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Sustainable Technology through Advanced Interdisciplinary Research

Coarse-Grained MD simulation of PET polymers

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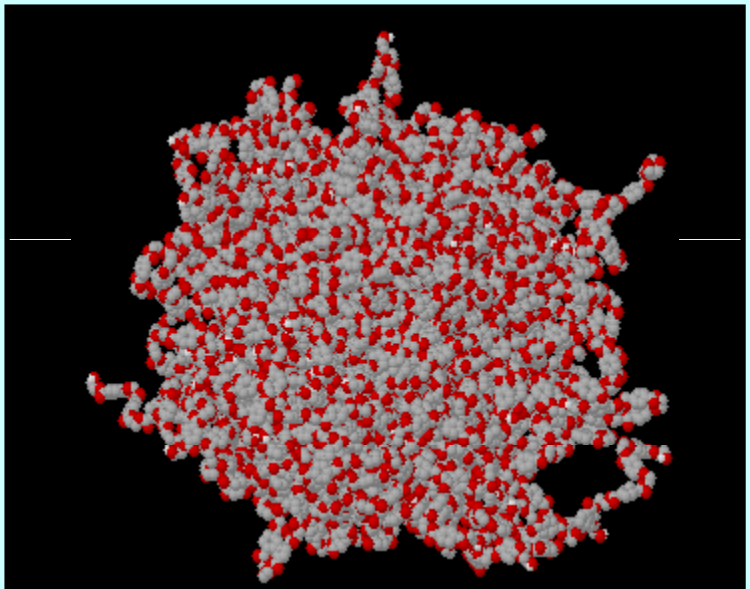
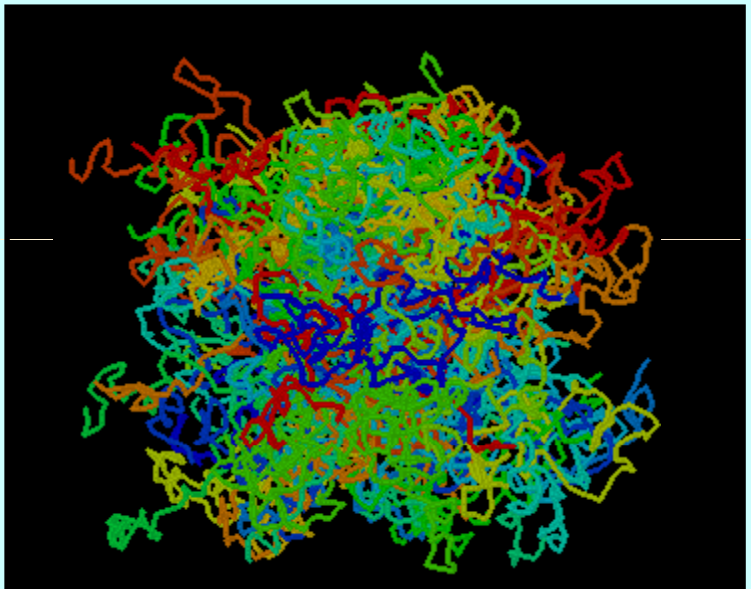
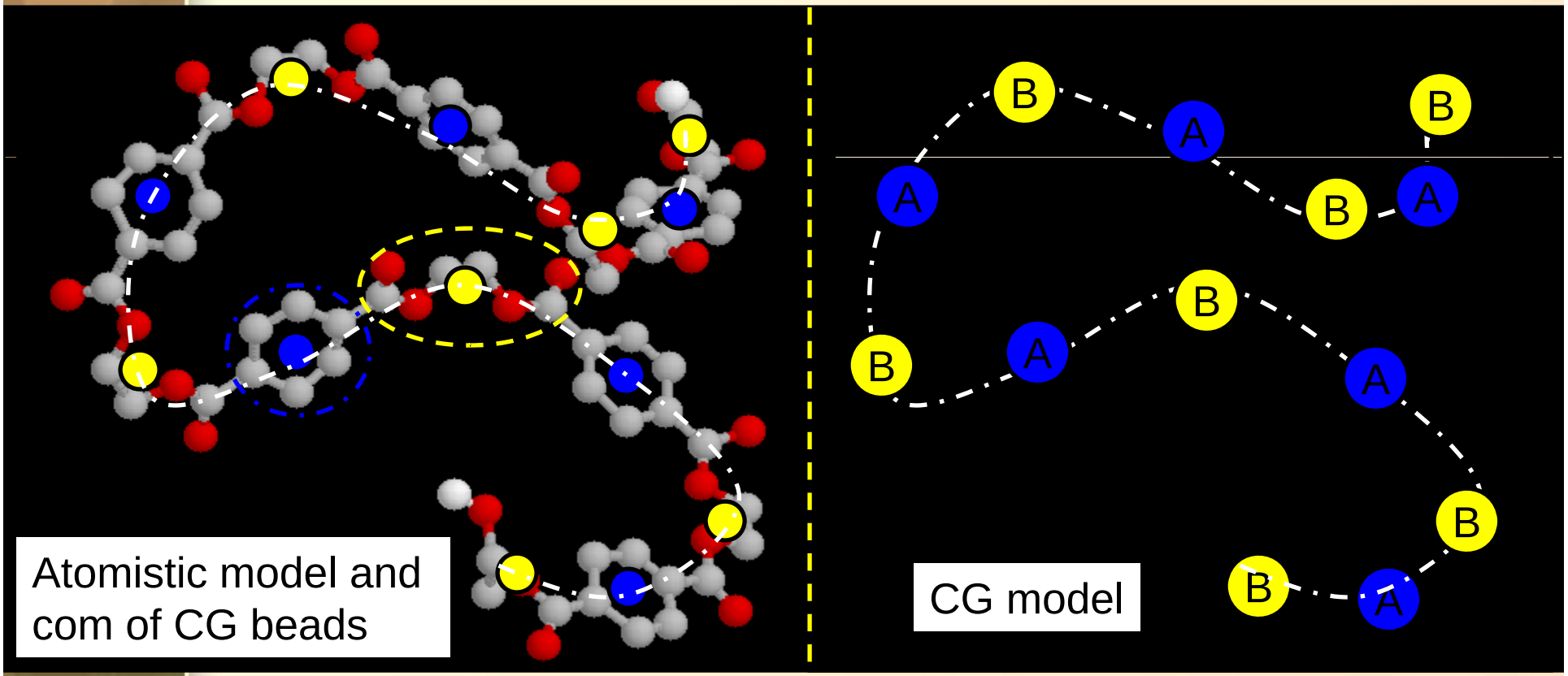
Motivation: Molecular vs. Coarse-Grained Simulations

Molecular System	Coarse-Grained System
 DP = 10, ~ 30 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)

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

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.

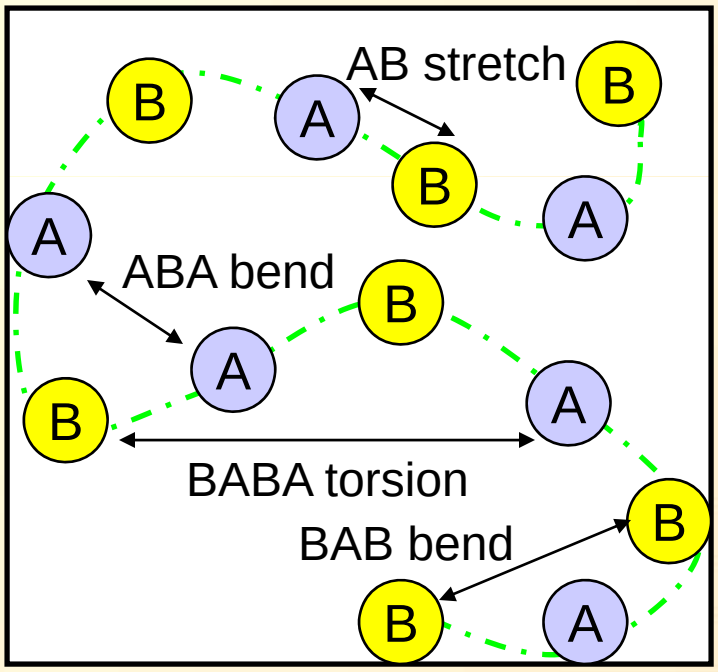


CG model on top of atomistic model for hexamer (DP=6)

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

Coarse-Grained Potentials: parameterization

We must figure out all interaction modes according to the CG model and parameterize the CG potentials for each mode (stretching, bending, torsion, non-bonded interactions) to match the structures of atomistic simulation.



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

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

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

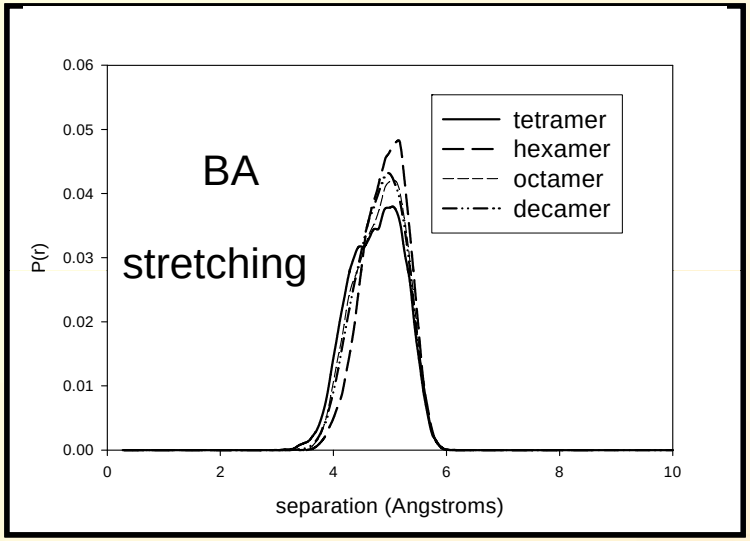
$$U^{CG}_{bend}(\theta,T) = -k_B T \ln P^{CG}_{bend}(\theta,T) + C_\theta$$

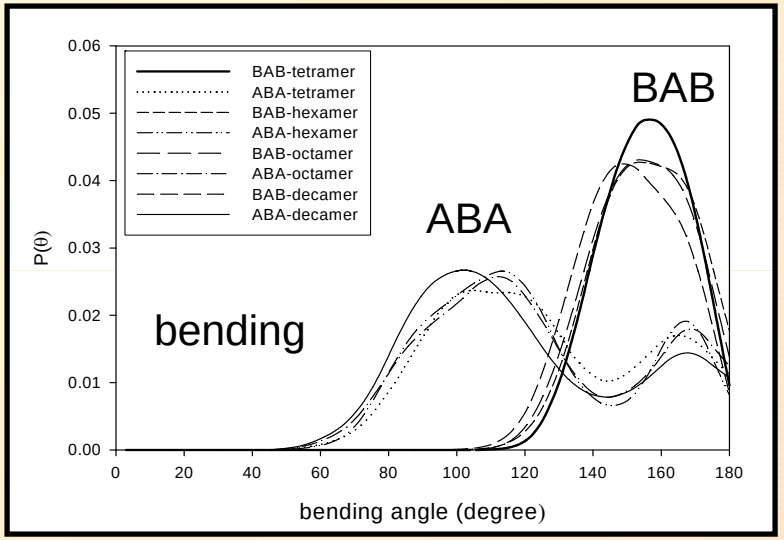
$$U^{CG}_{torsion}(\phi,T) = -k_B T \ln P^{CG}_{torsion}(\phi,T) + C_\phi$$

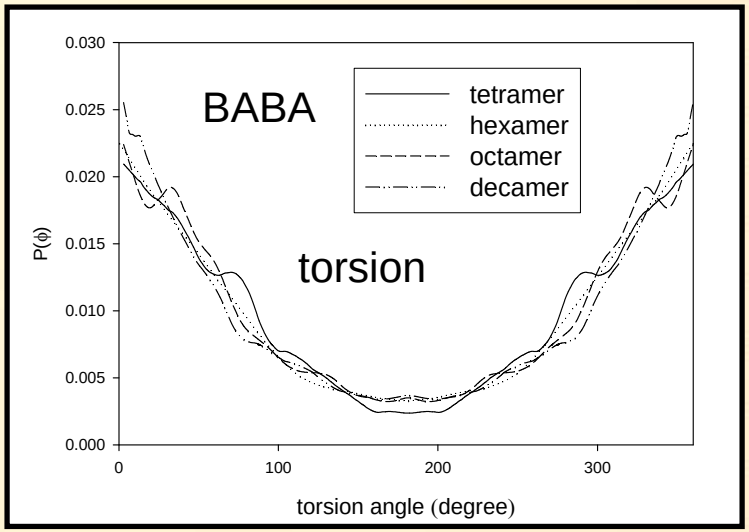
To get the potential of each mode, we have to obtain the distribution function first, this can be extracted by analyzing atomistic simulation configurations of short chains.

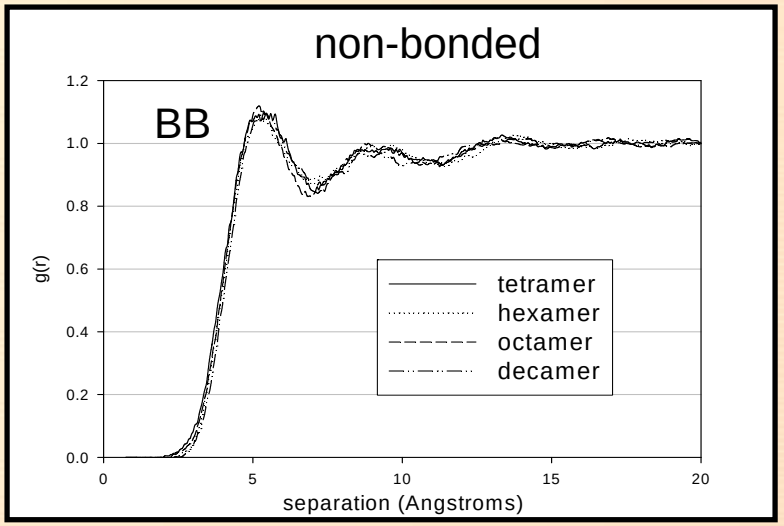
Coarse-Grained potentials: distributions of CG beads

We obtained $P(r)$, $P(\theta)$, $P(\phi)$, $g(r)$ based on atomistic MD simulation configurations.





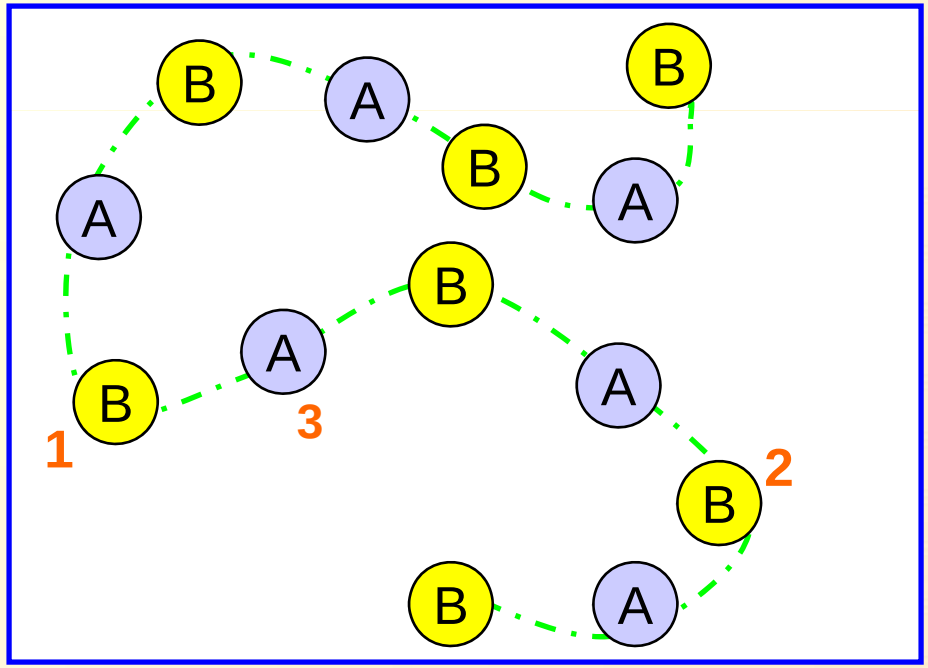




Coarse-Grained potentials: OZPY^{-1} method for CG polymers

OZ integral equation: exact relationship between pair correlation function (PCF) and interaction potential

$$g(r)-1=c(r)+n\int c(s)h(t)\,dV$$



OZPY: given U, find PCF
OZPY^{-1}: given PCF, find U
need to know:

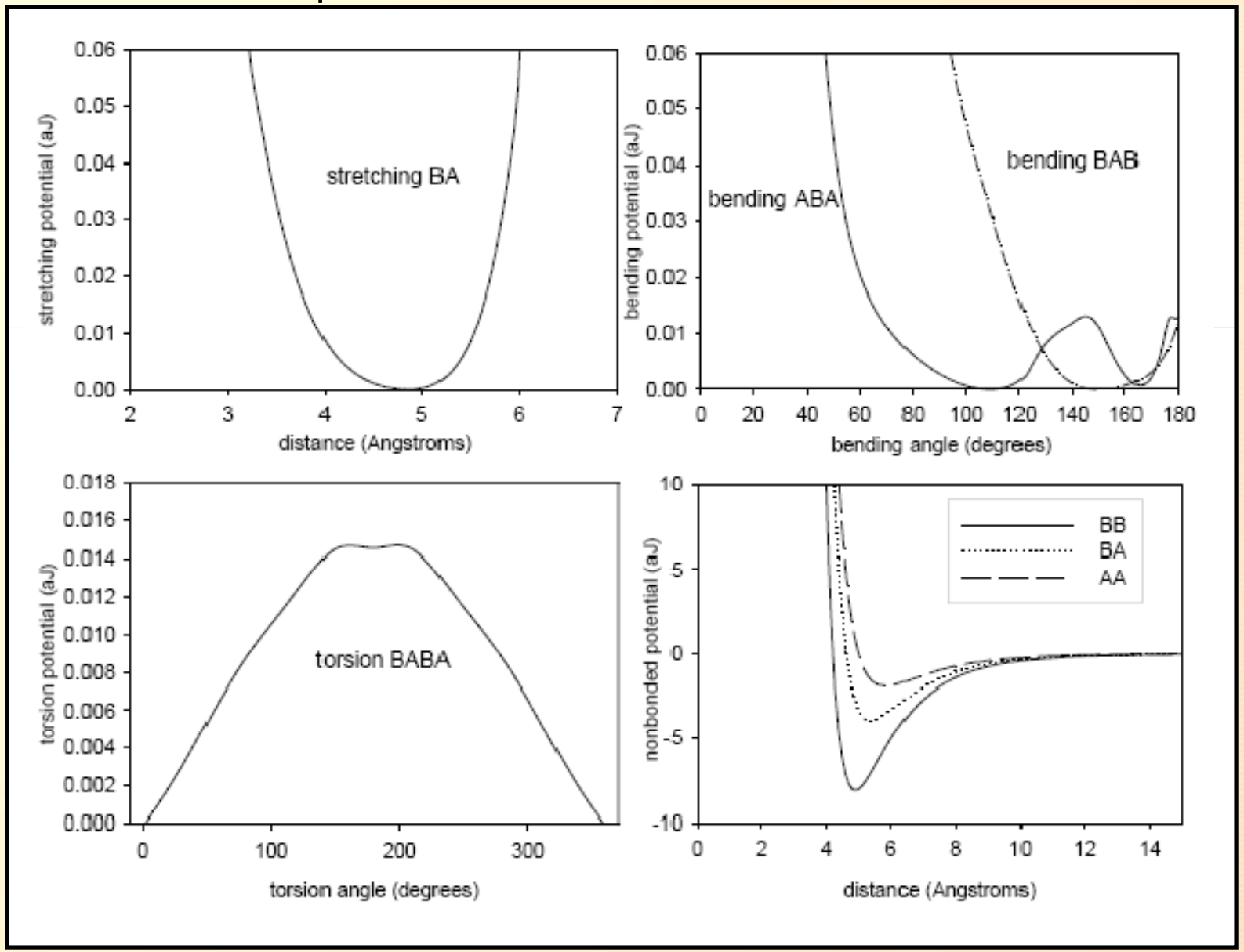
- PCFs
- allowable combinations

$(BA)_nB$ linear chain

various combinations of stretching, bending and torsion interactions

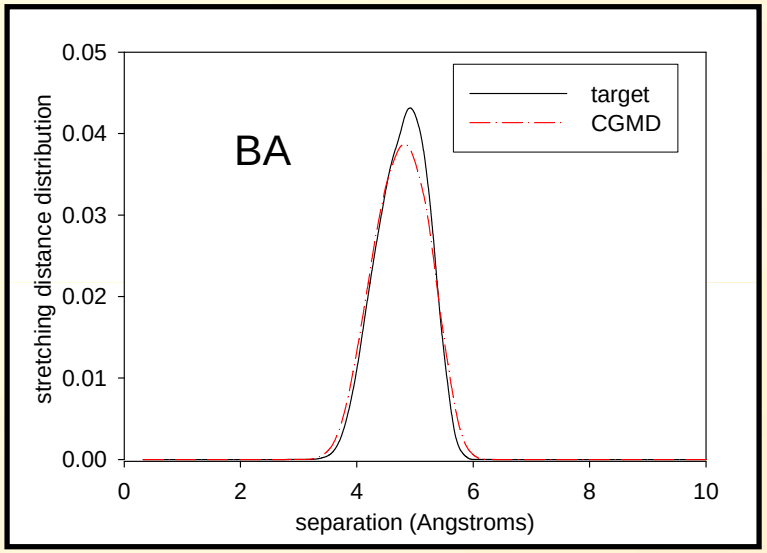
For this model, there are 34 allowable combinations that contribute to the indirect portion of the correlation.

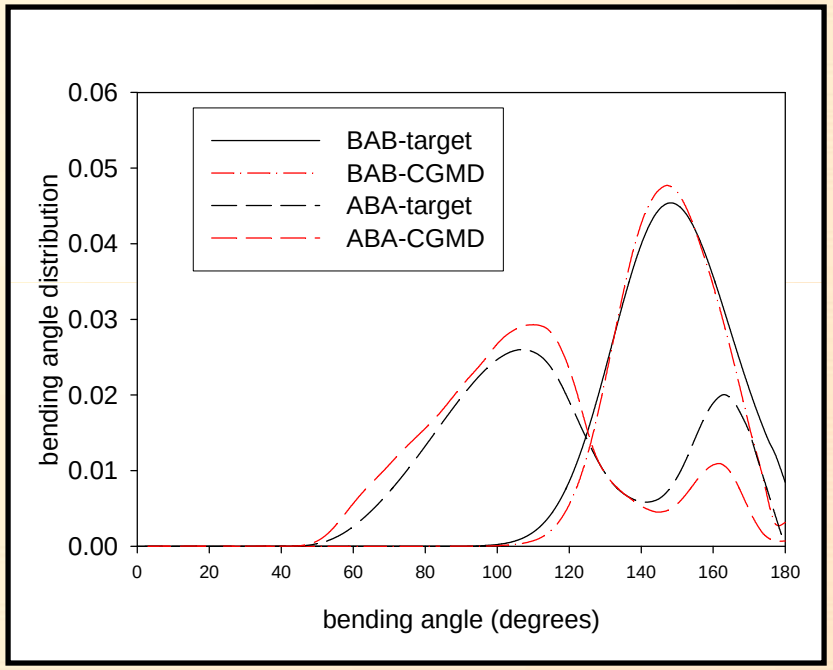
Coarse-Grained potentials: bonded and non-bonded.

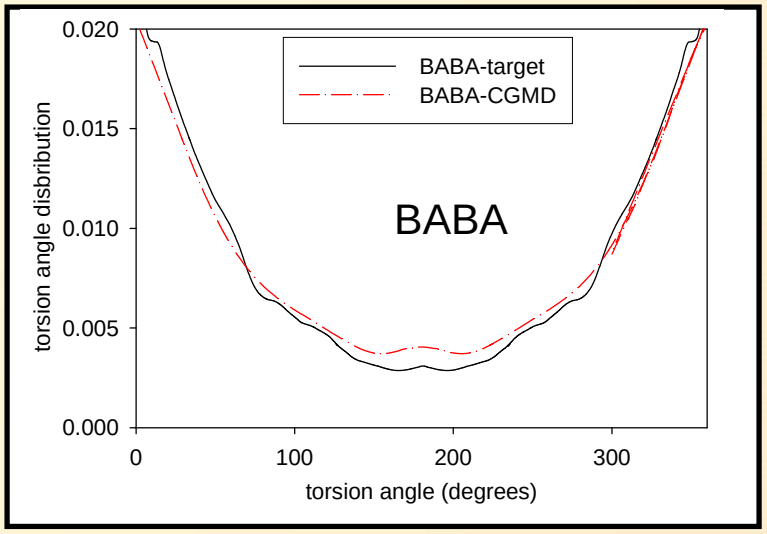


Coarse-Grained MD simulation: comparison of structures.

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



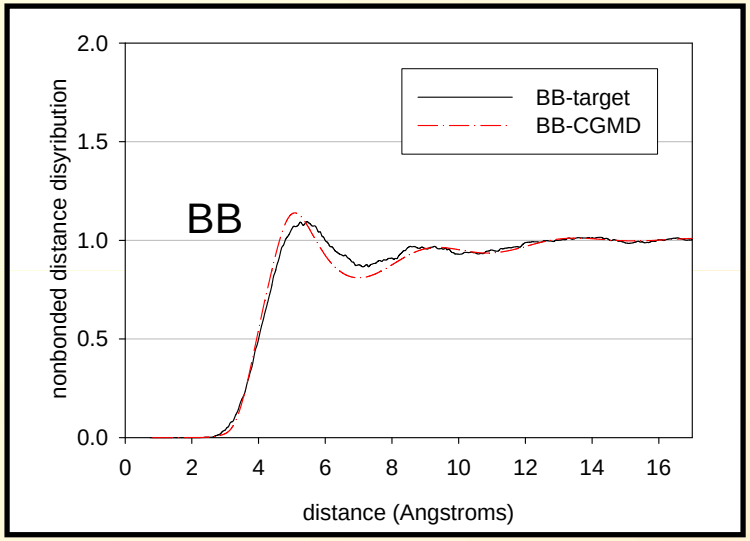


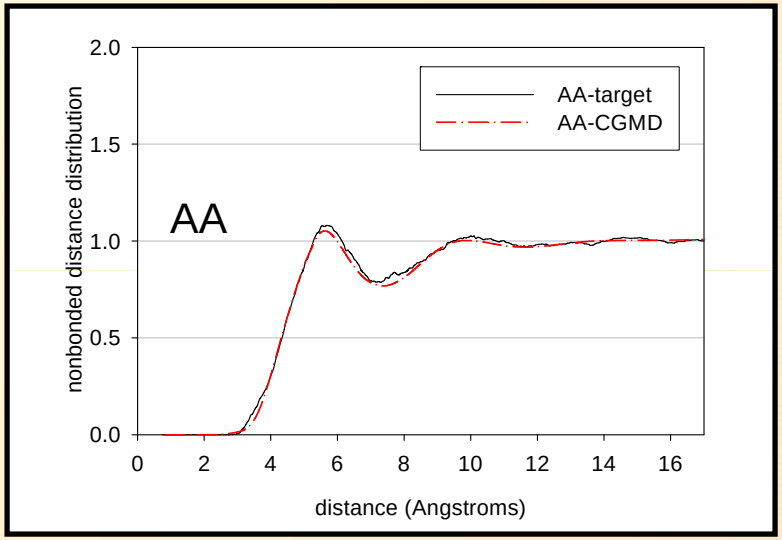


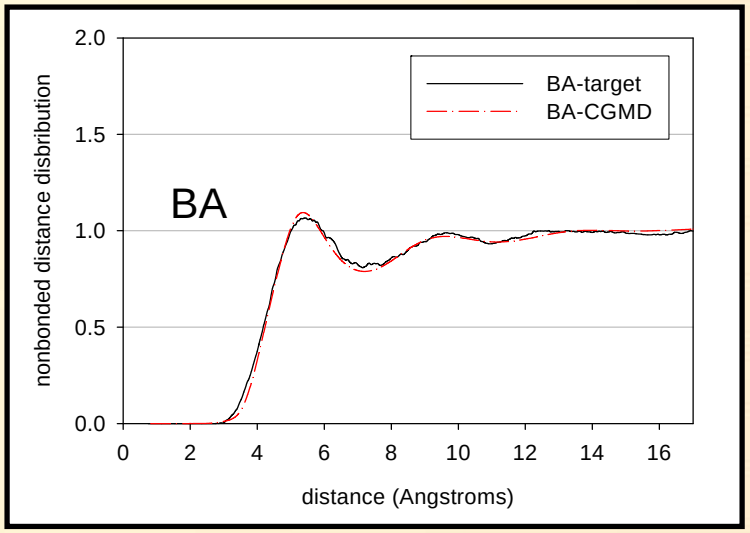
The distributions of beads with bonded interactions from MD simulations match relatively well.

Coarse-Grained MD simulation: comparison of structures

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



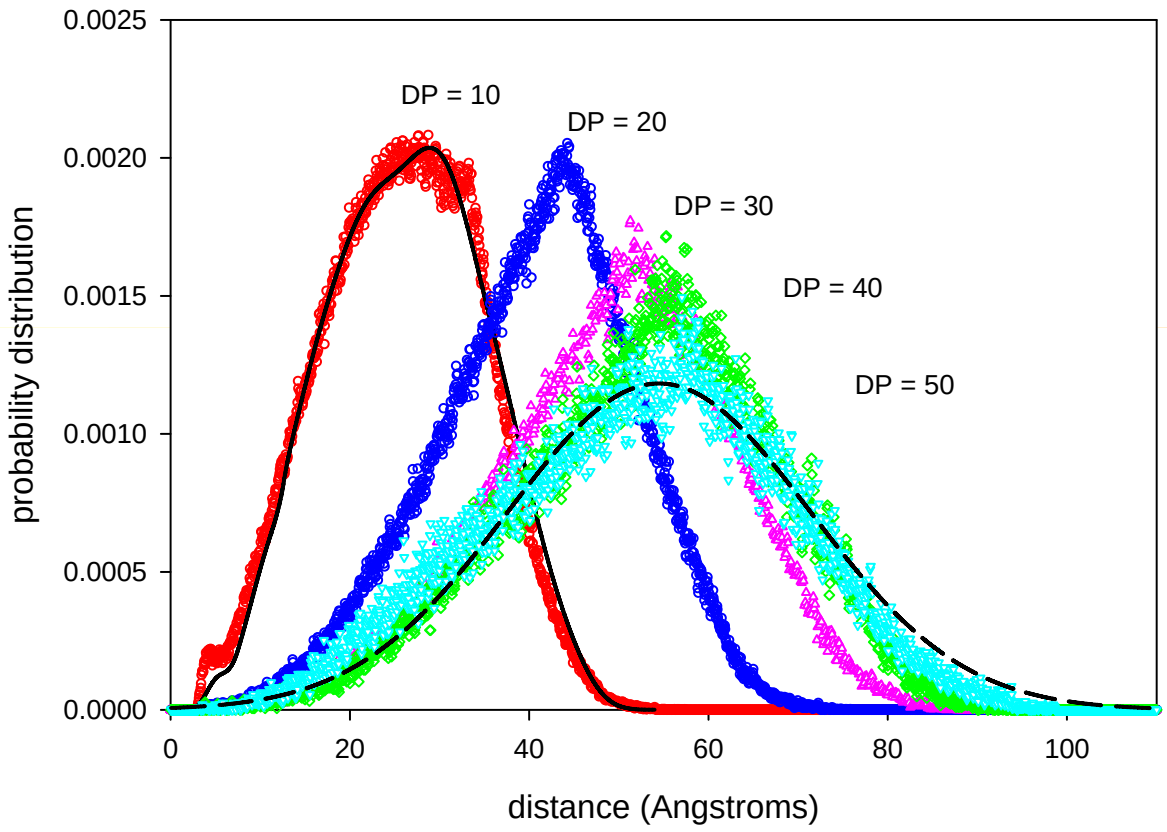




The non-bonded PCFs from CGMD and atomistic MD simulations match fairly well.

Solving the integral equations provides us a way to get a reliable non-bonded interaction potential for CGMD simulation.

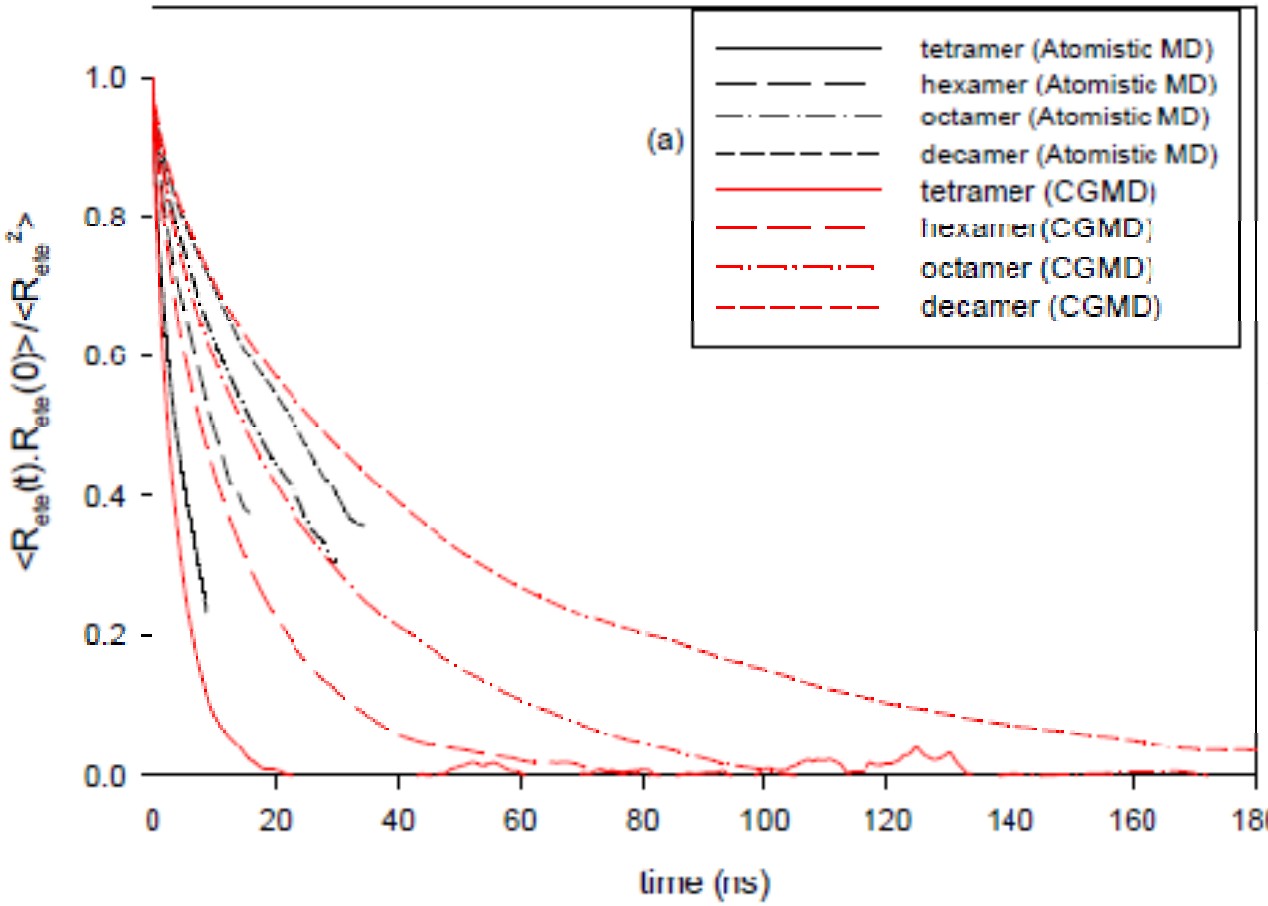
Coarse-Grained MD simulation: chain end-to-end distance distribution



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 factor and Scaling exponent (*b*)

Scaling factors: based on the ratio of the values of self-diffusivities from atomistic and CG simulations. The value 5.38 is used to scale the dynamic properties back to atomistic scope.

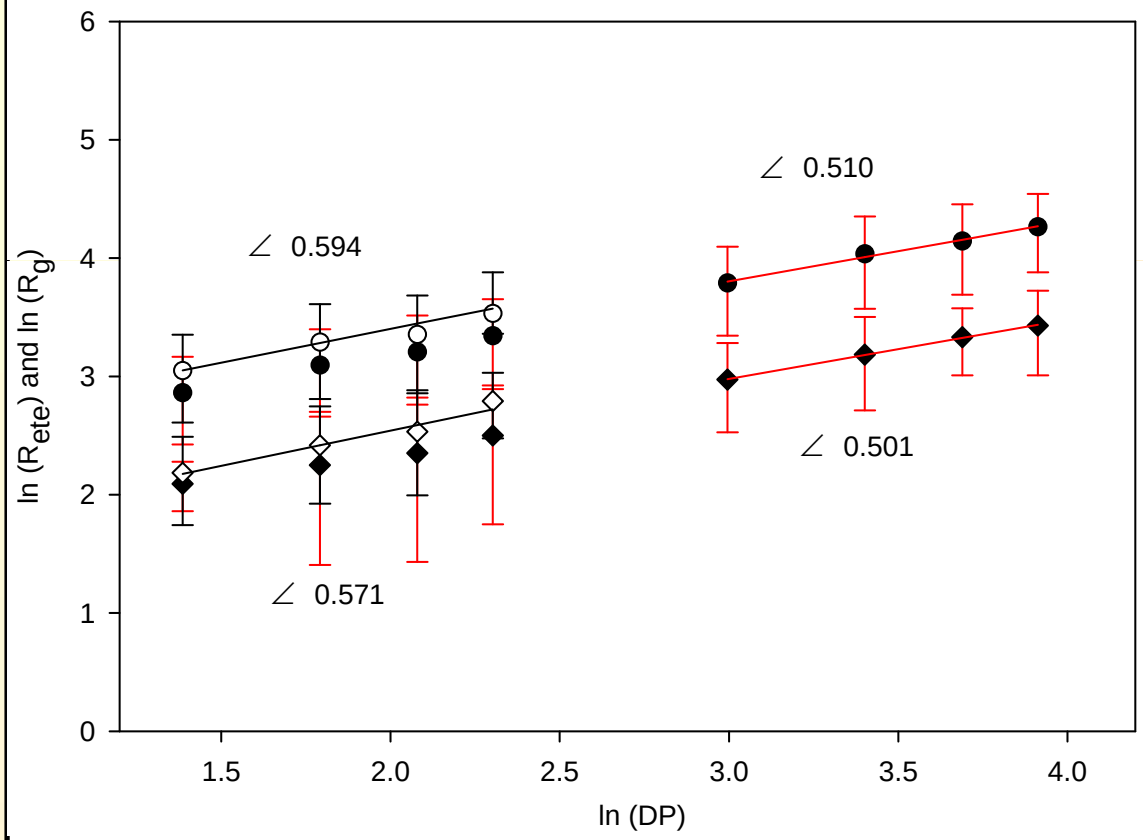
Scaling exponents: *b* from polymer physics.

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

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	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

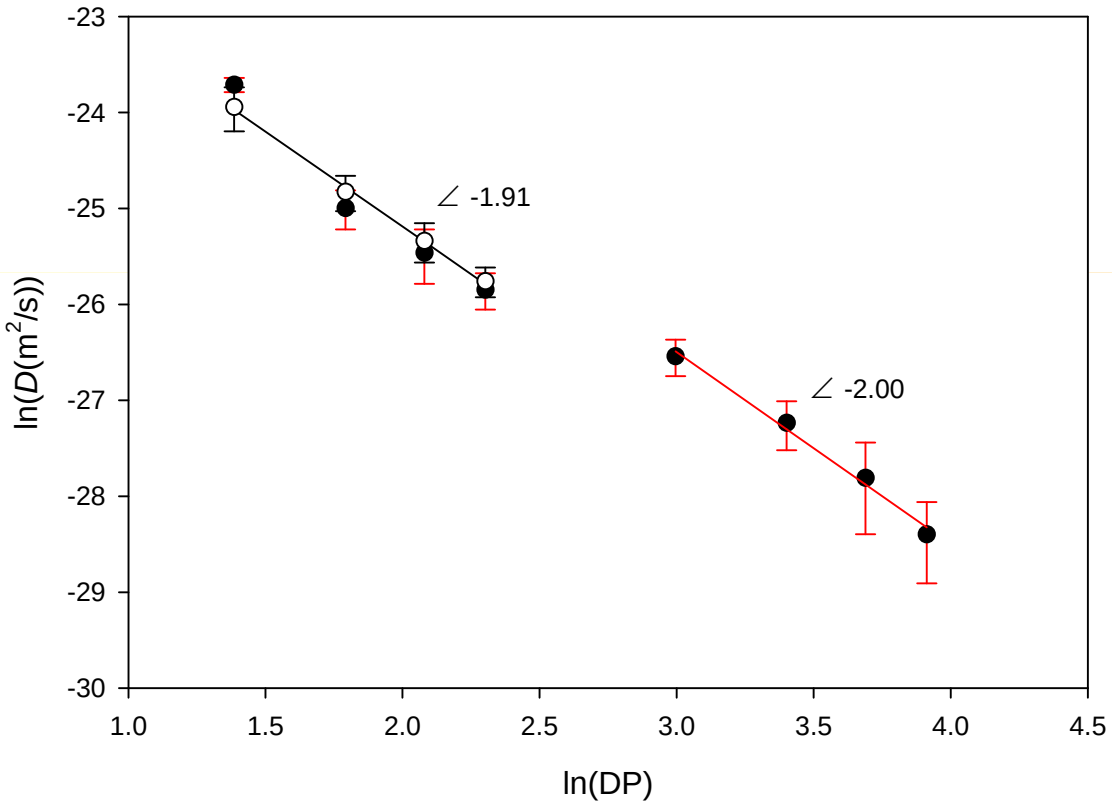


for Long chains: obtained *b* is close to 0.5

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

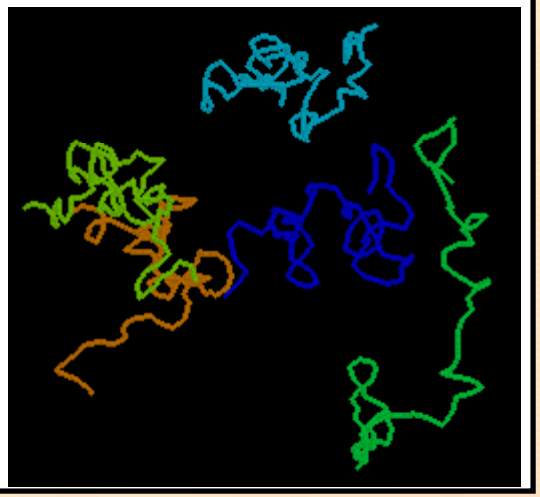
To further understand the reptation behavior, we can do entanglement analysis by extracting entanglement information directly from configurations of the chains.

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:

- A CG model of PET was developed and implemented in CGMD simulations of PET chains with DP up to 50. This allows simulation up to 1 ms.

- The CG potential is parameterized to structural distribution functions obtained from atomistic simulations using an inversion procedure based on (OZPY).

- The CGMD simulation of PET chains satisfactorily reproduces the structural and dynamic properties from atomistic MD simulation of the same systems.

- For the longest chains, we find the scaling exponents of 0.51, 0.50 and -2.00 for average chain end-to-end distance, radius of gyration and self-diffusivity respectively. The exponents are very close to the theoretical values of entangled polymer melt systems.

- The entanglement analysis shows that tube diameter (d), (Ne) and (N_{ES}) of long chain systems are very close to the reported values for entangled PET melts.

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