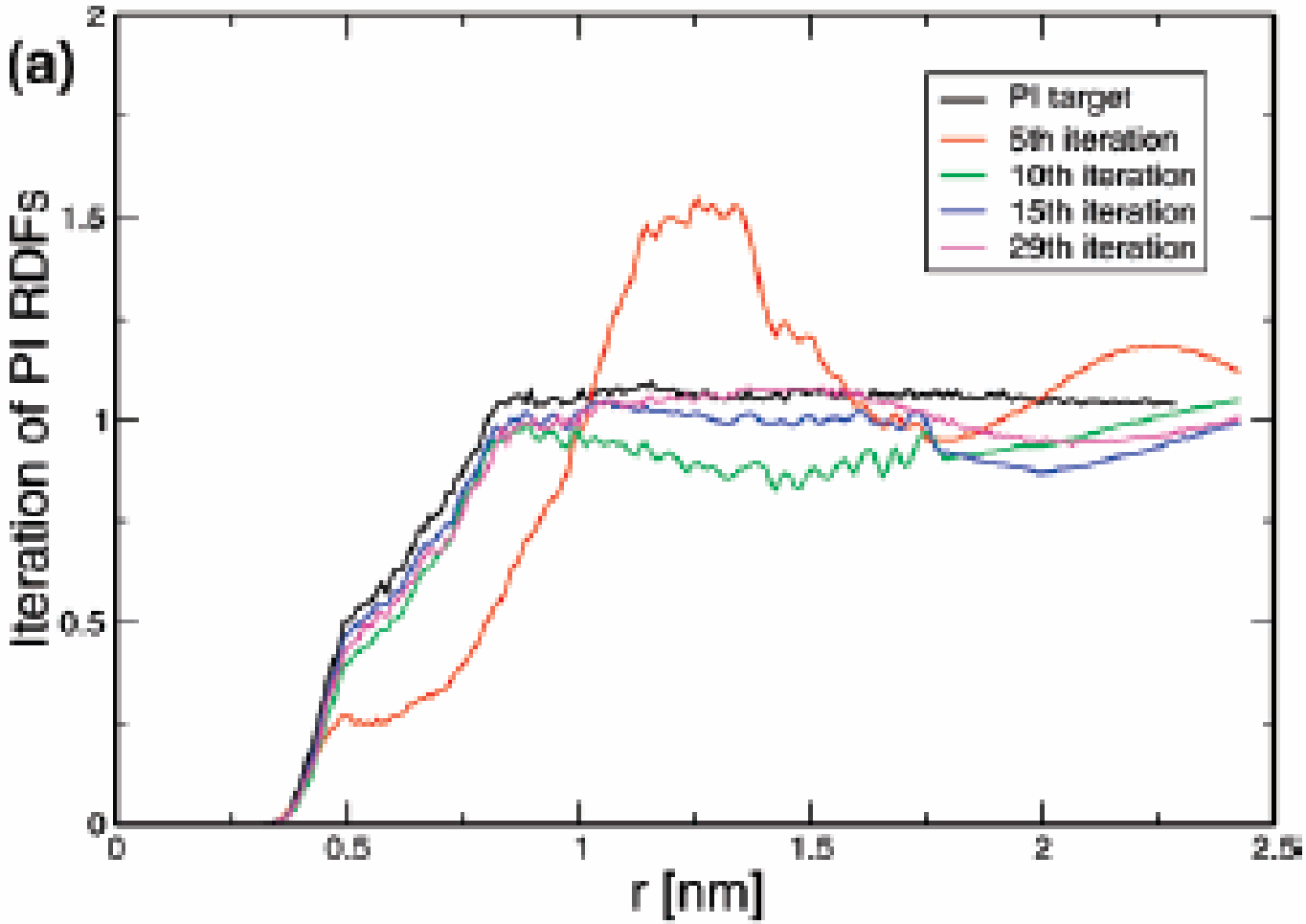
Homopolymer:
A-A interactions only



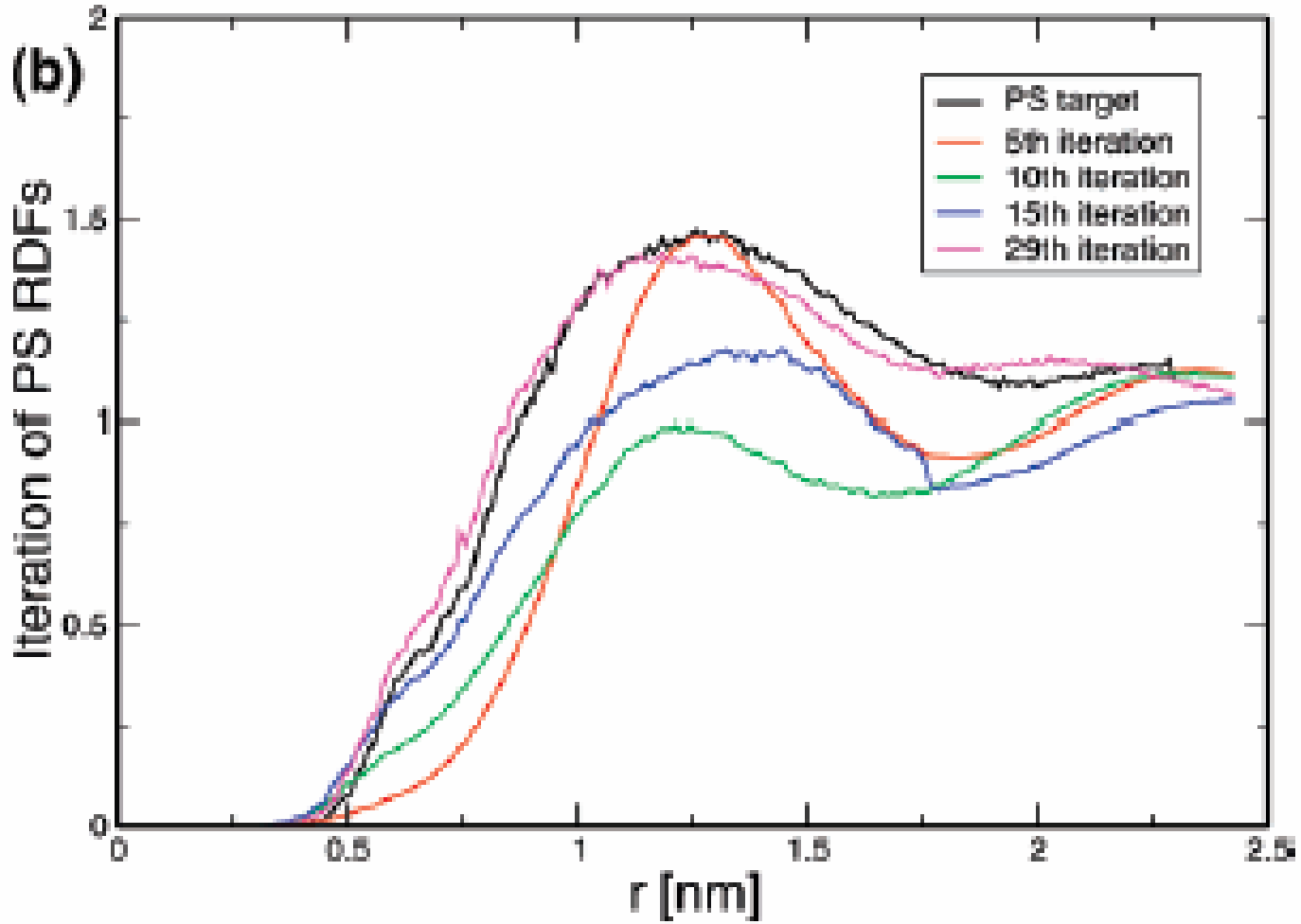
Polymer Mixture: A-A interactions also mediated by Bmers



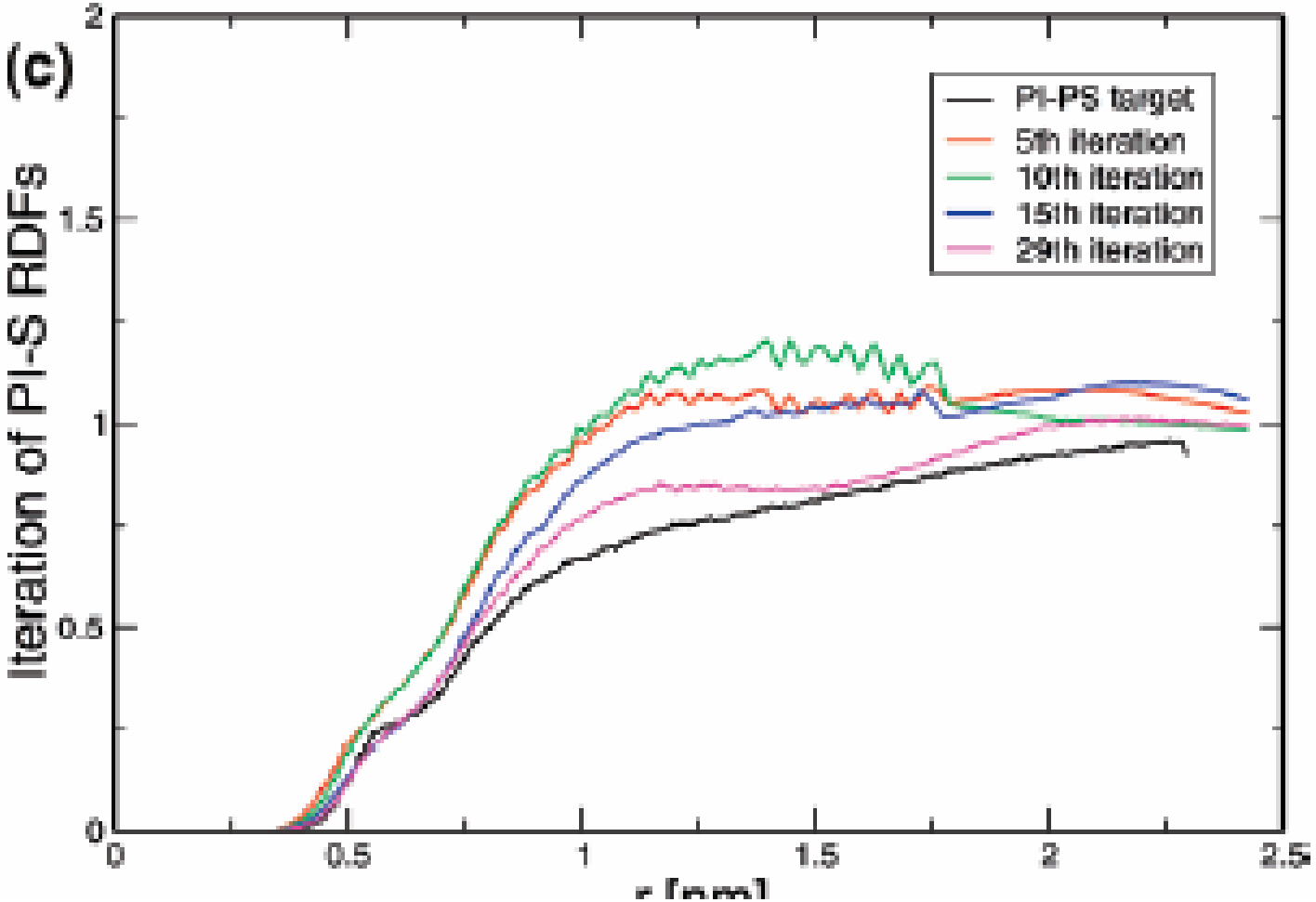
PI-PI RDFs


(a)
Iteration of PI RDFs
r [nm]
PI target
5th iteration
10th iteration
15th iteration
29th iteration
0
0.5
1
1.5
2
2.5

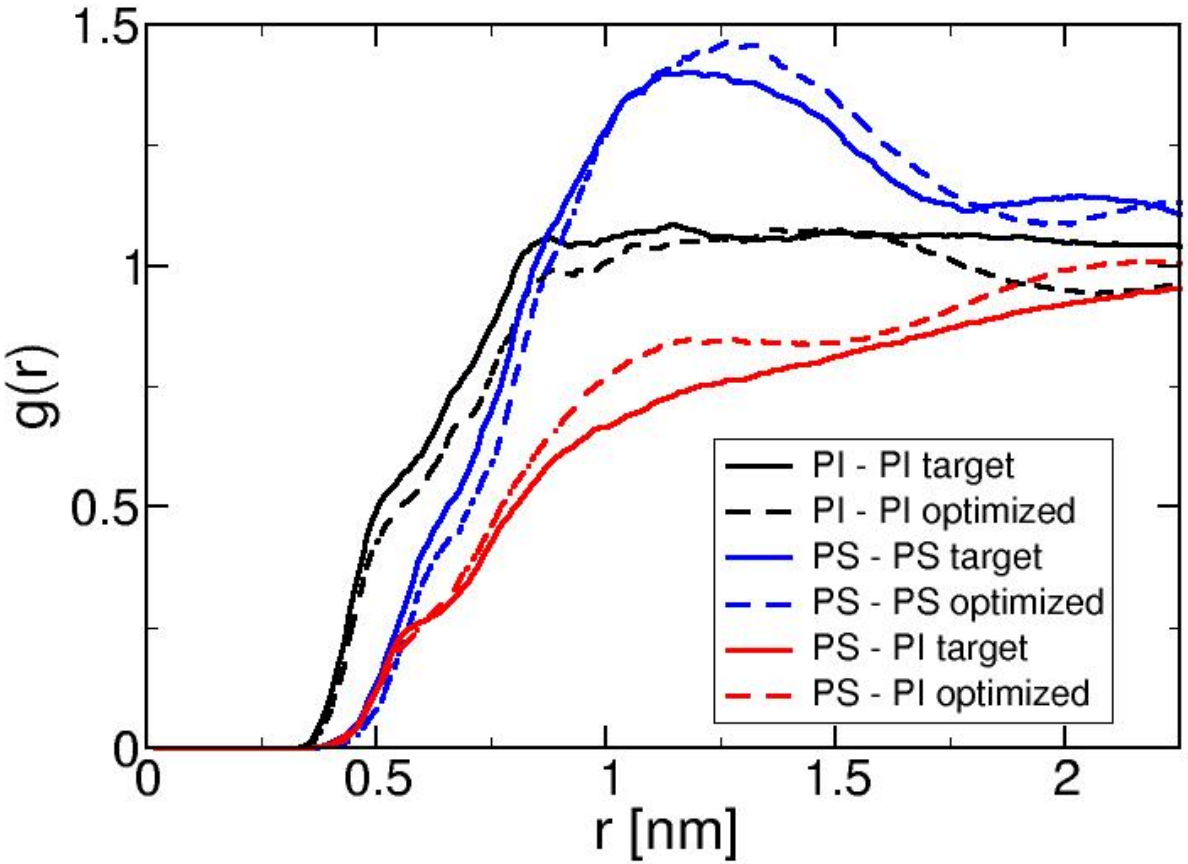
PS-PS RDFs


(b)
Iteration of PS RDFs
r [nm]
PS target
5th iteration
10th iteration
15th iteration
29th iteration
0
0.5
1
1.5
2
2.5

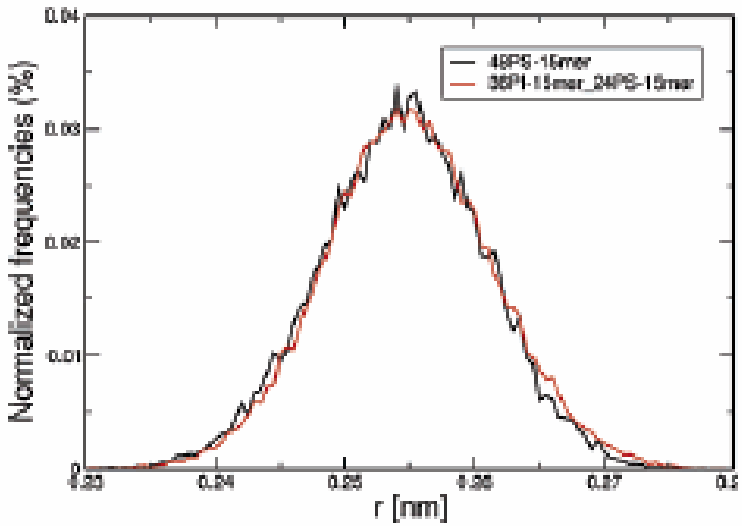
PI-PS RDFs


(c)
Iteration of PI-S RDFs
PI-PS target
5th iteration
10th iteration
15th iteration
29th iteration
0
0.5
1
1.5
2
2.5

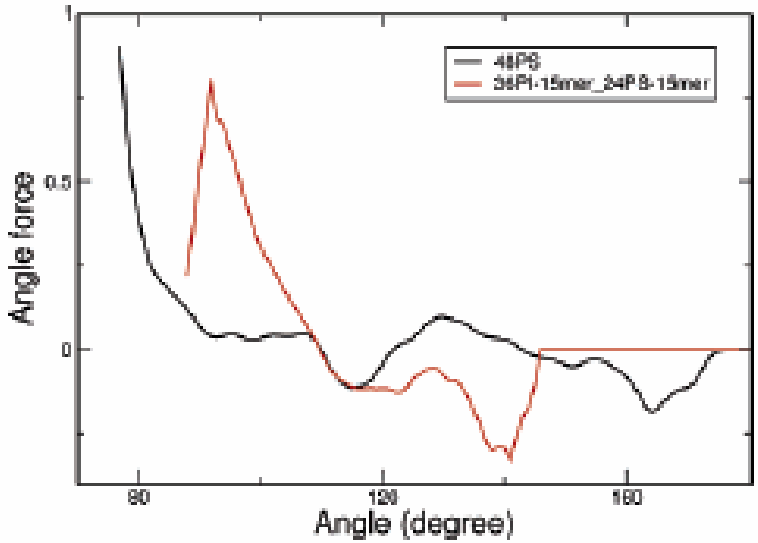
Influence of mixing on coarse-graining



Slight Changes in the Intra Potentials

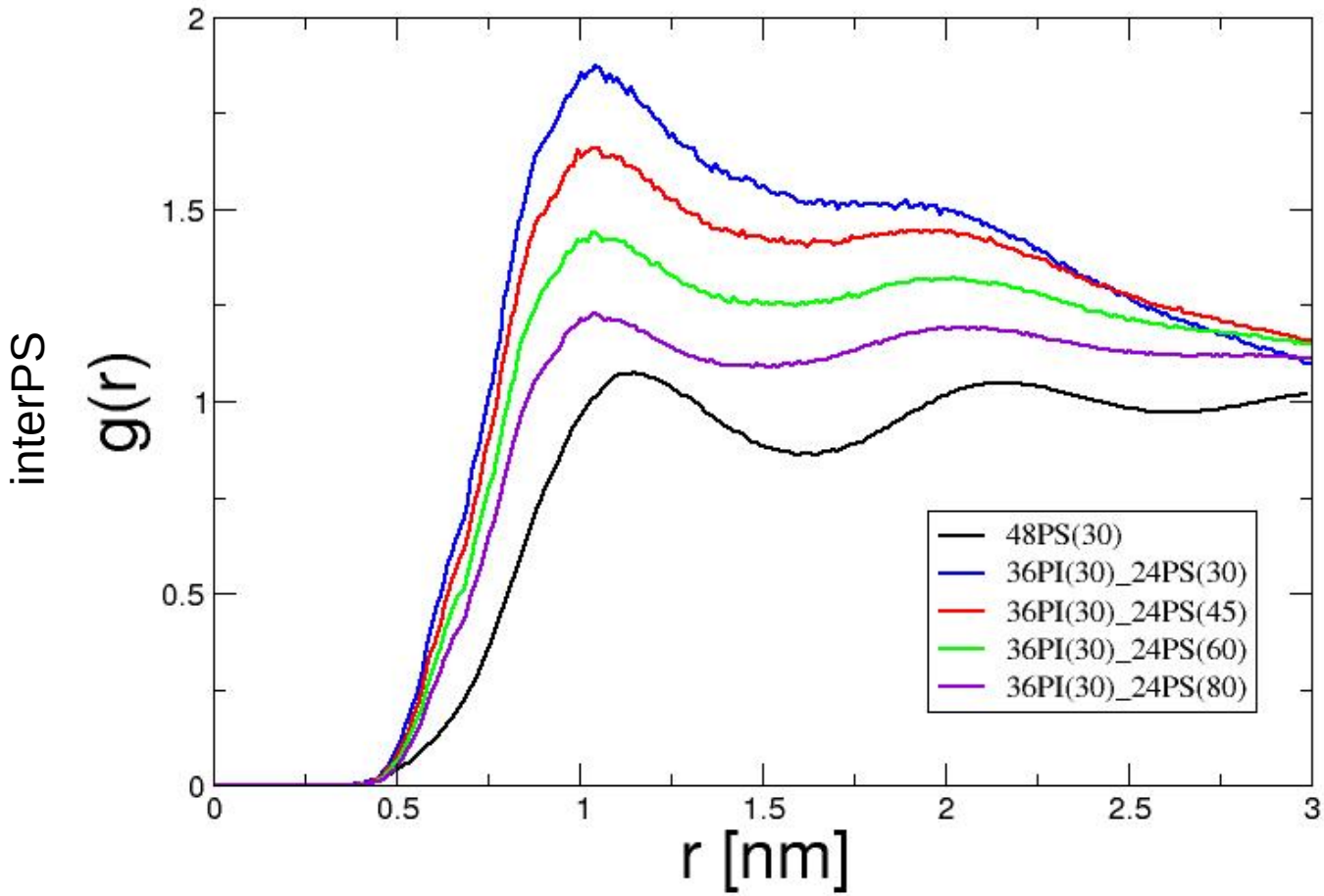


(a)



(b)

Chainlength influences in the mixture



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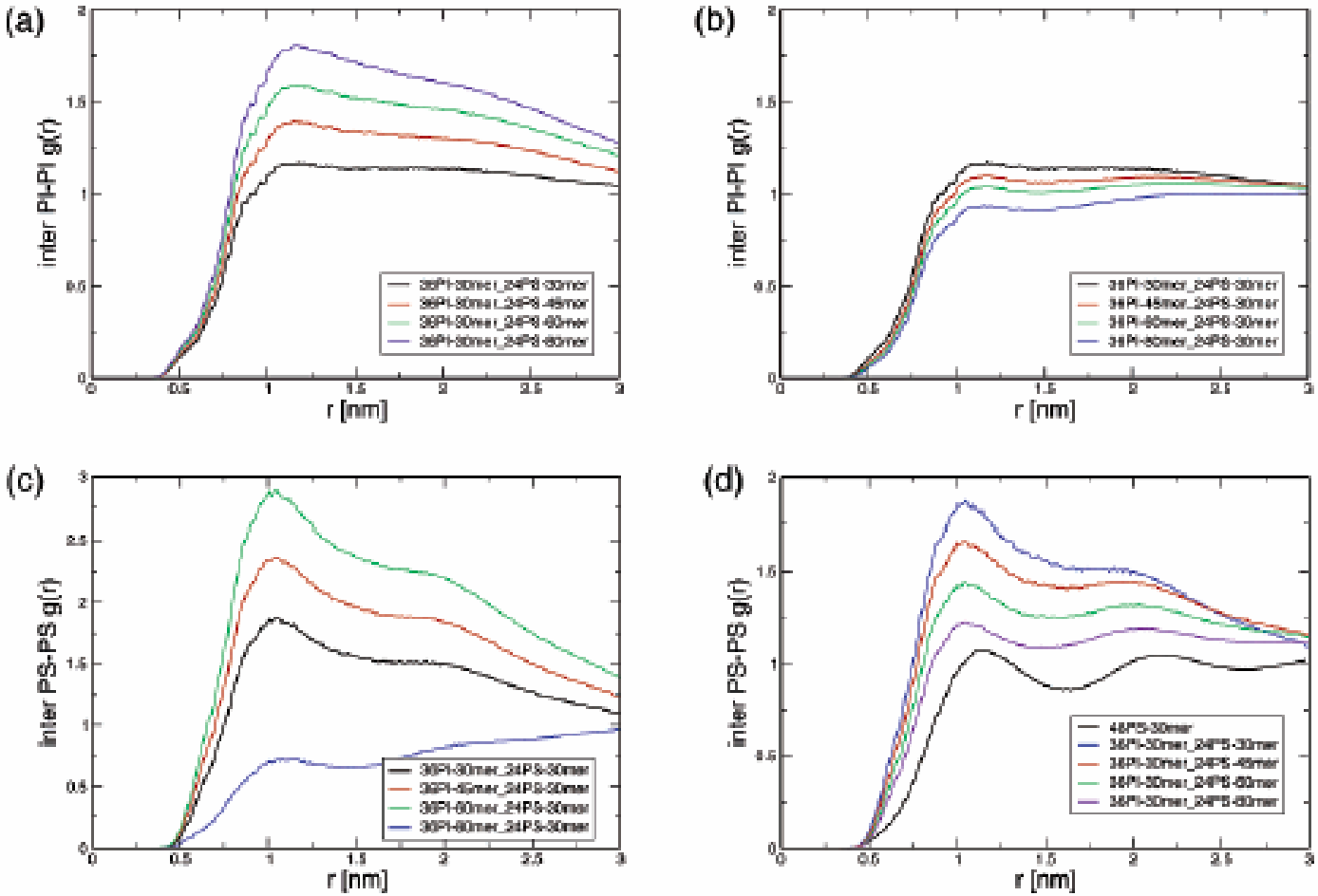
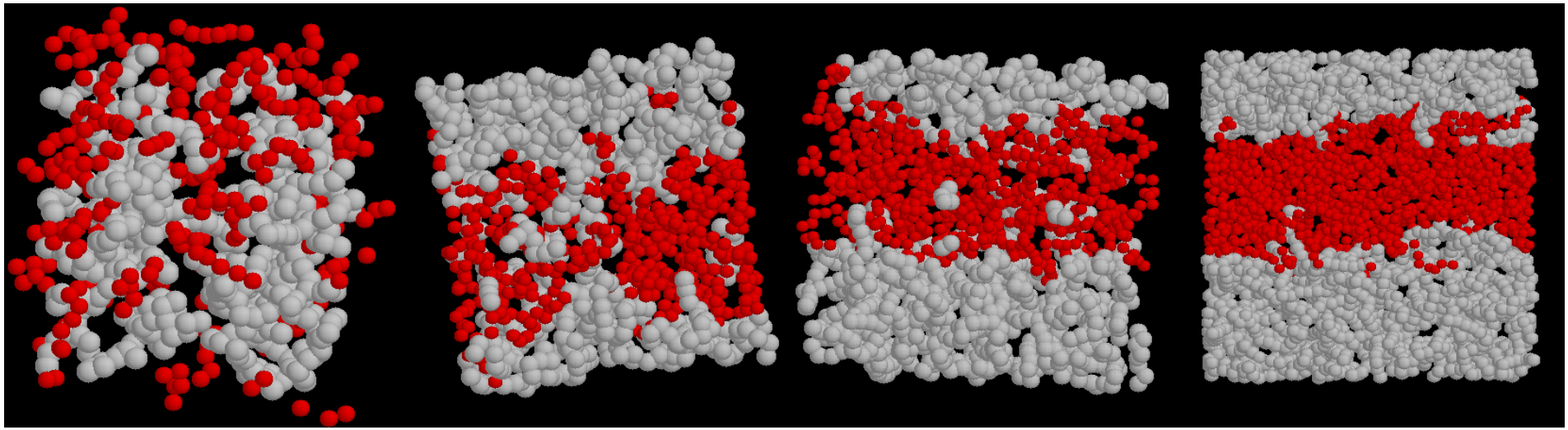
Chainlength influences in the mixture



Phase Separation with Increasing Chain Length



7 mers

10 mers

30 mers

60 mers

PS

PI

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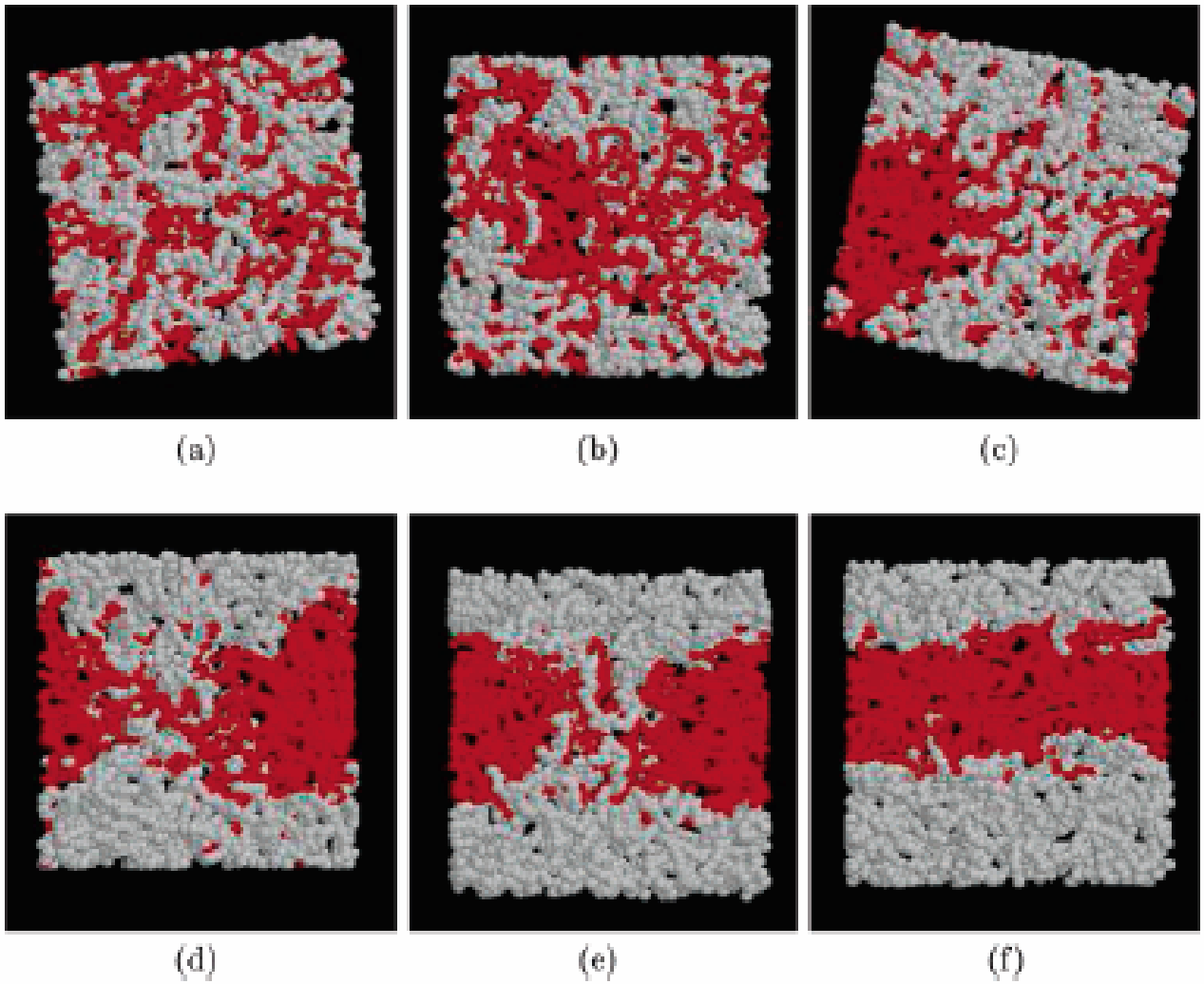
Dynamics of Phase Separation



Summary

- Different Environments lead to different coarse-grained potentials
- Mesoscale model effective for polymer dynamics (entanglement length)
- We can reproduce phase separation with chain length

Thank You!

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