Multiscale Materials Modeling

Lecture 06

Polymers

STAIR
Sustainable Technology through
Advanced Interdisciplinary Research

Fundamentals of Sustainable Technology

These notes created by David Keffer,
University of Tennessee, Knoxville, 2012.

Outline

Multiscale Modeling of Polymers

I. Introduction
II. Atomistic Simulation
III. Coarse-Grain Potential Generation
IV. Coarse-Grain Simulation
V. Validation
VI. More Examples
VII. Conclusions

Motivation

The dynamic phenomena of polymers span many orders of magnitude.

The shortest relaxation time, the vibration of individual chemical bonds in the polymer take place on a sub-femtosecond (10^{-15} s) time scale.

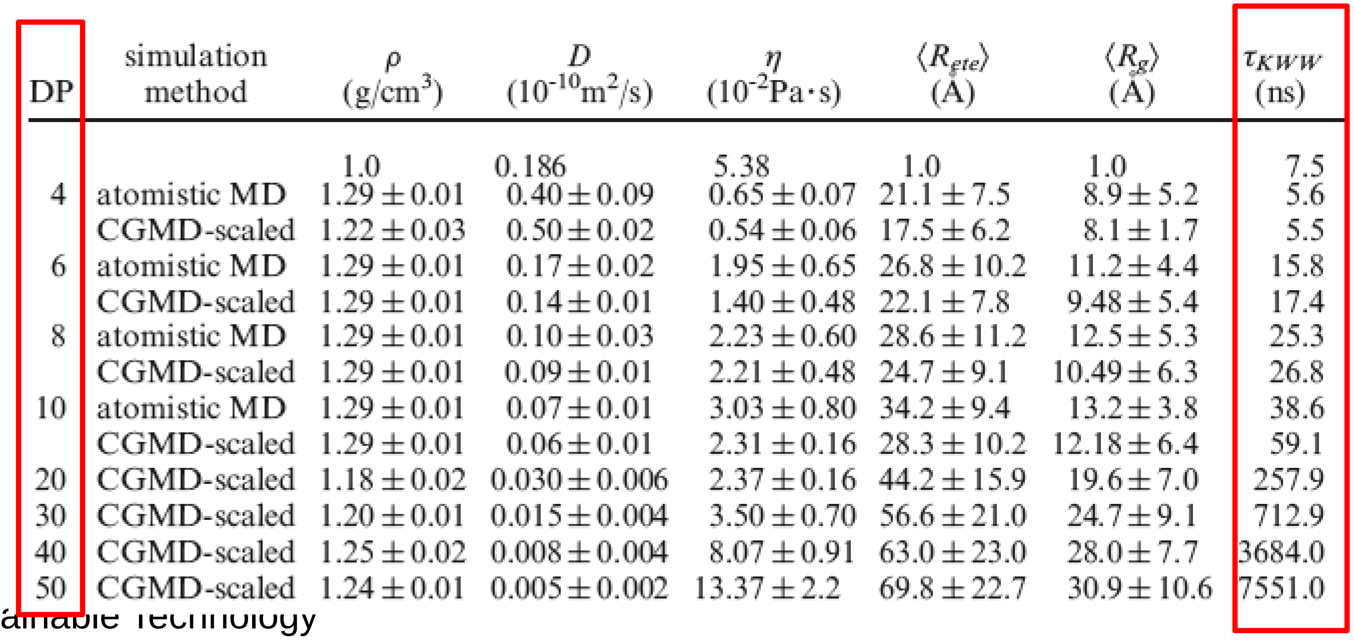
The longest relaxation, corresponding to the relaxation of the end-to-end vector of the polymer chain is much larger and is a strong function of polymer identity, degree of linearity, temperature, and chain length.

Motivation

The KWW model, a stretched exponential, is frequently use to describe the longest relaxation mode in a polymer.

$$X(t) = \exp\left(-\left(\frac{t}{\tau} \right)^{\beta} \right)$$

As an example, the relaxation time of PET at 1 atm and 563 K has a relaxation time of



DP	simulation method	ρ (g/cm^3)	D (10^{-10}m^2/s)	η (10^{-2}Pa·s)	$\langle R_{ete} \rangle$ (Å)	$\langle R_g \rangle$ (Å)	τ_{KWW} (ns)
		1.0	0.186	5.38	1.0	1.0	7.5
4	atomistic MD	1.29 ± 0.01	0.40 ± 0.09	0.65 ± 0.07	21.1 ± 7.5	8.9 ± 5.2	5.6
	CGMD-scaled	1.22 ± 0.03	0.50 ± 0.02	0.54 ± 0.06	17.5 ± 6.2	8.1 ± 1.7	5.5
6	atomistic MD	1.29 ± 0.01	0.17 ± 0.02	1.95 ± 0.65	26.8 ± 10.2	11.2 ± 4.4	15.8
	CGMD-scaled	1.29 ± 0.01	0.14 ± 0.01	1.40 ± 0.48	22.1 ± 7.8	9.48 ± 5.4	17.4
8	atomistic MD	1.29 ± 0.01	0.10 ± 0.03	2.23 ± 0.60	28.6 ± 11.2	12.5 ± 5.3	25.3
	CGMD-scaled	1.29 ± 0.01	0.09 ± 0.01	2.21 ± 0.48	24.7 ± 9.1	10.49 ± 6.3	26.8
10	atomistic MD	1.29 ± 0.01	0.07 ± 0.01	3.03 ± 0.80	34.2 ± 9.4	13.2 ± 3.8	38.6
	CGMD-scaled	1.29 ± 0.01	0.06 ± 0.01	2.31 ± 0.16	28.3 ± 10.2	12.18 ± 6.4	59.1
20	CGMD-scaled	1.18 ± 0.02	0.030 ± 0.006	2.37 ± 0.16	44.2 ± 15.9	19.6 ± 7.0	257.9
30	CGMD-scaled	1.20 ± 0.01	0.015 ± 0.004	3.50 ± 0.70	56.6 ± 21.0	24.7 ± 9.1	712.9
40	CGMD-scaled	1.25 ± 0.02	0.008 ± 0.004	8.07 ± 0.91	63.0 ± 23.0	28.0 ± 7.7	3684.0
50	CGMD-scaled	1.24 ± 0.01	0.005 ± 0.002	13.37 ± 2.2	69.8 ± 22.7	30.9 ± 10.6	7551.0

Wang et al., Macromolecules, 2010.

Motivation

This relaxation time scales nonlinearly with chain length.

$$\tau = a(DP)^{\beta}$$

As an example, the relaxation time of PET at 1 atm and 563 scales as

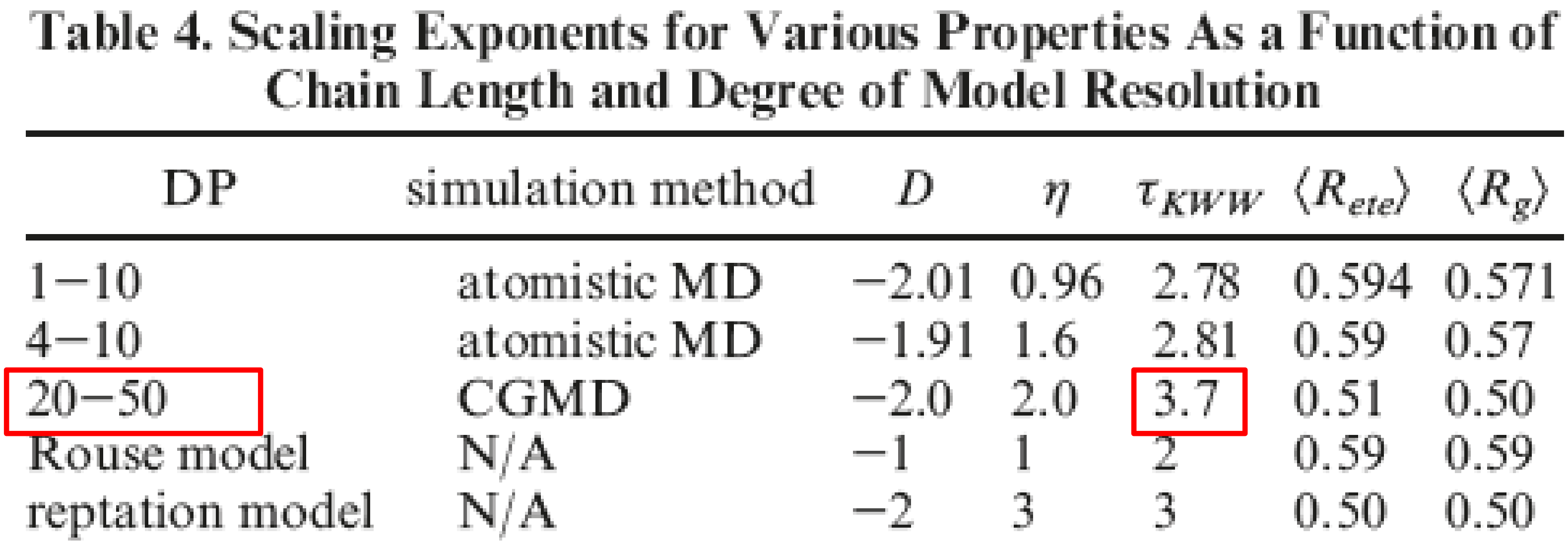


Table 4. Scaling Exponents for Various Properties As a Function of Chain Length and Degree of Model Resolution

DP	simulation method	D	η	τ_{KWW}	$\langle R_{ete}\rangle$	$\langle R_g\rangle$
1−10	atomistic MD	−2.01	0.96	2.78	0.594	0.571
4−10	atomistic MD	−1.91	1.6	2.81	0.59	0.57
20−50	CGMD	−2.0	2.0	3.7	0.51	0.50
Rouse model	N/A	−1	1	2	0.59	0.59
reptation model	N/A	−2	3	3	0.50	0.50

Wang et al., Macromolecules, 2010.

Motivation

relaxation time of PET at 1 atm and 563 as a function of chain length

degree of polymerization	t (ns)	t (s)
20	258	0.000000258
50	7551	0.00000755
100	92072.22	9.21E-05
500	35507300	0.036
1000	4.61E+08	0.461
5000	1.78E+11	178
10000	2.31E+12	2313

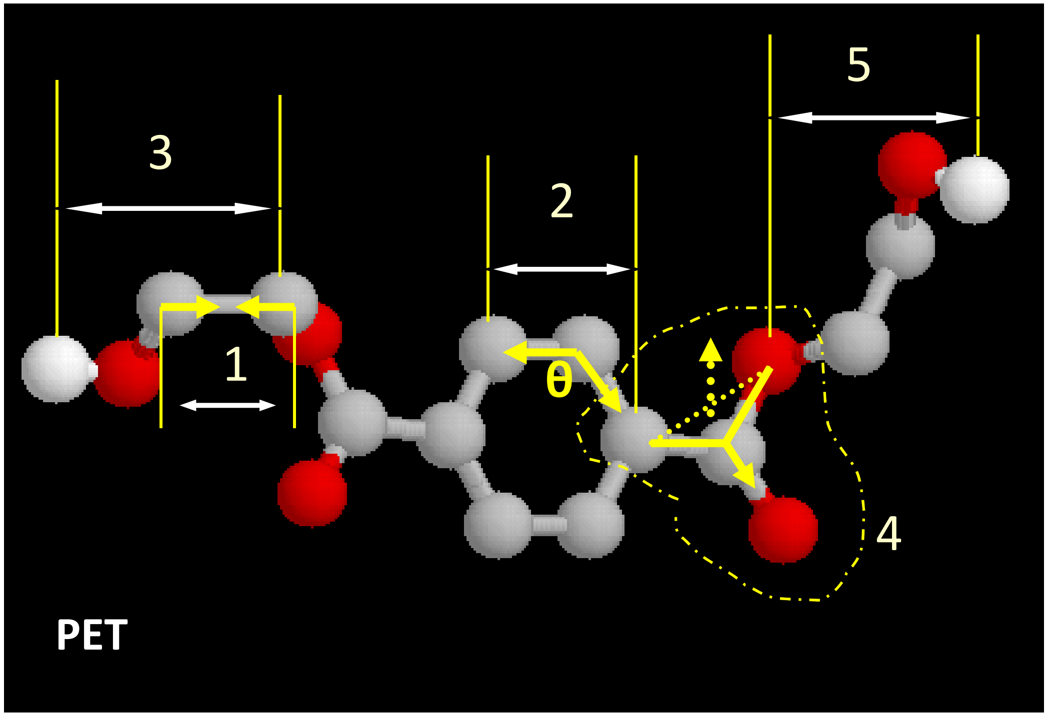
Clearly, long-chains are out of the reach of molecular simulation.

Wang et al., Macromolecules, 2010.

Multiscale Modeling of Polymers

Length and time scale in polymeric systems:

- simulation of long chain polymer is in order of μs
- dt = 0.2 fs for stretching interactions in molecular model
- from fs (10^{-15} s) to μs (10^{-6} s): 9 orders!



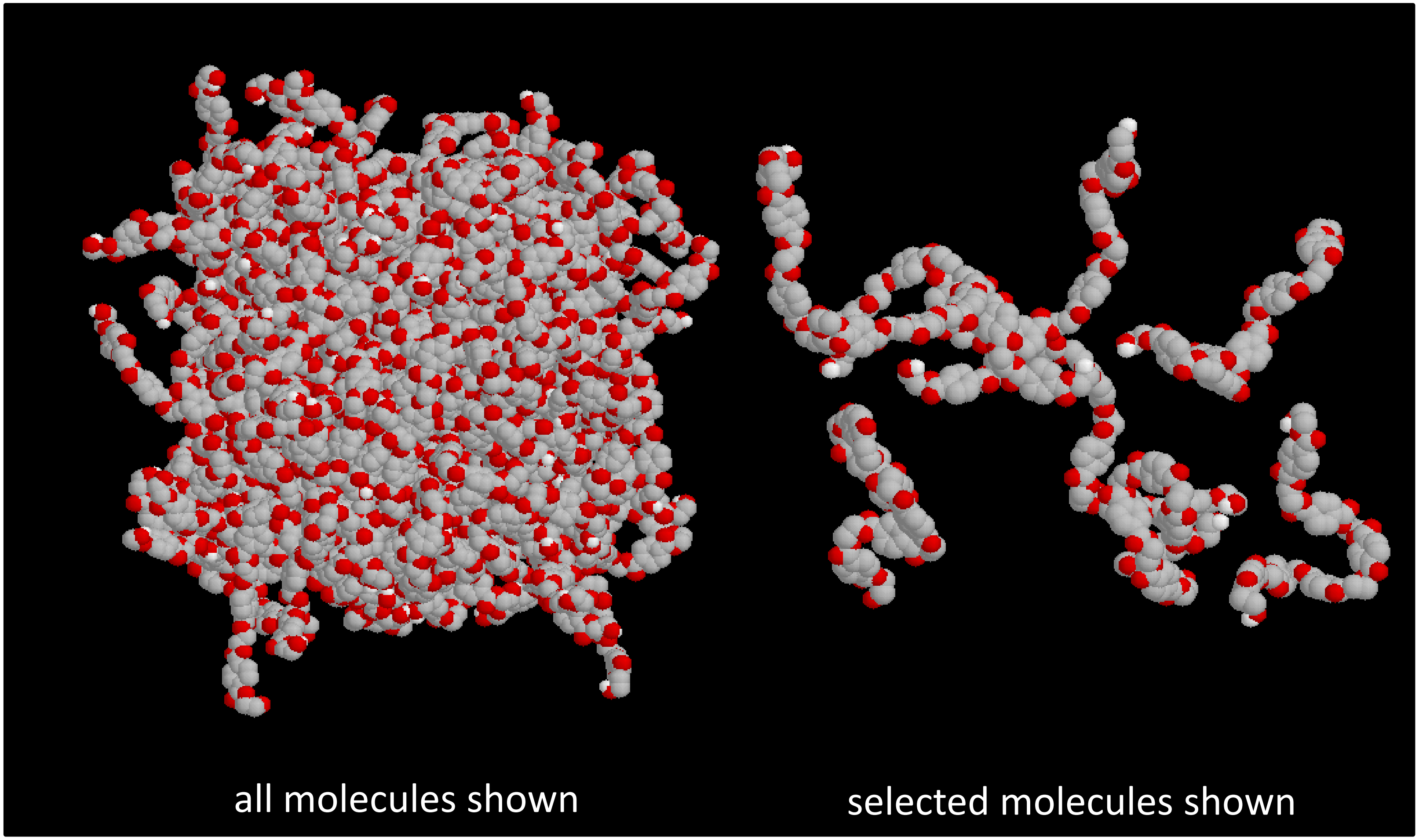
1: bond stretching
2: bond bending
3: bond torsion
4: out of plane bending
5: intramolecular L-J and electrostatic potential
(for atoms over four bonds)

Note: not all pairs are listed
O: red; C: grey; H: white

Hedenqvist *et al*. Macromolecules 1998. (neglected OH interactions)
OH interactions from Bin Chen et al. J. Phys. Chem. B, 2001

PET Properties

Molecular Dynamic Simulation Snapshots



Snapshots of PET hexamer at T = 563 K and p = 0.13 kPa.

PET Properties: Structural Information

MD Simulation data for PET (DP = 1, 2, 3, 4, 6, 8 and 10) at *p* = 0.13 kPa, *T* = 563 K.

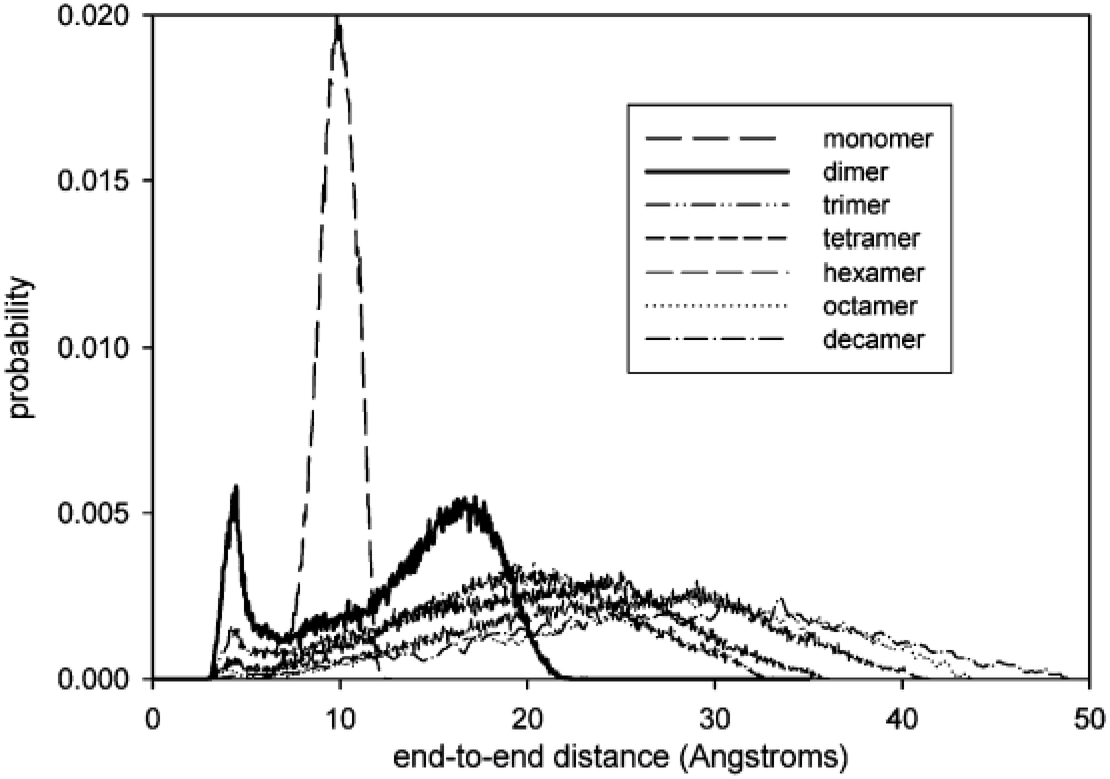


Figure 3. Chain end-to-end distance distributions as a function of degree of polymerization (DP).

Wang, Q., Keffer, D.J., Petrovan, S., Thomas, J.B., in preparation, 2009.

PET Properties: Dynamic Information

MD Simulation data for PET (DP = 1, 2, 3, 4, 6, 8 and 10) at p = 0.13 kPa, T = 563 K.

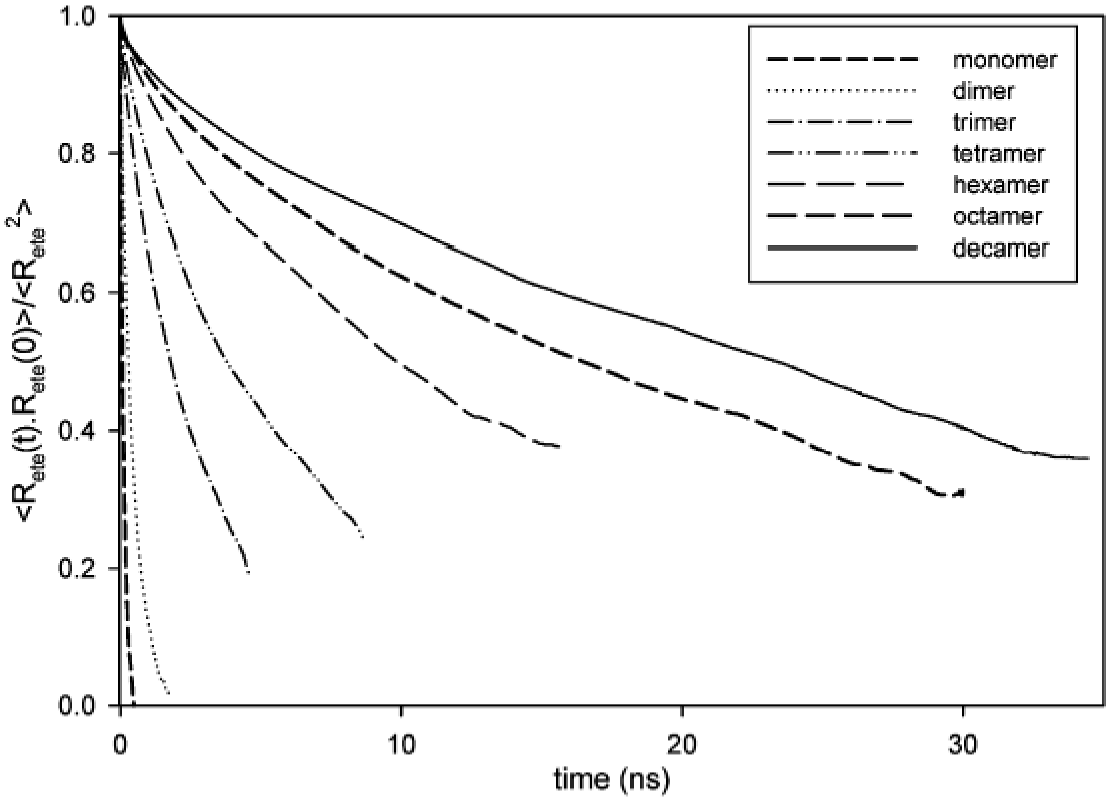


Figure 5. Chain end-to-end distance (R_{ete}) autocorrelation functions as a function of observation time for all DPs studied.

Wang, Q., Keffer, D.J., Petrovan, S., Thomas, J.B., in preparation, 2009.

PET Properties: Thermodynamic Information

MD Simulation data for PET (DP = 1, 2, 3, 4, 6, 8 and 10) at *p* = 0.13 kPa, *T* = 563 K.

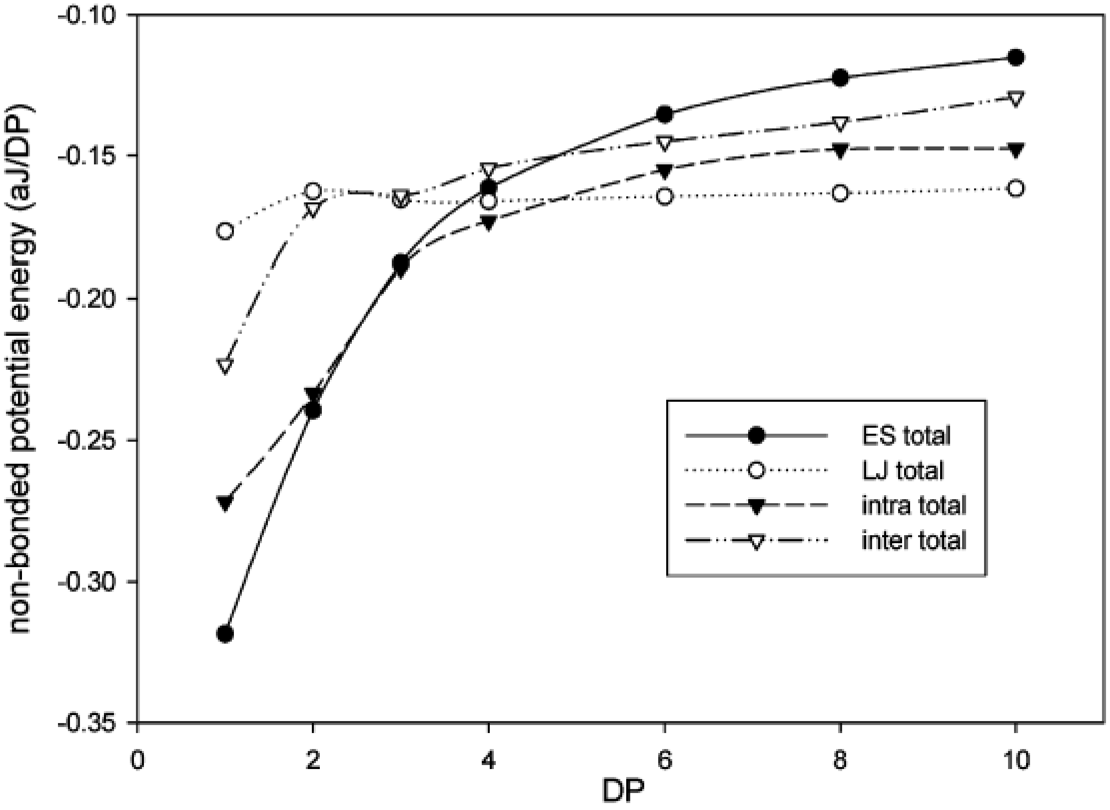


Figure 8. Individual nonbonded contributions to the potential energy as a function of DP. ES = electrostatic; LJ = Lennard-Jones; intra = intramolecular; inter = intermolecular. These contributions are normalized by the degree of polymerization.

Wang, Q., Keffer, D.J., Petrovan, S., Thomas, J.B., in preparation, 2009.

PET Properties: Transport Information

MD Simulation data for PET (DP = 1, 2, 3, 4, 6, 8 and 10) at *p* = 0.13 kPa, *T* = 563 K.

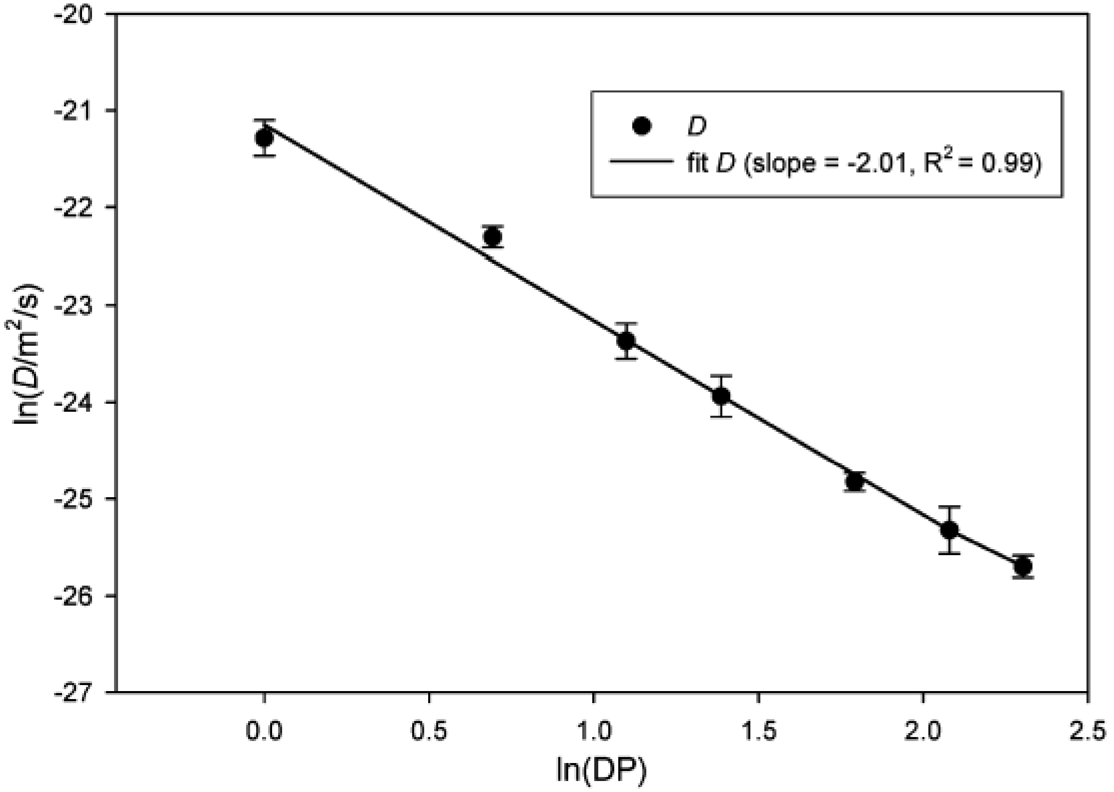
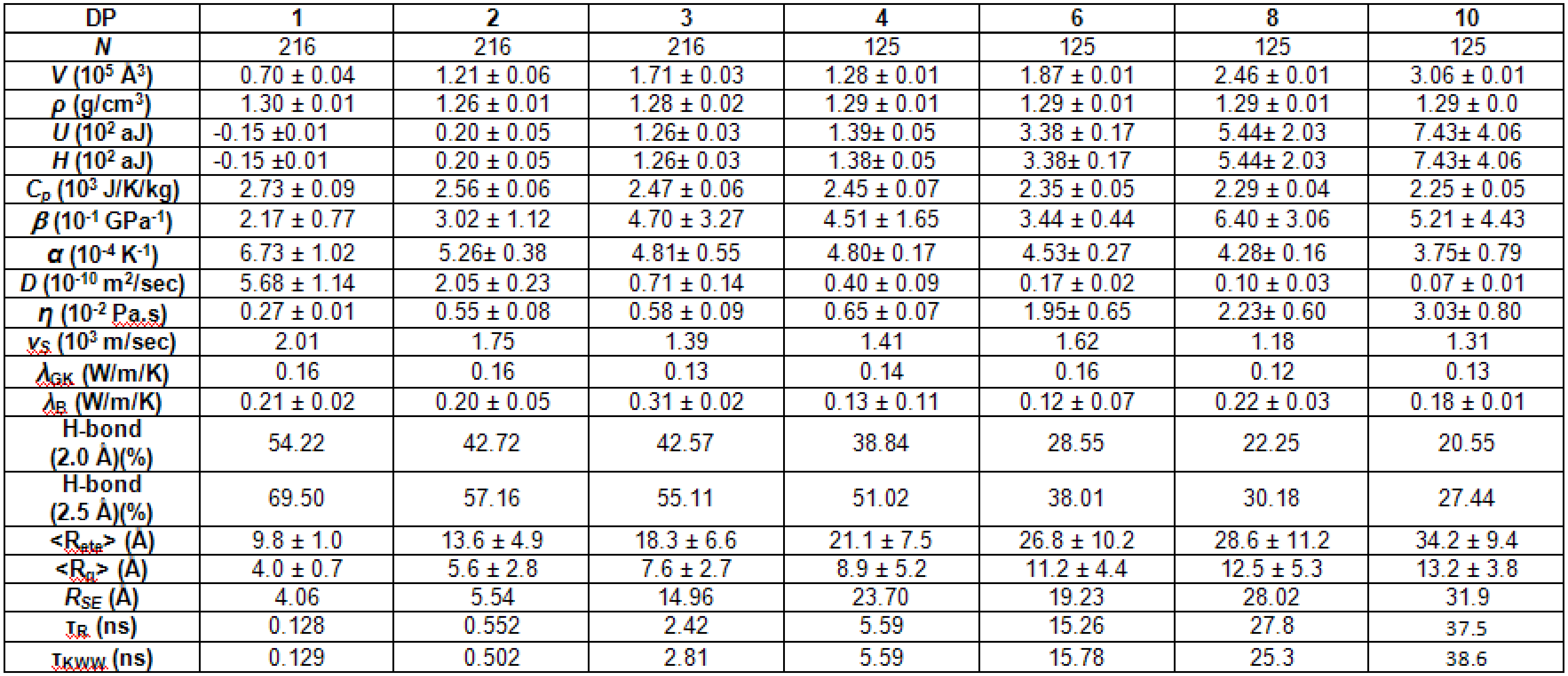


Figure 12. Self-diffusivity (*D*) as a function of DP.

Wang, Q., Keffer, D.J., Petrovan, S., Thomas, J.B., in preparation, 2009.

PET Properties

MD Simulation data for PET (DP = 1, 2, 3, 4, 6, 8 and 10) at *p* = 0.13 kPa, *T* = 563 K.



DP	1	2	3	4	6	8	10
N	216	216	216	125	125	125	125
V (10^5 Å^3)	0.70 ± 0.04	1.21 ± 0.06	1.71 ± 0.03	1.28 ± 0.01	1.87 ± 0.01	2.46 ± 0.01	3.06 ± 0.01
ρ (g/cm^3)	1.30 ± 0.01	1.26 ± 0.01	1.28 ± 0.02	1.29 ± 0.01	1.29 ± 0.01	1.29 ± 0.01	1.29 ± 0.0
U (10^2 aJ)	-0.15 ±0.01	0.20 ± 0.05	1.26± 0.03	1.39± 0.05	3.38 ± 0.17	5.44± 2.03	7.43± 4.06
H (10^2 aJ)	-0.15 ±0.01	0.20 ± 0.05	1.26± 0.03	1.38± 0.05	3.38± 0.17	5.44± 2.03	7.43± 4.06
C_p (10^3 J/K/kg)	2.73 ± 0.09	2.56 ± 0.06	2.47 ± 0.06	2.45 ± 0.07	2.35 ± 0.05	2.29 ± 0.04	2.25 ± 0.05
β (10^{-1} GPa^{-1})	2.17 ± 0.77	3.02 ± 1.12	4.70 ± 3.27	4.51 ± 1.65	3.44 ± 0.44	6.40 ± 3.06	5.21 ± 4.43
α (10^{-4} K^{-1})	6.73 ± 1.02	5.26± 0.38	4.81± 0.55	4.80± 0.17	4.53± 0.27	4.28± 0.16	3.75± 0.79
D (10^{-10} m^2/sec)	5.68 ± 1.14	2.05 ± 0.23	0.71 ± 0.14	0.40 ± 0.09	0.17 ± 0.02	0.10 ± 0.03	0.07 ± 0.01
η (10^{-2} Pa.s)	0.27 ± 0.01	0.55 ± 0.08	0.58 ± 0.09	0.65 ± 0.07	1.95± 0.65	2.23± 0.60	3.03± 0.80
v_S (10^3 m/sec)	2.01	1.75	1.39	1.41	1.62	1.18	1.31
λ_{GK} (W/m/K)	0.16	0.16	0.13	0.14	0.16	0.12	0.13
λ_B (W/m/K)	0.21 ± 0.02	0.20 ± 0.05	0.31 ± 0.02	0.13 ± 0.11	0.12 ± 0.07	0.22 ± 0.03	0.18 ± 0.01
H-bond (2.0 Å)(%)	54.22	42.72	42.57	38.84	28.55	22.25	20.55
H-bond (2.5 Å)(%)	69.50	57.16	55.11	51.02	38.01	30.18	27.44
$\langle R_{ete} \rangle$ (Å)	9.8 ± 1.0	13.6 ± 4.9	18.3 ± 6.6	21.1 ± 7.5	26.8 ± 10.2	28.6 ± 11.2	34.2 ± 9.4
$\langle R_g \rangle$ (Å)	4.0 ± 0.7	5.6 ± 2.8	7.6 ± 2.7	8.9 ± 5.2	11.2 ± 4.4	12.5 ± 5.3	13.2 ± 3.8
R_{SE} (Å)	4.06	5.54	14.96	23.70	19.23	28.02	31.9
τ_R (ns)	0.128	0.552	2.42	5.59	15.26	27.8	37.5
τ_{KWW} (ns)	0.129	0.502	2.81	5.59	15.78	25.3	38.6

Wang, Q., Keffer, D.J., Petrovan, S., Thomas, J.B., in preparation, 2009.

Outline

Multiscale Modeling of Polymers

I. Introduction
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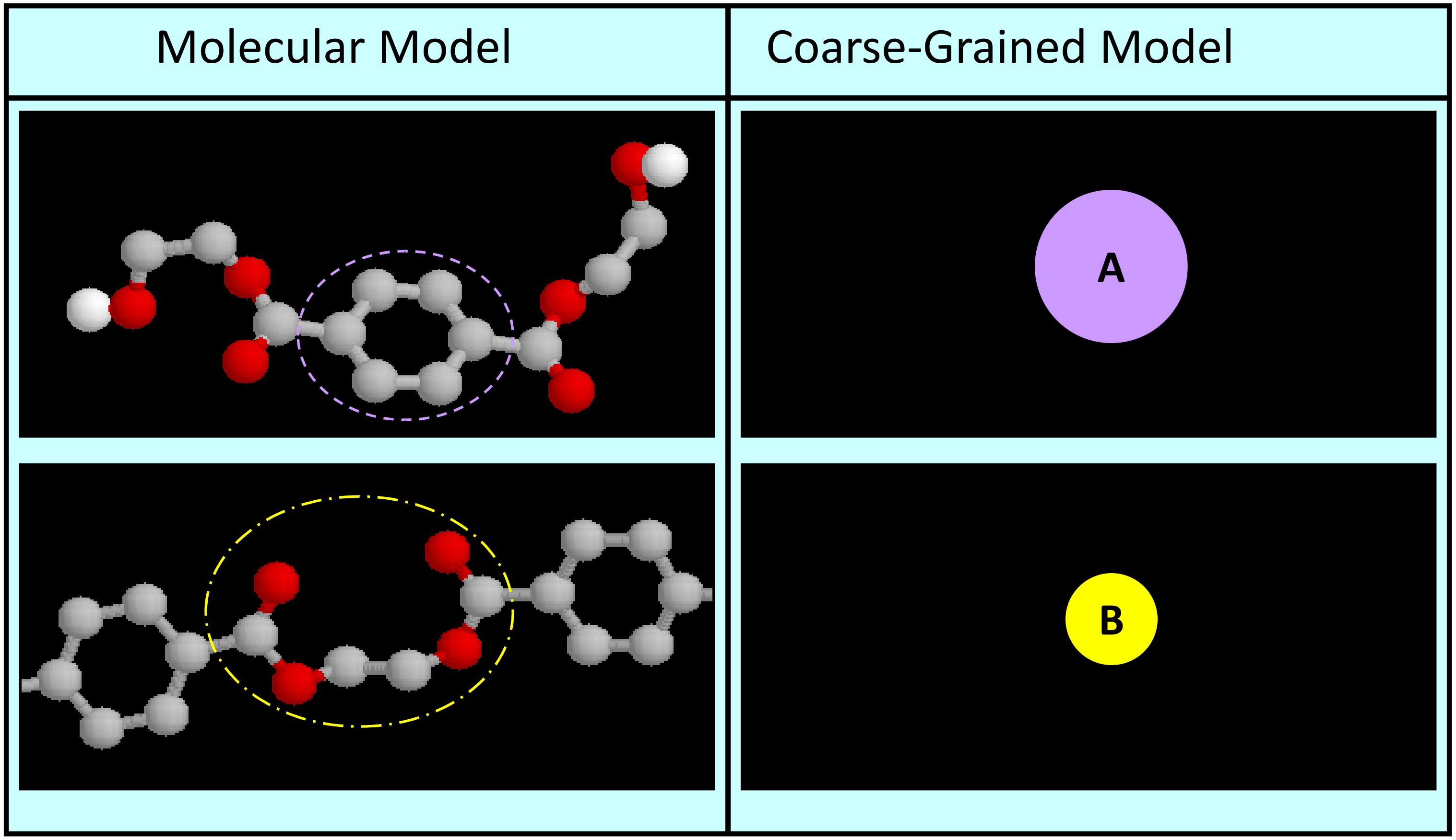
VI. More Examples
VII. Conclusions

Polymer Mesoscale Models

Example: PET

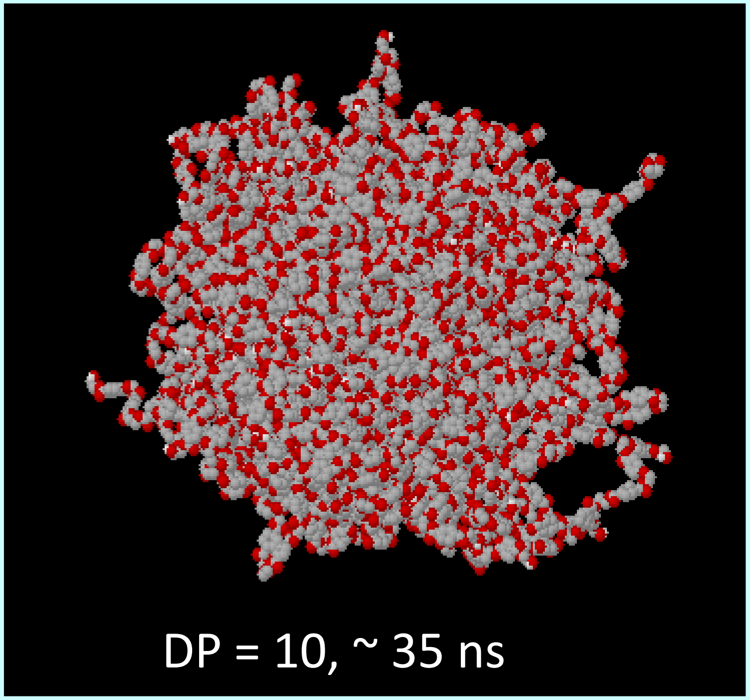
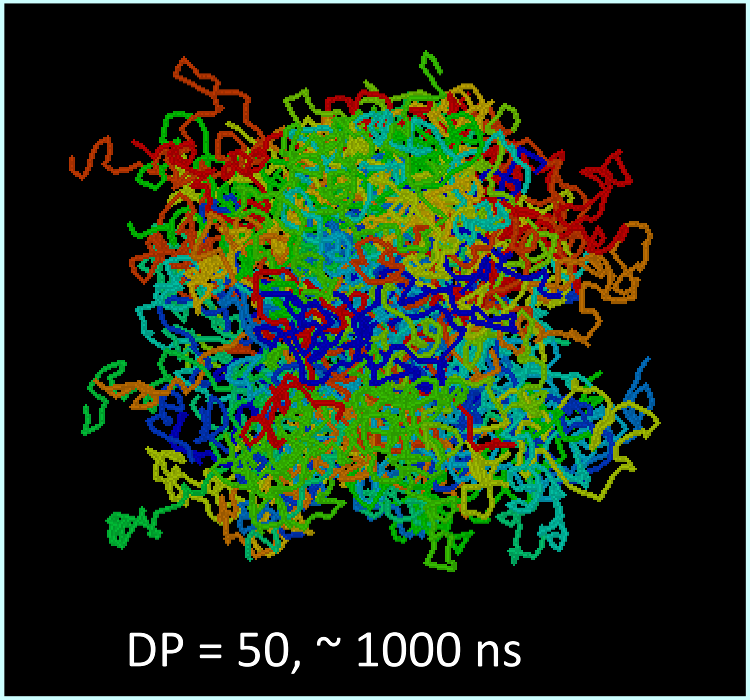


Wang, Q., Keffer, D.J., Petrovan, S., Thomas, J.B., in progress, 2009.

Motivation: Molecular vs. Coarse-Grained Simulations

Polymer Mesoscale Models

Exampl

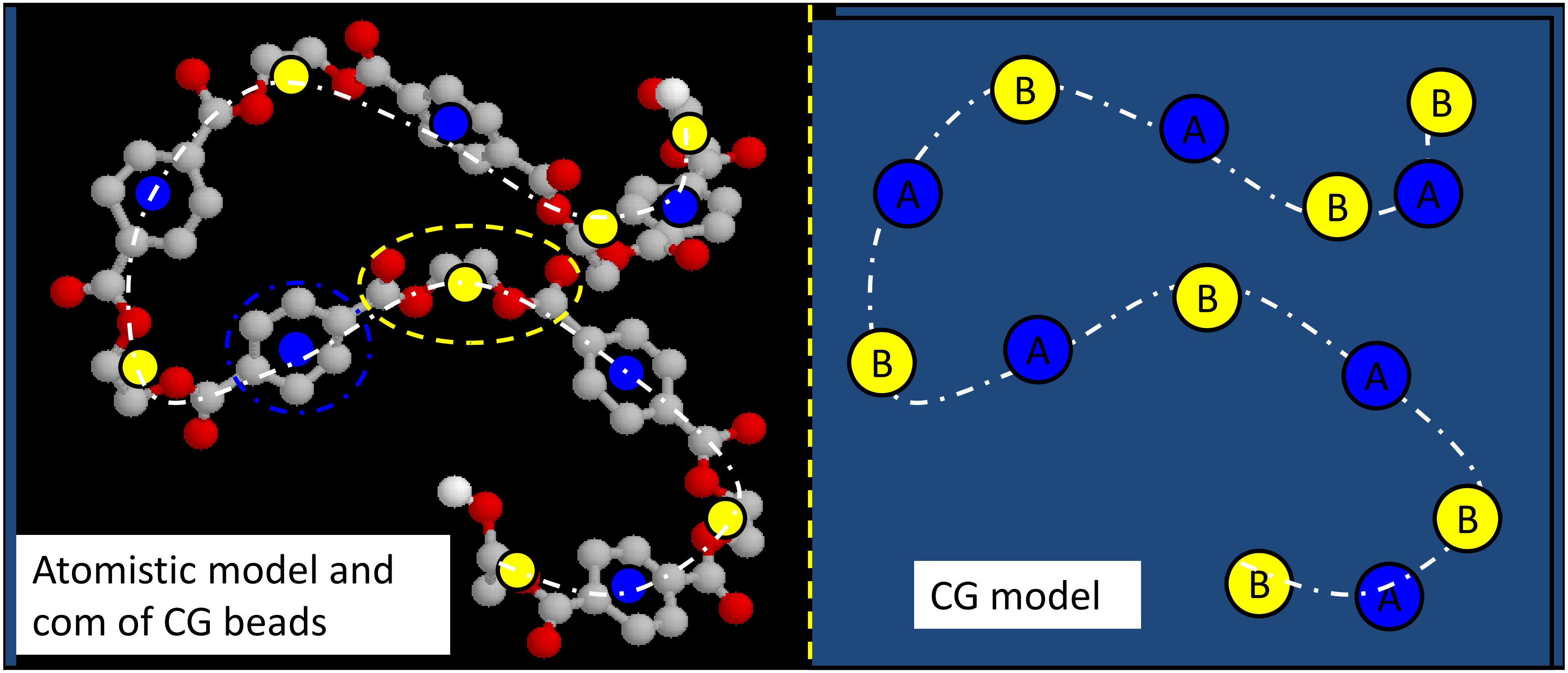
Molecular System	Coarse-Grained System
 DP = 10, ~ 35 ns	 DP = 50, ~ 1000 ns
• many degrees of freedom • computationally expensive • limited to short chains (1-10)	• fewer degrees of freedom • computationally modest • long chains (25-50 or longer)

$$F = ma \qquad F \equiv -\nabla U \qquad \frac{d^2 x_{i,\alpha}}{dt} = -\frac{1}{m}\frac{\partial U}{\partial x_{i,\alpha}}$$

Harmandaris, Adhikari, van der Vegt, Kremer, Macromolecules, 2006.

Coarse-Grained model: based on atomistic MD simulation

Atomistic MD simulation is limited to DP up to 10, CG MD simulation will allow us to get to DP from 25 to 50 or even longer chains by neglecting some local degrees of freedom.

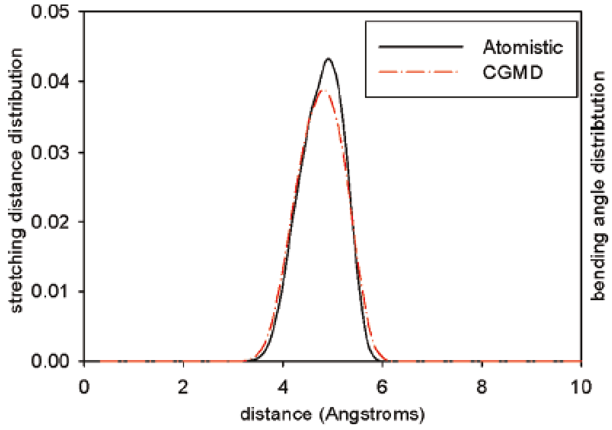


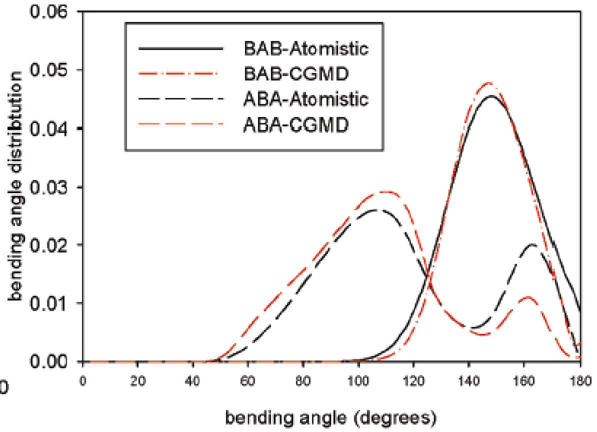
CG model on top of atomistic model for hexamer (DP=6)

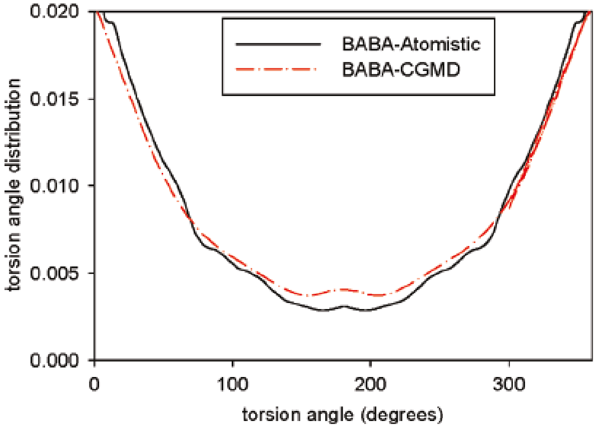
CG chain for hexamer, total interaction centers is 13 for each molecule (original:90).

Coarse-Grained Potentials: parameterization

Step 1. Run atomistic MD simulations on short chains.
Generate Pair Correlation functions of center-of-mass of molecular fragments corresponding to beads.







Stretching, bending and torsion modes indicate distributions of intramolecular degrees of freedom.

This is a representation of the structure of the material.

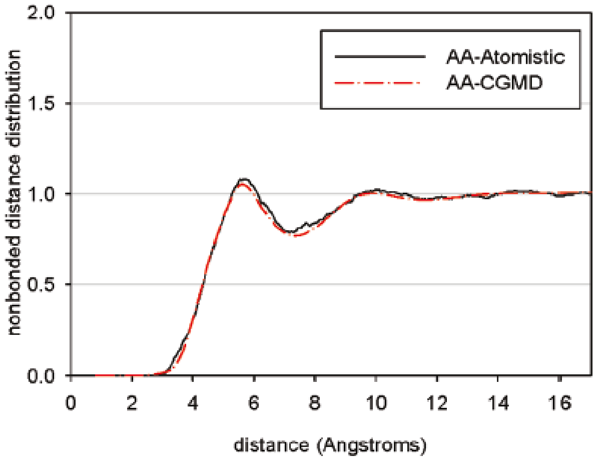
Remember: PET is an ABABABA polymer.

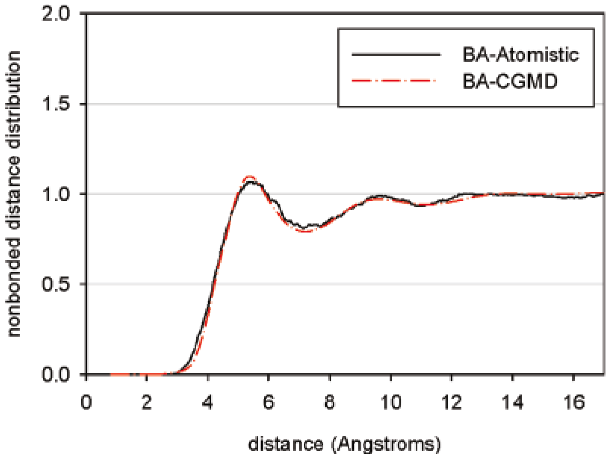
Coarse-Grained Potentials: parameterization

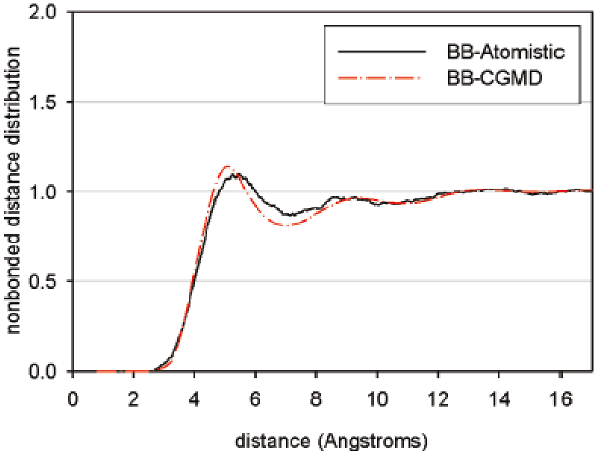
Step 1. Run atomistic MD simulations on short chains.
Generate Pair Correlation functions of center-of-mass of molecular fragments corresponding to beads.

Non-bonded distributions of intermolecular (and distant intramolecular) degrees of freedom.

Remember: PET is an ABABABA polymer.

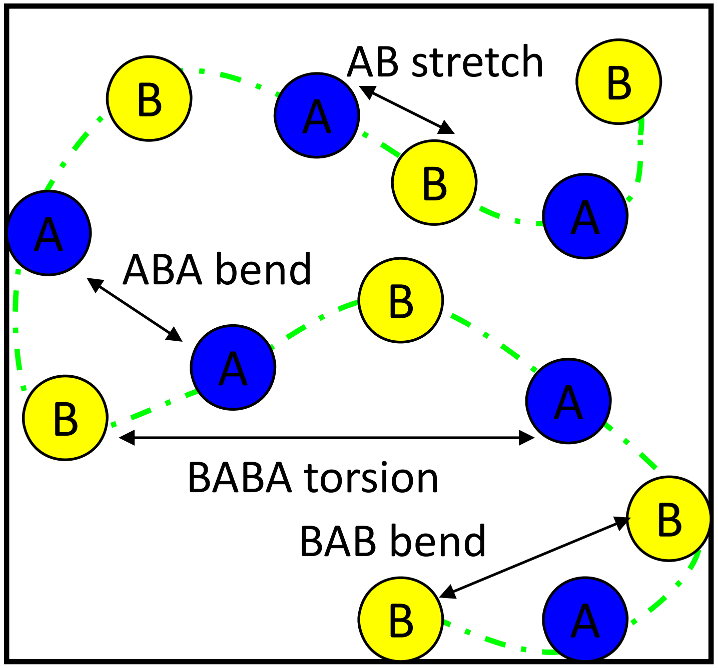






Coarse-Grained Potentials: parameterization

Step 2. From the PCFs obtained from atomistic simulations, estimate the CG interaction potential.



CG chain model and intramolecular interaction for hexamer,
1: bond stretching (BA);
2: bond bending (BAB and ABA);
3: bond torsion (BABA)

$$U^{CG} = U^{CG}_{stretch} + U^{CG}_{bend} + U^{CG}_{torsion} + U^{CG}_{non-bond}$$

$$U^{CG}_{stretch}(r,T) = -k_B T \ln P^{CG}_{stretch}(r,T) + C_r$$

$$U^{CG}_{bend}(\theta,T) = -k_B T \ln P^{CG}_{bend}(\theta,T) + C_\theta$$

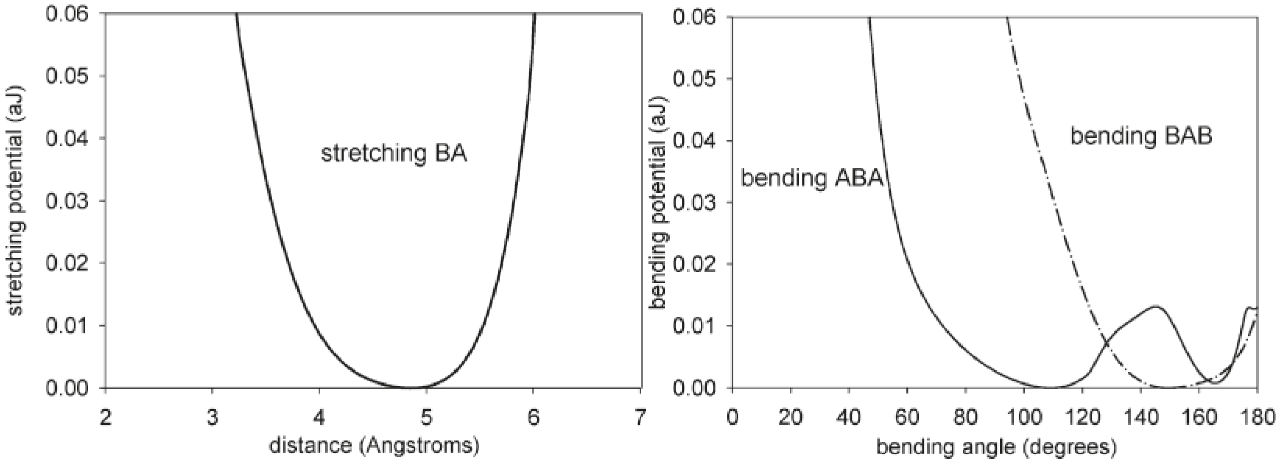
$$U^{CG}_{torsion}(\phi,T) = -k_B T \ln P^{CG}_{torsion}(\phi,T) + C_\phi$$

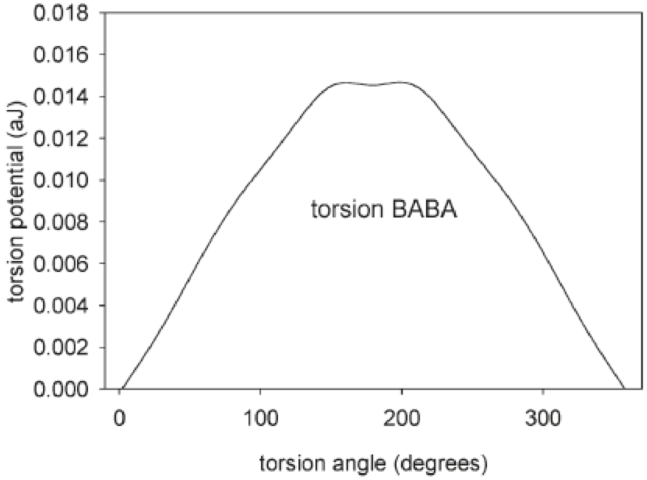
For bonded modes, we use a simple Boltzmann distribution, which assumes that all of the bonded modes are decoupled.

This assumption won’t work for non-bonded modes.

Coarse-Grained Potentials: parameterization

Step 2. From the PCFs obtained from atomistic simulations, estimate the CG interaction potential.

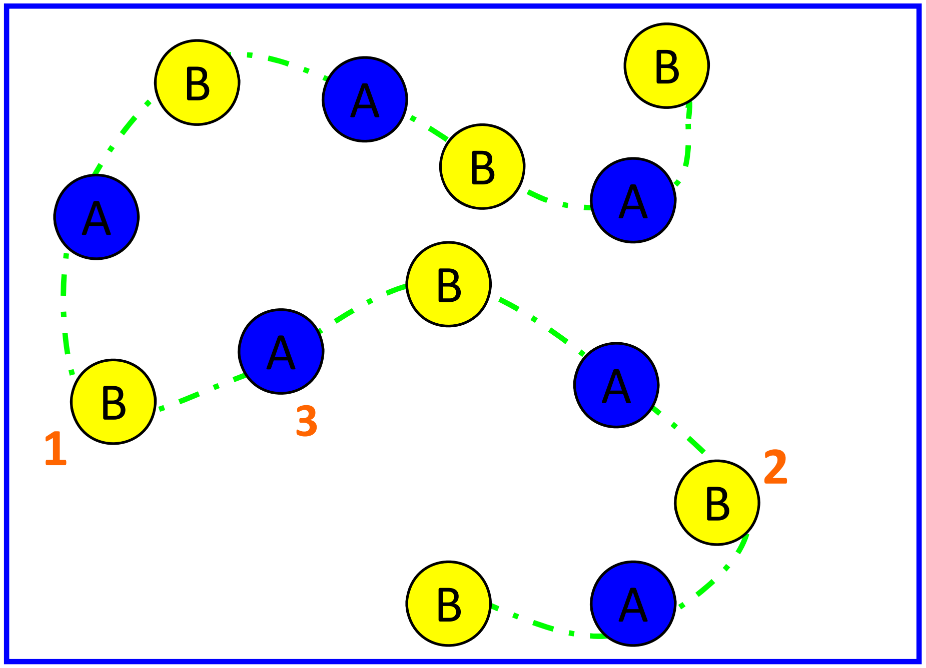




The CG potentials have low energy where the probability of finding the configuration is high.

Coarse-Grained Potentials: parameterization

Step 2. From the PCFs obtained from atomistic simulations, estimate the CG interaction potential.



There are a variety of ways to obtain the non-bonded interaction potentials from the PCFs.

One of the most-common is iterative Boltzmann inversion.

Coarse-Grained Potentials: parameterization

Iterative Boltzmann Inversion

IBI: iterative, can reproduce structures from atomistic simulation.[1]

$$U_{\alpha\beta,i+1}(r) = U_{\alpha\beta,i}(r) + k_B T \ln\left(\frac{g_{\alpha\beta,i}(r)}{g_{\alpha\beta}(r)}\right)$$

$$U_{\alpha\beta,0}(r) = -k_B T \ln\left(g_{\alpha\beta}(r)\right)$$

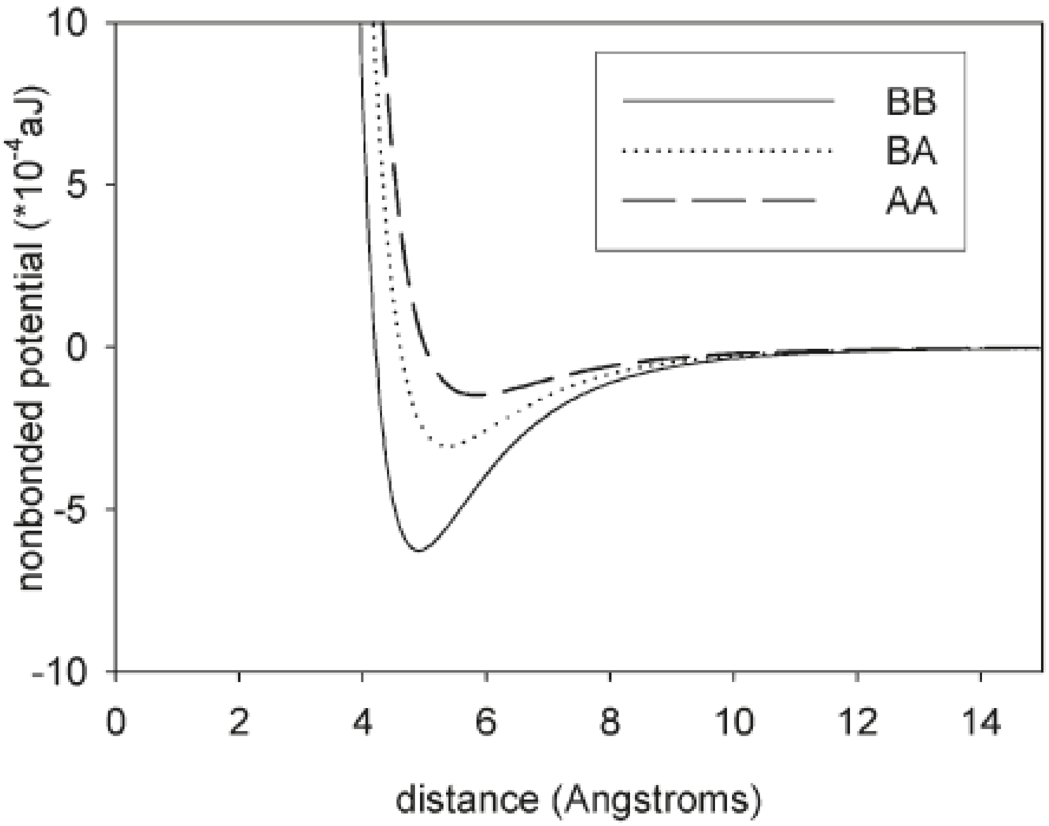
Potential is iteratively refined to reproduce the target PCF.

May involve many CG simulations to obtain the PCFs.

Computationally expensive, may not work for Inhomogeneous multi-component system

1 D. Reith, M. Putz and F. Muller-Plathe, *J. Comput. Chem.* **24**, 1624 (2003)

Coarse-Grained Potentials: parameterization



The IBI method or an alternative procedure leads to a non-bonded interaction potential for the coarse-grained beads.

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Motivation: Molecular vs. Coarse-Grained Simulations

The Coarse Grain Simulations use the same code as the atomistic molecular dynamics simulations because both are solving Newton's equations of motion given an interaction potential.

In the atomistic simulation, the particles are atoms and the interaction potentials are atom-atom potentials.

In the CG simulation, the particles are CG beads and the interaction potentials are bead-bead potentials.

$$F = ma \qquad F \equiv -\nabla U \qquad \frac{d^2 x_{i,\alpha}}{dt} = -\frac{1}{m}\frac{\partial U}{\partial x_{i,\alpha}}$$

Before Analyzing results, you must verify that your coarse-grained potential can correctly reproduce the structure of the atomistic system.

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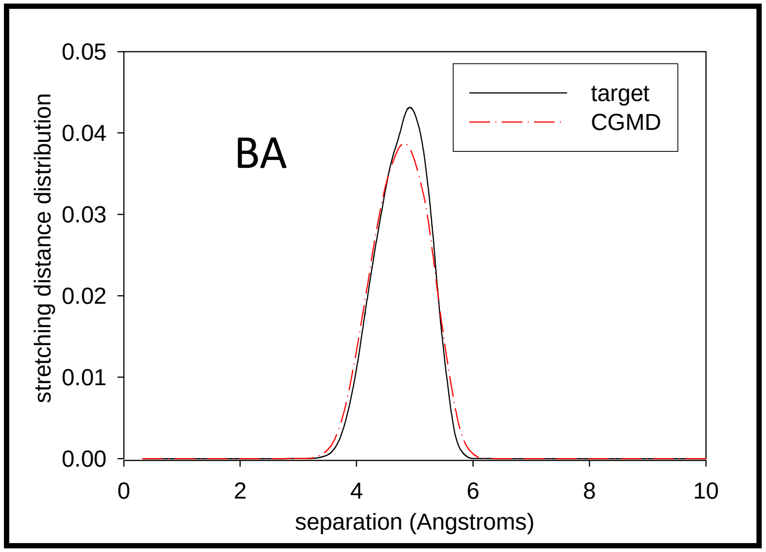
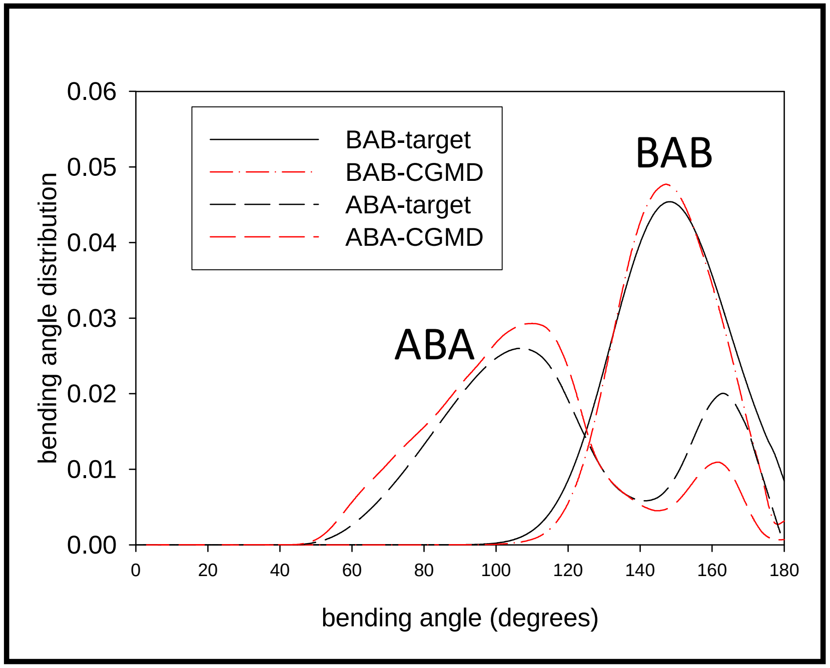
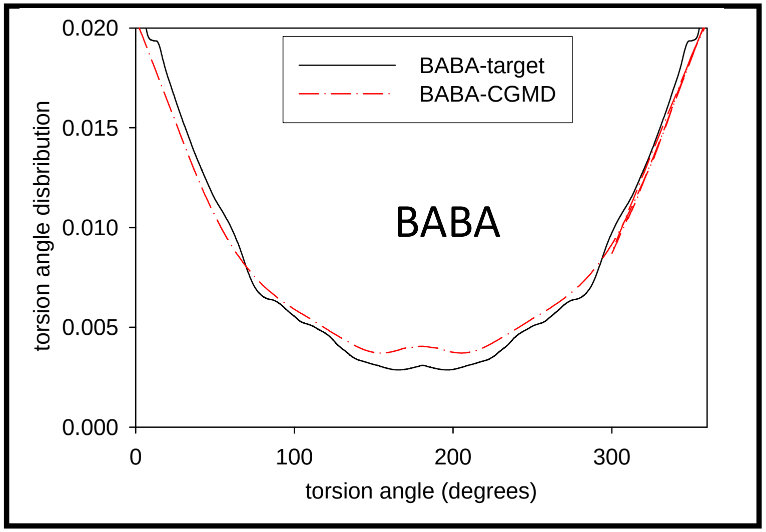
Coarse-Grained MD simulation: validation

We compared the $P(r)$, $P(\theta)$ and $P(\phi)$ from CG and atomistic MD simulation.



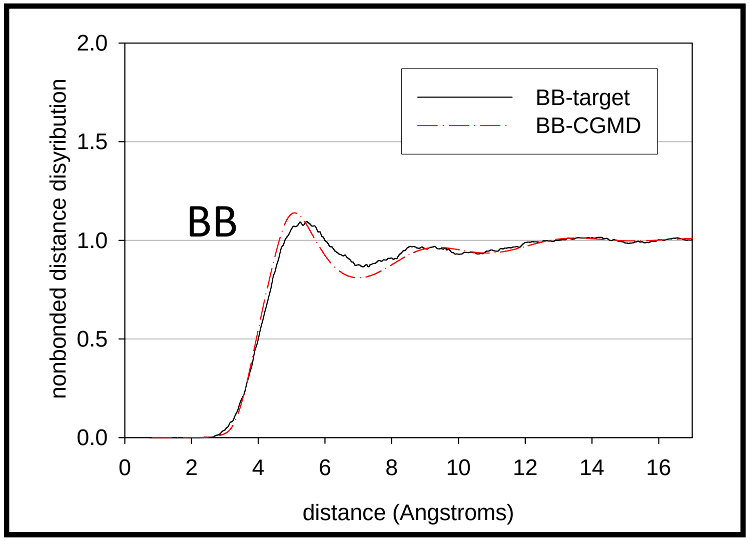


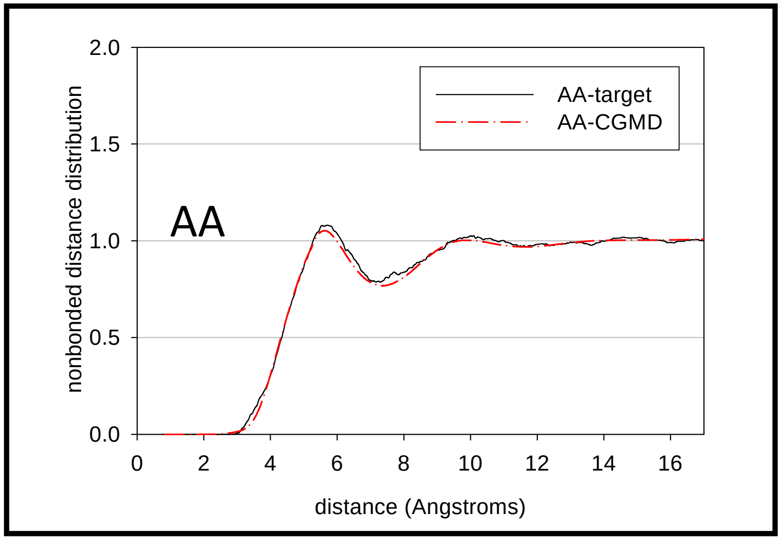


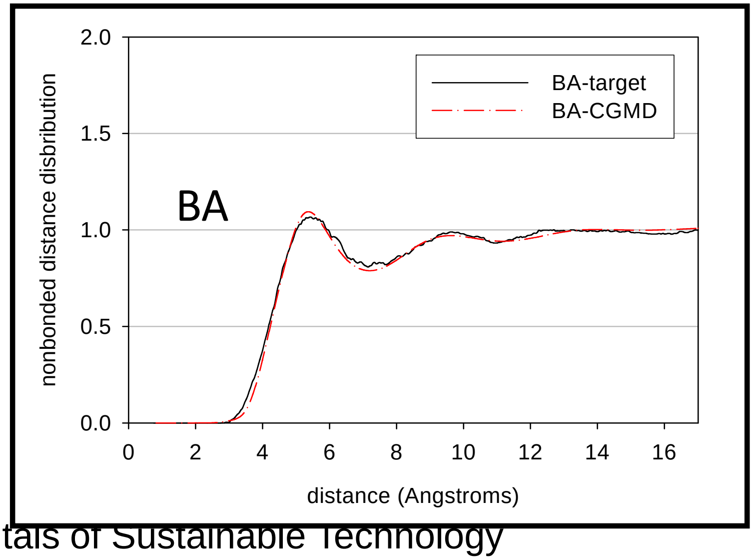
The distributions of beads with bonded interactions from MD simulations match relatively well.

Coarse-Grained MD simulation: validation

Comparison of non-bonded PCFs (BB, BA and AA) from CGMD and atomistic MD simulations.







The non-bonded PCFs from CGMD and atomistic MD simulations match fairly well.

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Sustainable Technology through Advanced Interdisciplinary Research

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VI. More Examples
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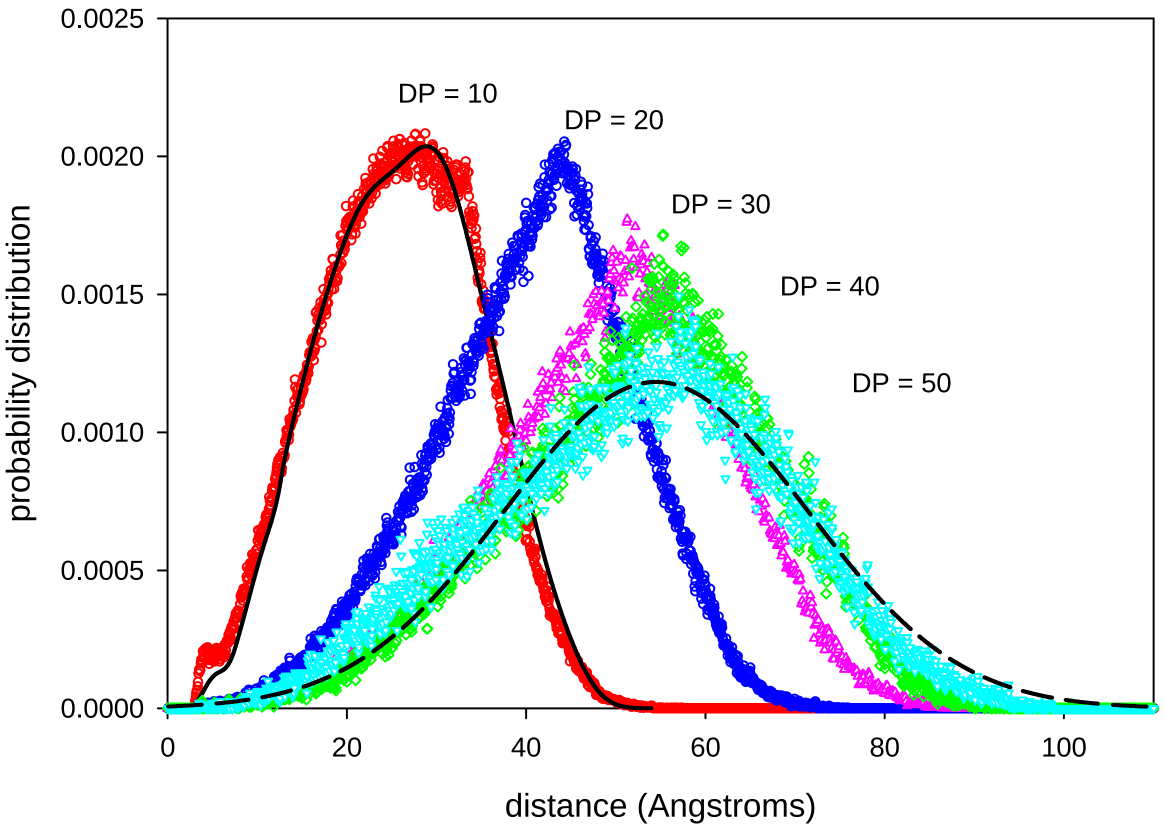
Coarse-Grained MD simulation: chain end-to-end distance distribution

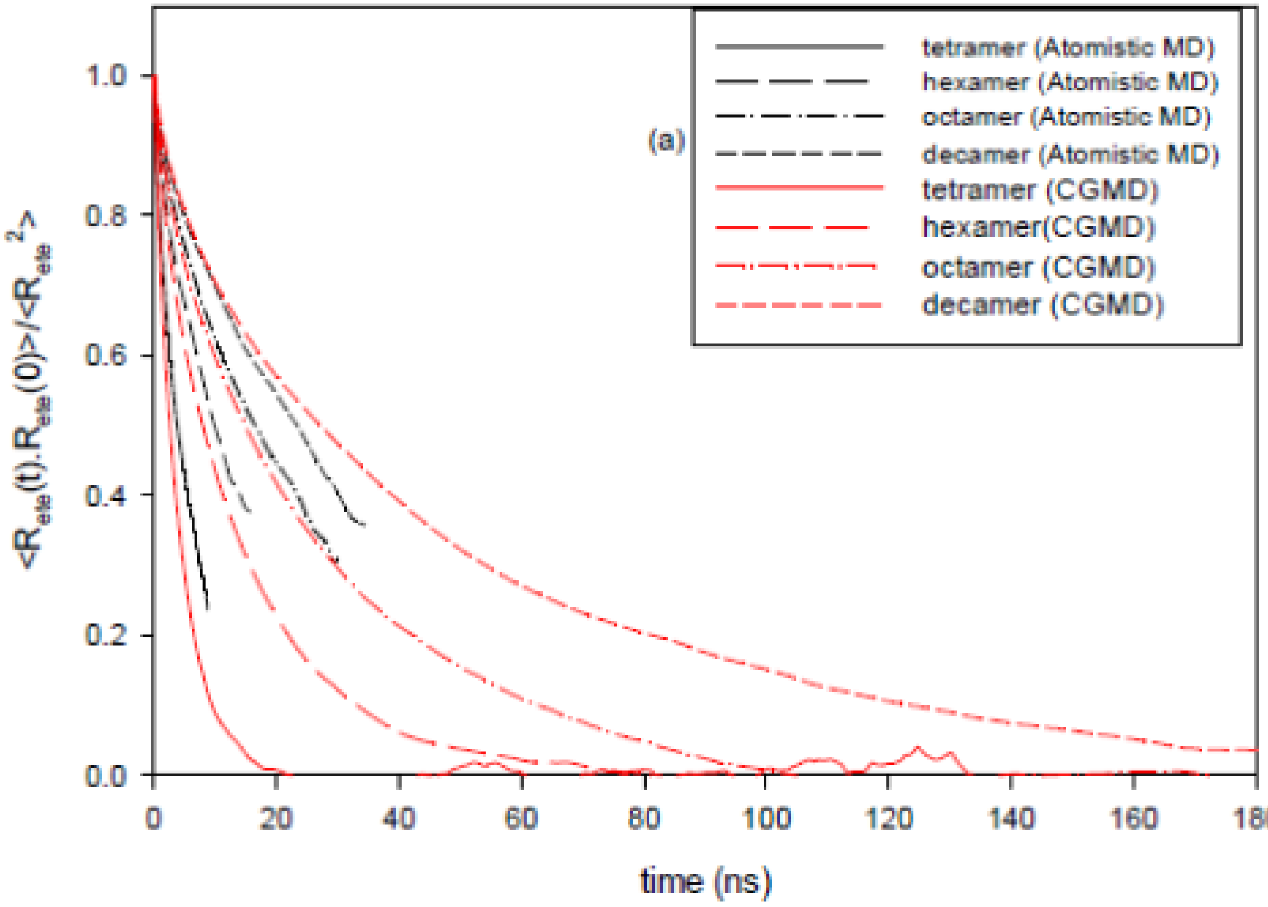


Decamer:

Comparison of chain end-to-end distance distributions from CGMD and atomistic MD match fairly well.

➢**The distributions are not typical Gaussian distributions, with chain length increases, they become more Gaussian like.**

CGMD simulation: comparison of dynamic property chain end-to-end distance auto-correlation function (ACF)



Note: We must scale time in CGMD simulation (Harmandaris *et al. Macromol. Chem. Phys.* (2007)).
5.38 (based on ratio of the values of self-diffusivities)

Atomistic MD: ACFs for long chain systmems can not reach 0 in short times. For decamer, it took roughly 6 months to finish a run of 30ns

CGMD: simulations of the same systems. Apparent speed up is observed. All ACFs can reach 0 in short times. For decamer, it took just 2 weeks to finish a run of 180 ns.

Scaling exponent (*b*)

Scaling exponents: *b* from polymer physics.

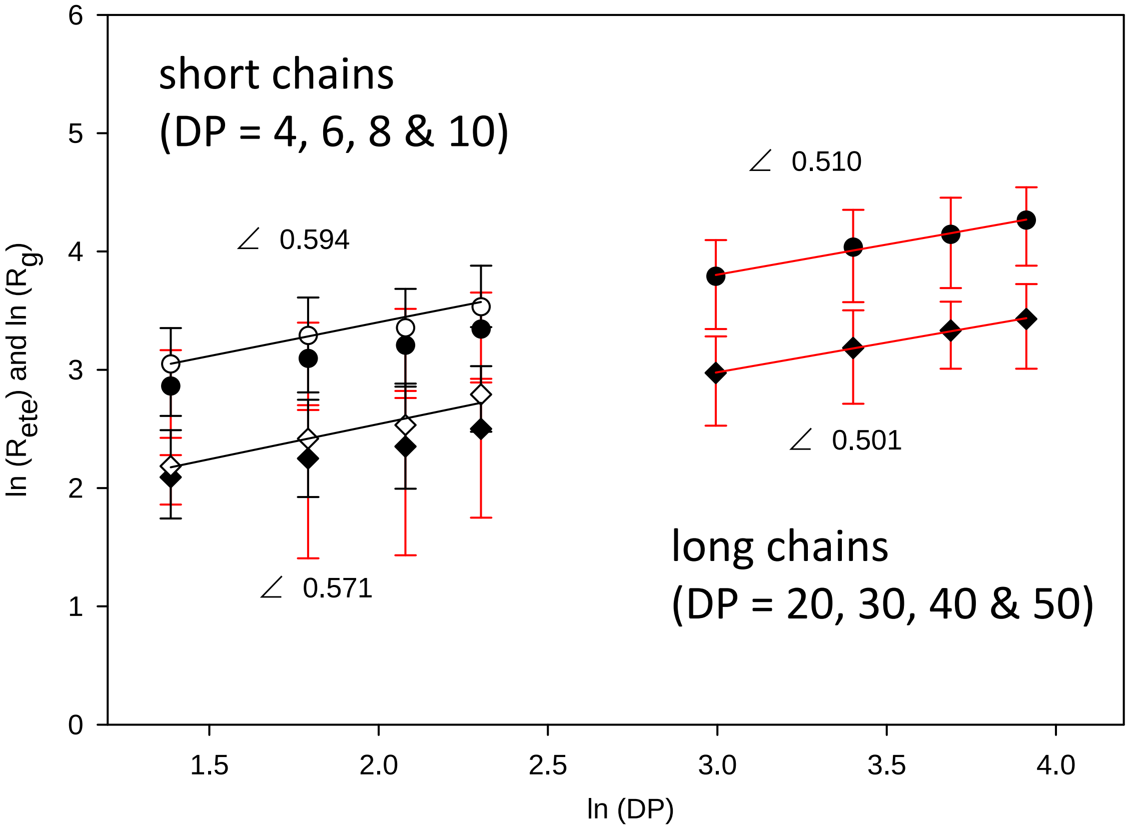
$$X = a(DP)^b$$

DP	Simulation method	D	η	τ_{KWW}	$<R_{ete}>$	$<R_g>$
1~10	Atomistic MD	-2.01	0.96	2.78	0.594	0.571
4~10	CGMD	-1.91	1.6	2.81	0.59	0.57
20~50	CGMD	-2.0	2.0	3.7	0.51	0.50
Rouse Model (1, 2)	N/A	-1	1	2	0.59	0.59
Reptation Model (1, 2)	N/A	-2	3	3	0.50	0.50

1 Tzoumanekas *et al.* Macromolecules 2009

2 Lahmar *et al.* Macromolecules 2009

Coarse-Grained MD simulation: Scaling exponents of R_{ete} and R_g

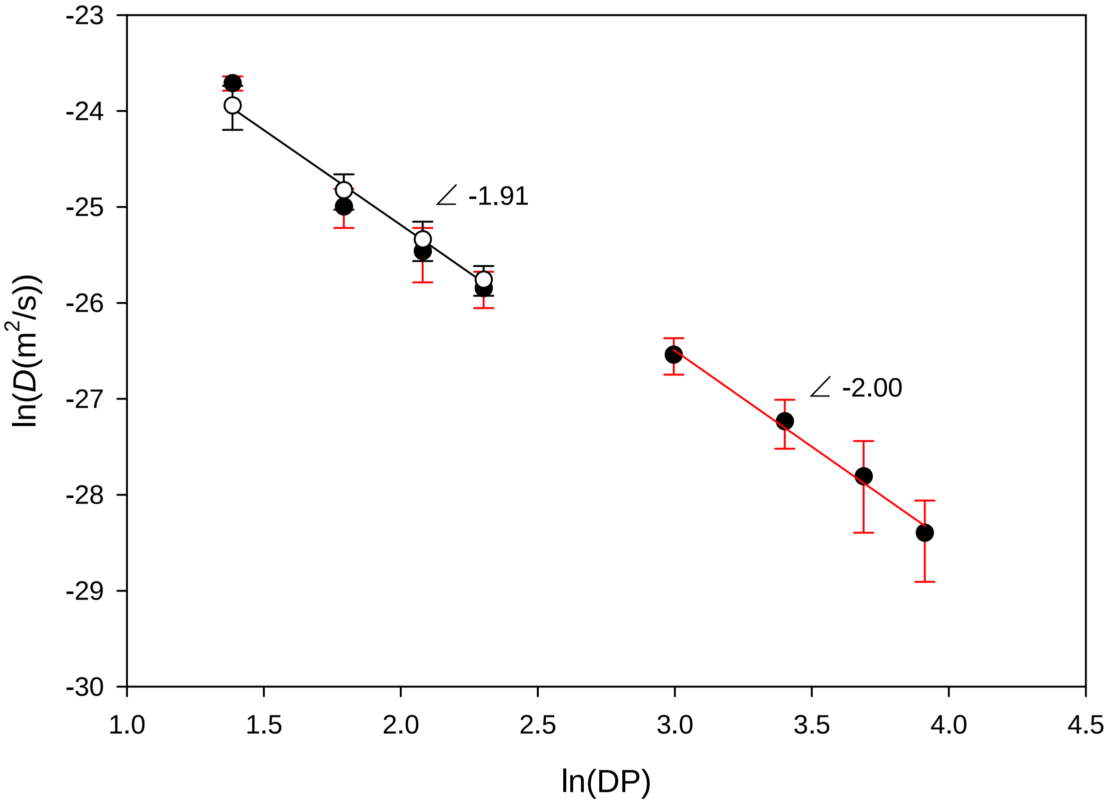


for Long chains: obtained *b* is close to 0.5

for short chains: obtained *b* is in the range of 0.57~0.60

- **The values for both short chains and long chains agree with the Rouse and Reptation theory respectively.**

Coarse-Grained MD simulation: Scaling exponent of self-diffusivity



Rouse model:
for short chains,
***b* = -1**

Reptation model:
for long chains,
***b* = -2**

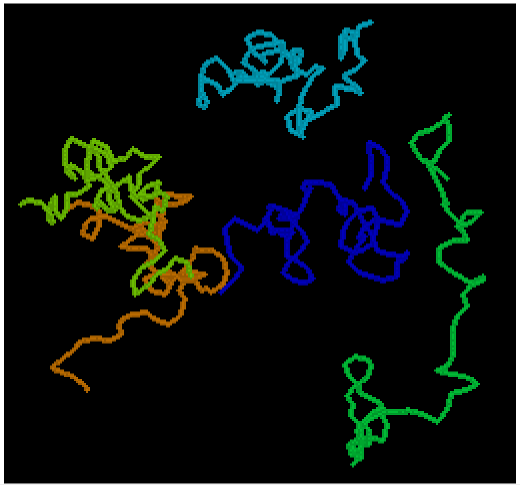
➢**Obtained *b* deviates from Rouse theory for short chains, agrees with reptation theory for long chains.**

Coarse-Grained MD simulation: entanglement analysis

To further understand the reptation behavior, we can do entanglement analysis by extracting entanglement information directly from configurations of the chains.

The Z-code: A common algorithm to study the entanglements in polymeric systems (Kroger, M. *Comput. Phys. Commun.* **2005**)

What can we get from Z-code?
mean contour length of primitive path (<*Lpp*>), tube diameter (*d*), number of monomers between entanglement points (N_e), interentanglement strand length (N_{ES}), defined as:



$$N_{ES} = \frac{N(N-1)}{Z(N-1)+N}$$

Kamio *et al*. Macromolecules **2007**, 40, 710.

Coarse-Grained MD simulation: entanglement analysis

DP	**$\langle L_{pp} \rangle$ (Å)**	**d (Å)**	**N_e**	**Z**	**N_{ES}**
10	31.99	19.07	8.82	1.87	7.19
20	62.08	33.08	14.60	2.44	11.16
30	92.17	35.38	18.67	3.51	13.48
40	110.22	38.49	22.16	4.34	15.13
50	133.23	34.74	22.60	6.02	14.37
rheology models	N/A	35[a], 38-43[b]	30.2[a], 24.2[b], 25.0[c]	N/A	14.9[d]

- For DP = 10, unentangled system. for DP = 20 to 50, (d), (Ne) and (N_{ES}) are very close to the reported values for entangled PET melts.

a Fetters *et al.* In *Physical Properties of Polymers Handbook*; James E. Mark, 2007
b Fetters *et al. Macromolecules* **1994,** *27,* 4639.
c Lorentz, G.; Tassin, J. F. *Polymer* **1994,** *35,* 3200.
d Kamio *et al*. Macromolecules 2007, 40, 710.

Conclusions:

- In this example, a multiscale modeling approach was used to model PET.

- Atomistic MD simulations were used to model short chains, up to DP=10. From these simulations, PCFs of the proposed CG beads were generated.

- A technique (Iterative Boltzmann Inversion, or in this case the Ornstein-Zernike equation) was used to generate interaction potential for the CG beads.

- CG dynamic simulations of short chains were performed. From these simulations, PCFs of the CG system were generated.

- The PCFs from the atomistic and CG simulations of short chains were compared to validate the CG potentials.

- Once validated, the CG potentials were used to simulate long chains, which could be compared to reptation theory and entanglement models.

Acknowledgments

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