



**Modeling of Electrochemical Cells:  
Proton Exchange Membrane Fuel Cells  
HYD7007 – 01**

**Lecture 10. Atomistic and Coarse-Grained Models  
of Polymers**

**Dept. of Chemical & Biomolecular Engineering  
Yonsei University  
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- Atomistic simulations
  - method
  - sample results (Wang, Q., Keffer, D.J., Petrovan, S., Thomas, J.B., “Molecular Dynamics Simulation of Polyethylene Terephthalate Oligomers”, *J. Phys. Chem. B.* **114**(2) 2010 pp. 786–795.)
- Coarse-graining Procedure (Wang, Q., Keffer, D.J., Nicholson, D.M., Thomas, J.B., “Use of the Ornstein-Zernike Percus-Yevick Equation to Extract Interaction Potentials from Pair Correlation Functions”, *Phys. Rev. E* **81**(6) 2010 article # 061204. )
- Coarse-grained simulations
  - method
  - sample results (Wang, Q., Keffer, D.J., Nicholson, D.M., Thomas, J.B., “Coarse-grained Molecular Dynamics Simulation of Polyethylene Terephthalate (PET)”, *Macromolecules* **43**(24) 2010 pp. 10722–10734.)



The simulations presented thus far in the course have focused on the structure and dynamics within the aqueous phase. The movement of water and ions occurs on a much faster timescale than the movement of the polymer. Thus, in those analyses, the polymer is considered to be essentially rigid.

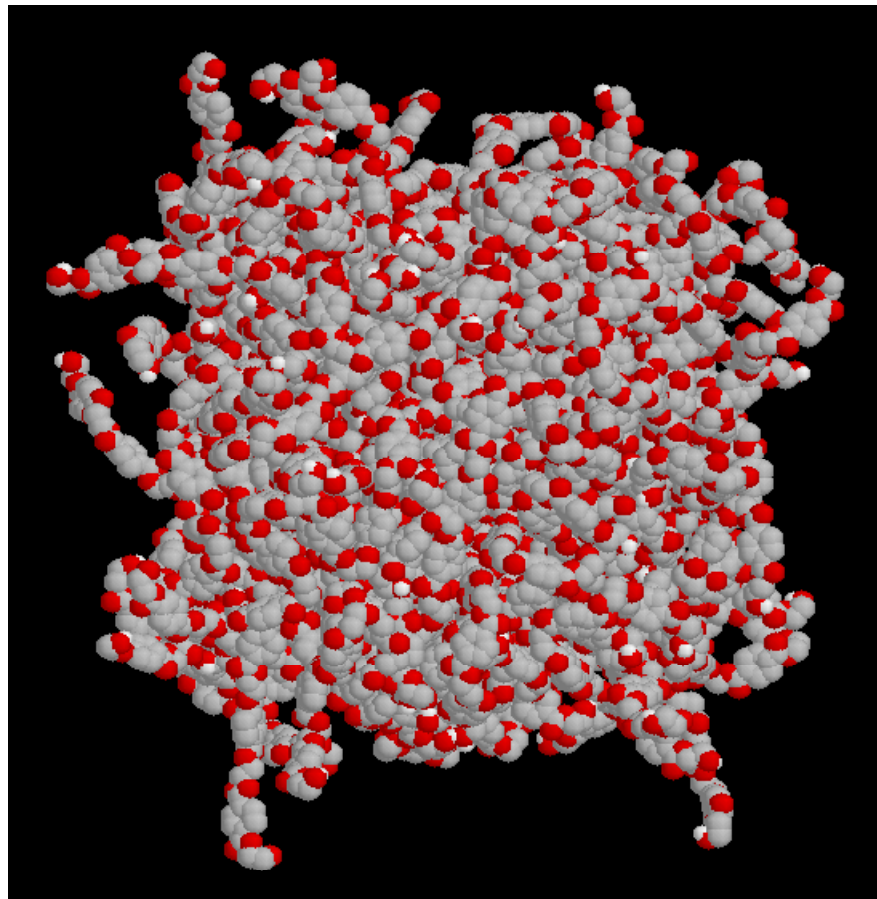
If we are interested in understanding processes that require polymer mobility, such as the response of the membrane to a sustained applied electric field, then we must implement simulations that are capable of much longer timescales.

This is one motivation for moving to coarse-grained simulations of polymers.



## Molecular Level Simulation :

Atomistic MD simulation: Small system, short time.



system size ~ 6 nm

number of oligomers  
125 to 216

number of atoms  
4320 to 18250

simulation duration  
1 to 100 ns

The use of periodic boundary conditions allows bulk properties to be extracted from these simulations.



## Can't Simulate long chains with Atomistic Model

Why?

Longest relaxational time of polymers scales with chain length to the 3-4 power.

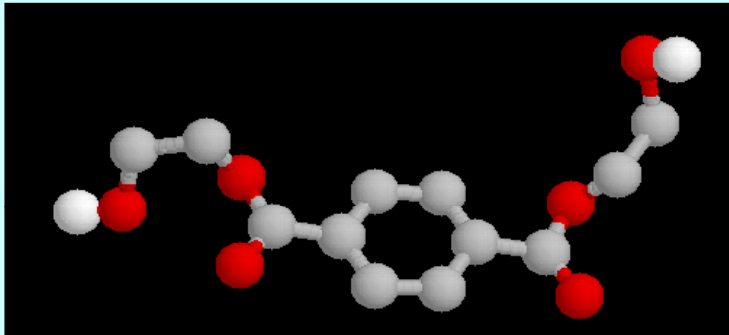
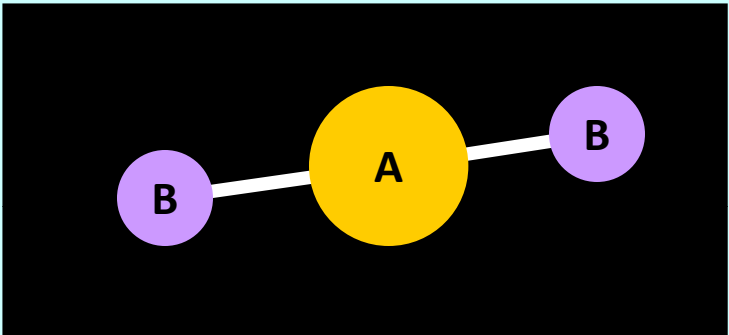
For long chains (DP > 10), the relaxation time is longer than the maximum simulation time available on modern computational resources.

What is the solution?

Coarse-grained models.

DP	time (ns)
1	0.129
2	0.502
3	2.81
4	5.59
6	15.78
8	28.30
10	66.20

## Molecular vs. Coarse-Grained Models: Example Polymer: PET

Molecular Model	Coarse-Grained Model
	
<ul style="list-style-type: none"><li>• atomistic detail</li><li>• structure is known</li><li>• interaction potentials known</li> <li>• many degrees of freedom</li><li>• computationally expensive</li><li>• limited to short chains</li> <li>• use for DP 1 to 10</li></ul>	<ul style="list-style-type: none"><li>• particles are molecular groups</li><li>• grouping is based on intuition</li><li>• interaction potentials unknown</li> <li>• fewer degrees of freedom</li><li>• computationally modest</li><li>• works for long chains</li> <li>• use for DP 25 to 50</li></ul>



## Procedure

1. Run molecular-level simulation for DP = 1 to 10
2. Parameterize coarse-grained potential based on molecular-level simulations
3. Run coarse-grained simulations for DP = 25 to 50



## Molecular Dynamics Simulation:

Based on solving Newton's equation of motion

To simulate  $N$  atoms in 3-D, you must solve a set of  $3N$  coupled nonlinear ordinary differential equations.

$$F = ma$$

The force is completely determined by an interaction potential.

$$F \equiv -\nabla U$$

The ODE for particle  $i$  in dimension  $\alpha$  is thus

$$\frac{d^2 x_{i,\alpha}}{dt^2} = -\frac{1}{m} \frac{\partial U}{\partial x_{i,\alpha}}$$

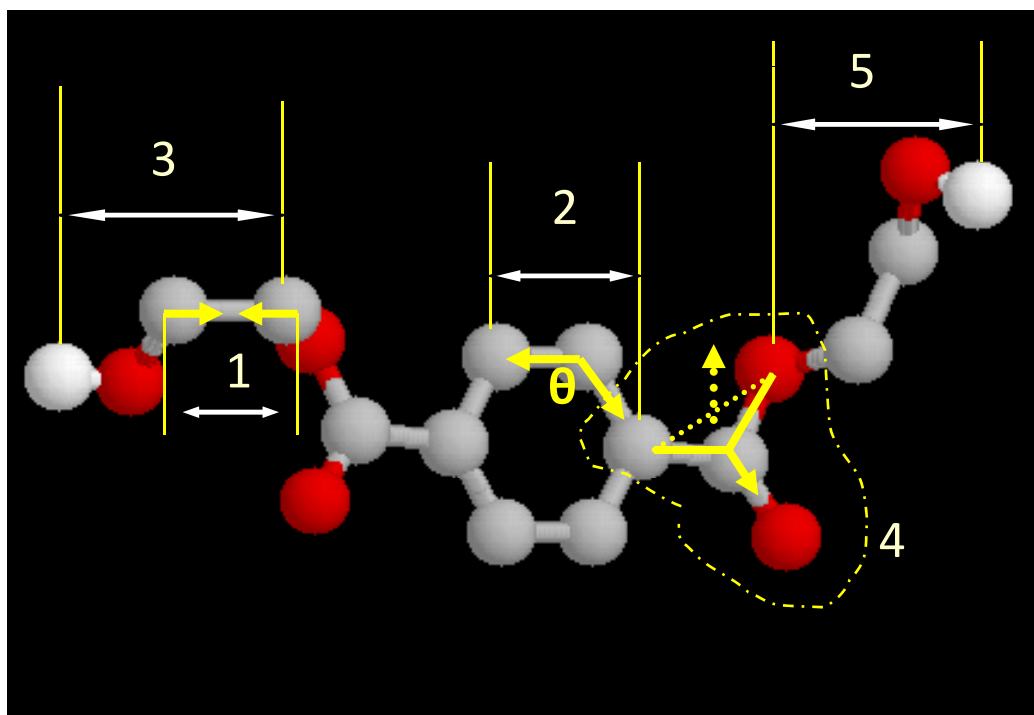
We must provide an interaction potential from either theory, quantum mechanical calculations or experiment.





## Molecular Dynamics Simulation: Intramolecular potential

We use the anisotropic united atom (AUA) potential model developed by Hedenqvist, Bharadwaj and Boyd for PET to describe the intramolecular and intermolecular potential of BHET molecules. Namely, all atoms of BHET molecule are explicitly represented except for the hydrogen connected to carbons



- 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



## Collaboration with Oak Ridge National Laboratory



OAK RIDGE NATIONAL LABORATORY

Managed by UT-Battelle for the Department of Energy



### National Center for Computational Science

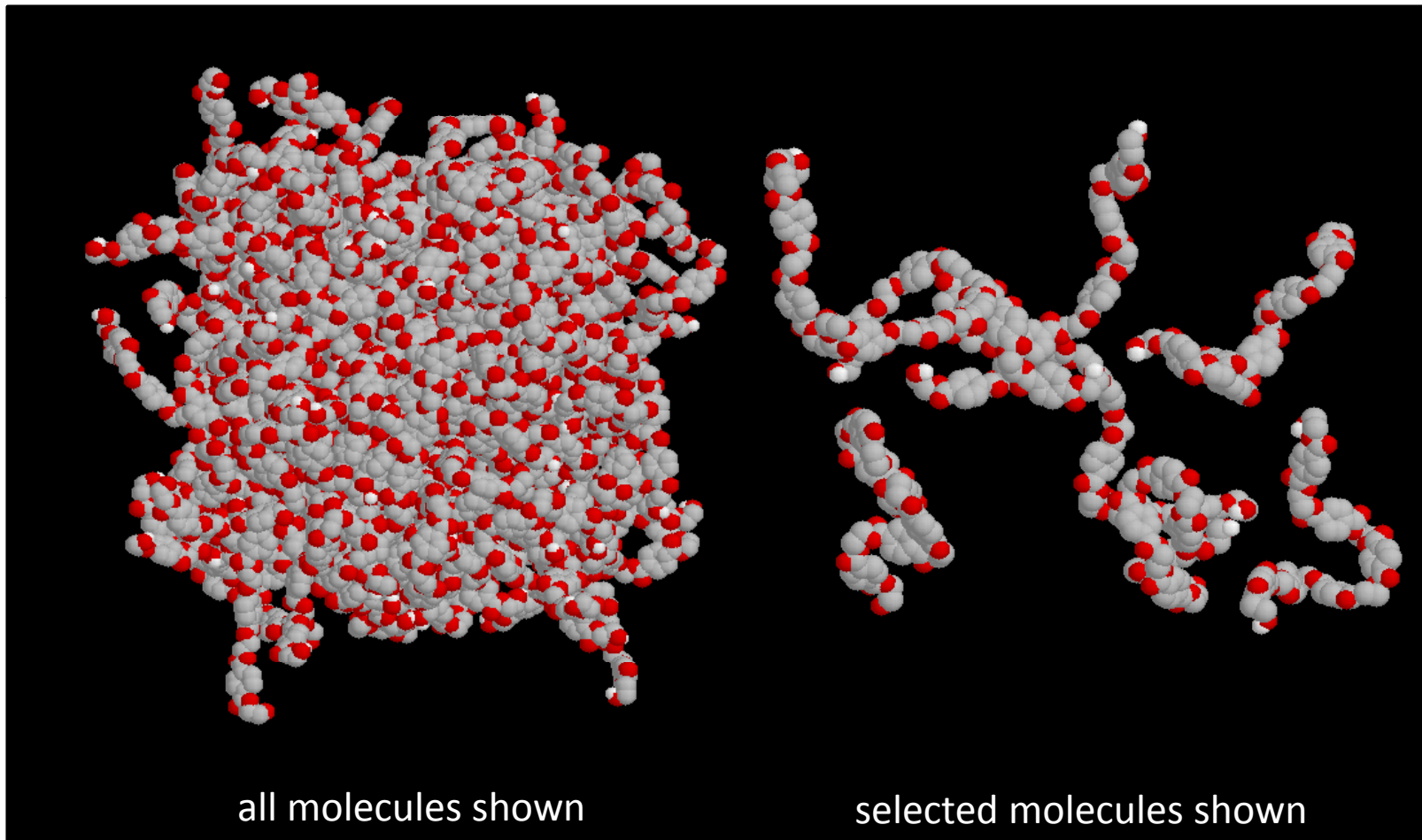
Today the computing resources of the NCCS are among the fastest in the world, able to perform more than 119 trillion calculations per second.

To solve the thousands of ODEs (largest system thus far is 55,000), we use the massively parallel supercomputers at ORNL, both Cray and IBM.

These resources are available to researchers at UT through discretionary accounts of the program directors.



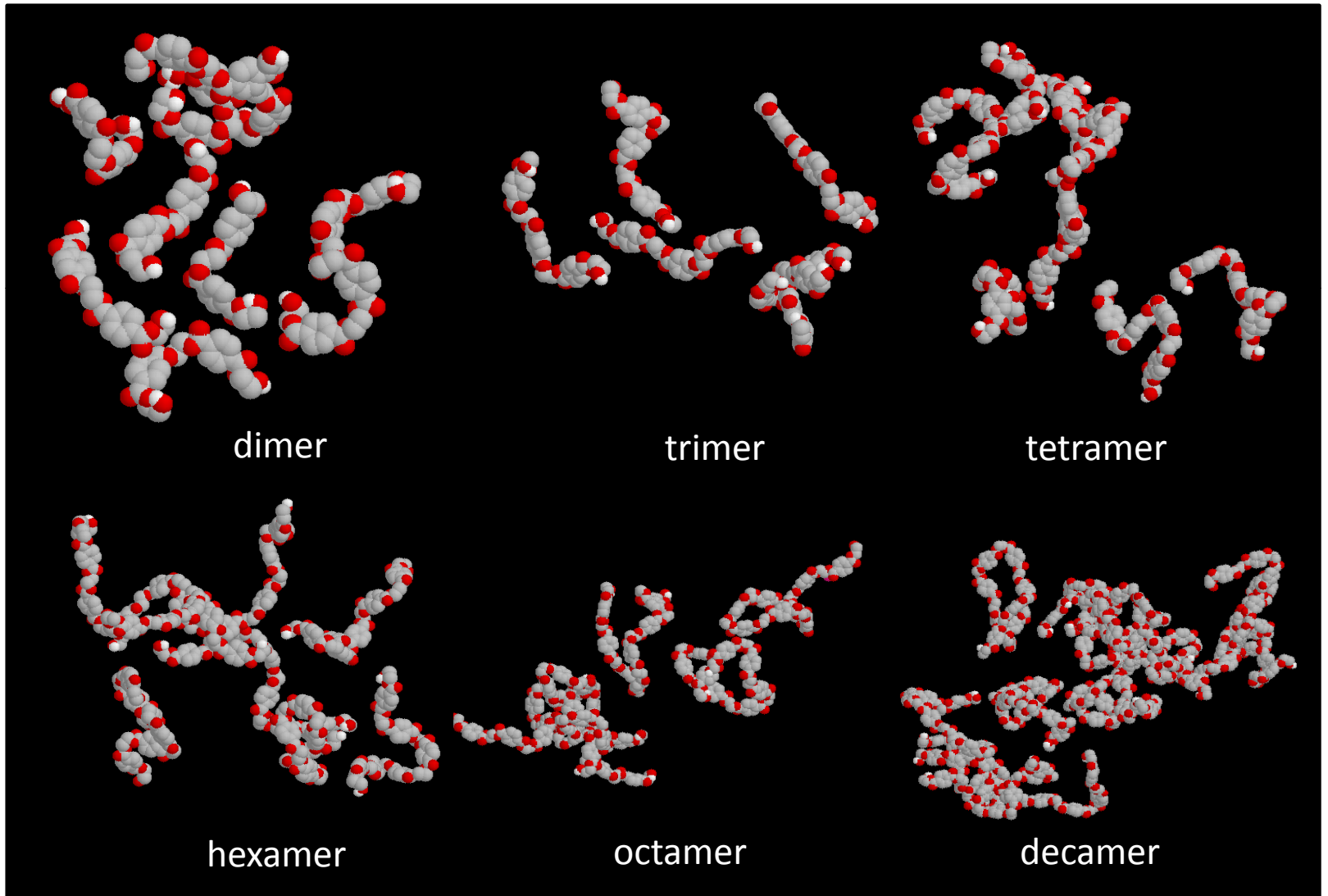
## Molecular Dynamic Simulation Snapshots



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



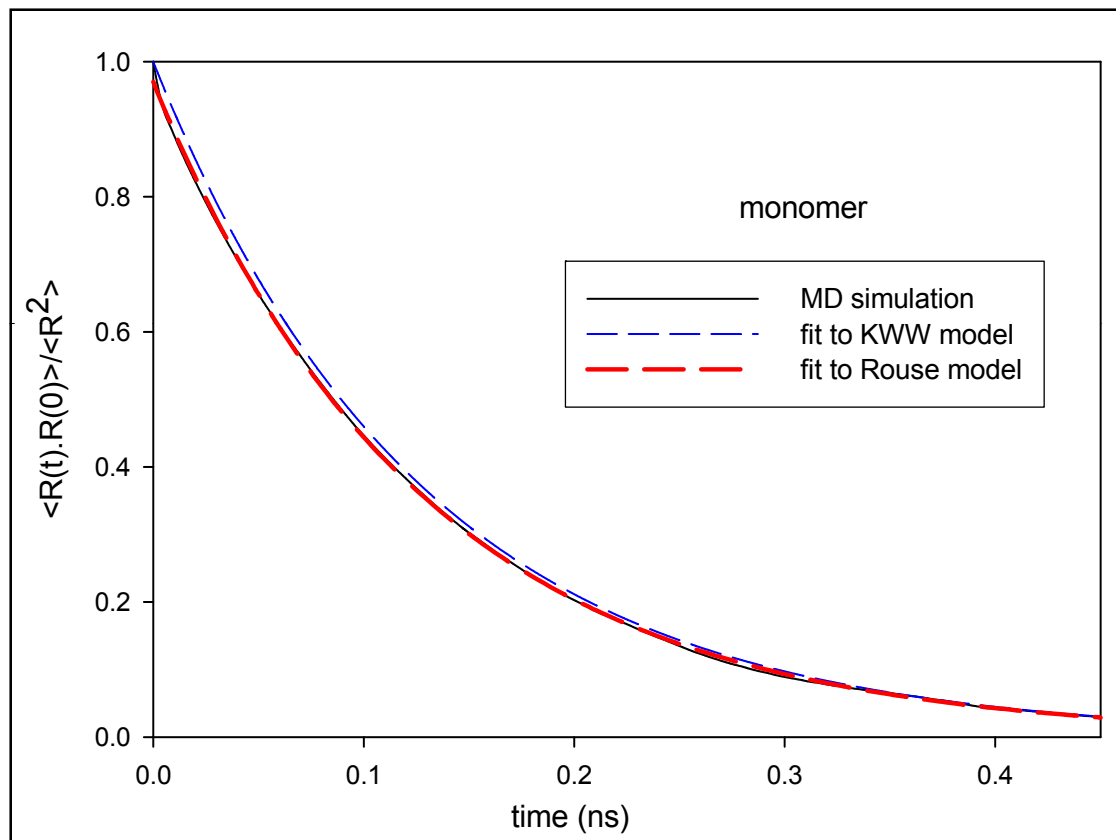
## Molecular Dynamic Simulation Snapshots



All snapshots at  $T = 563 \text{ K}$  and  $p = 0.13 \text{ kPa}$ .



## Structural properties: Relaxation Times



Two traditional models:  
both fit well

$$\exp(-t/\tau_R)$$

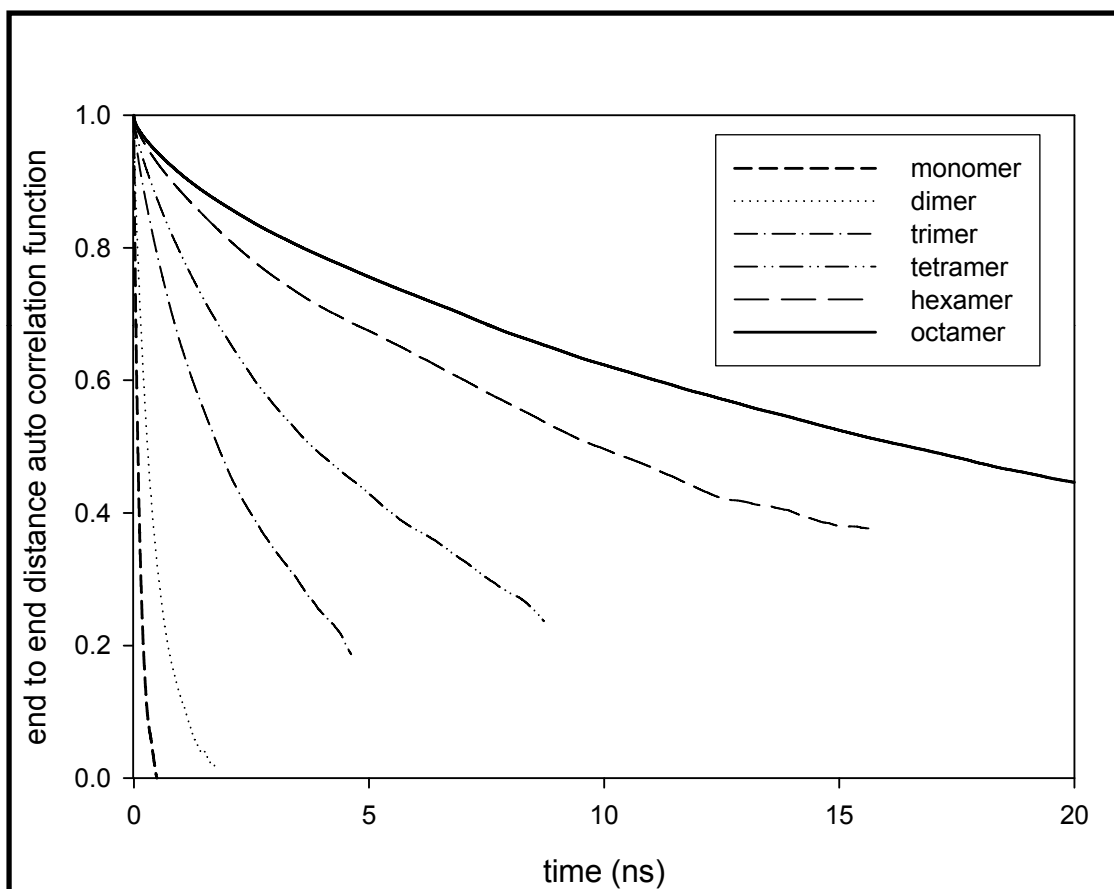
$$\exp(-(t/\tau_{KWW})^\beta)$$

Tsolou, V.G. *et al.*  
Macromolecules,  
2005

MD simulations provide characteristic relaxation times through the analysis of the decay of structural auto-correlation functions.  
For polymers, longest relaxation time is due to rotation.



## Structural properties: Relaxation Times



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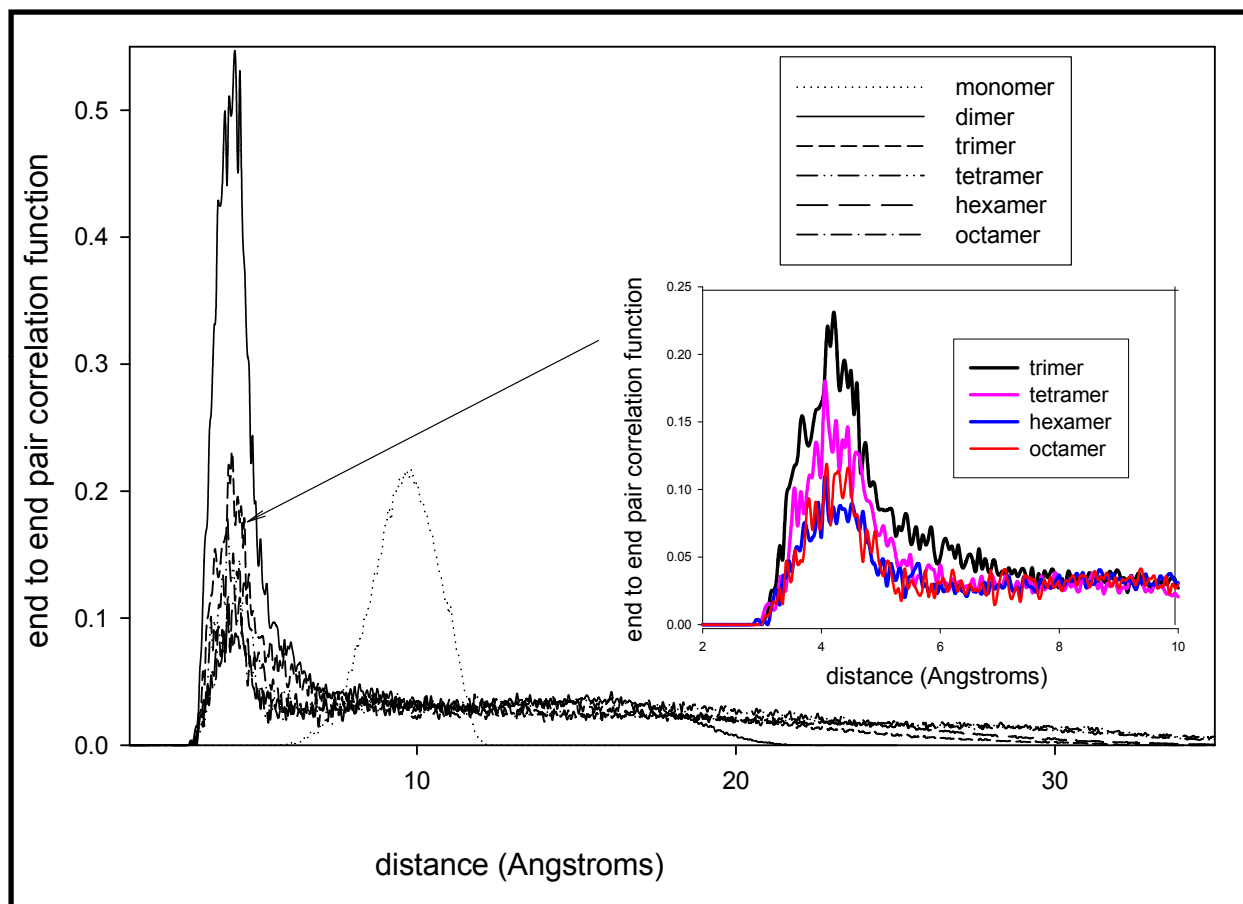
DP	time (ns)
1	0.129
2	0.502
3	2.81
4	5.59
6	15.78
8	28.30
10	66.20

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Characteristic relaxations times increase dramatically with DP, creating difficulties for MD simulation of longer chain molecules.



## Structural properties: End-to-end Pair Correlation Function



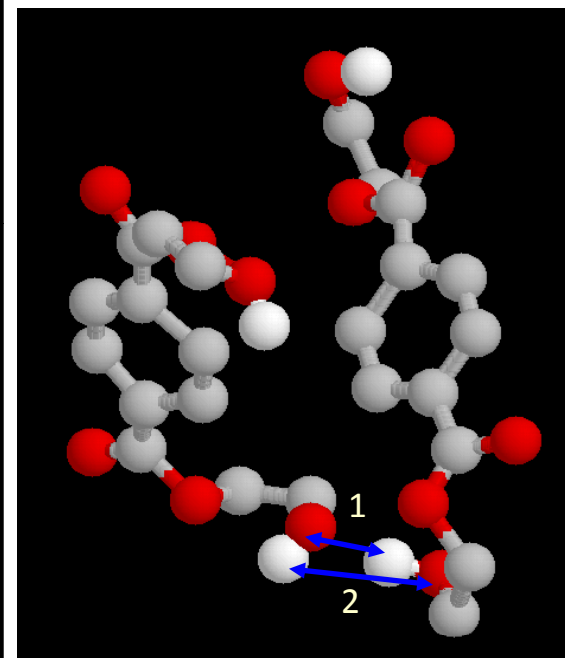
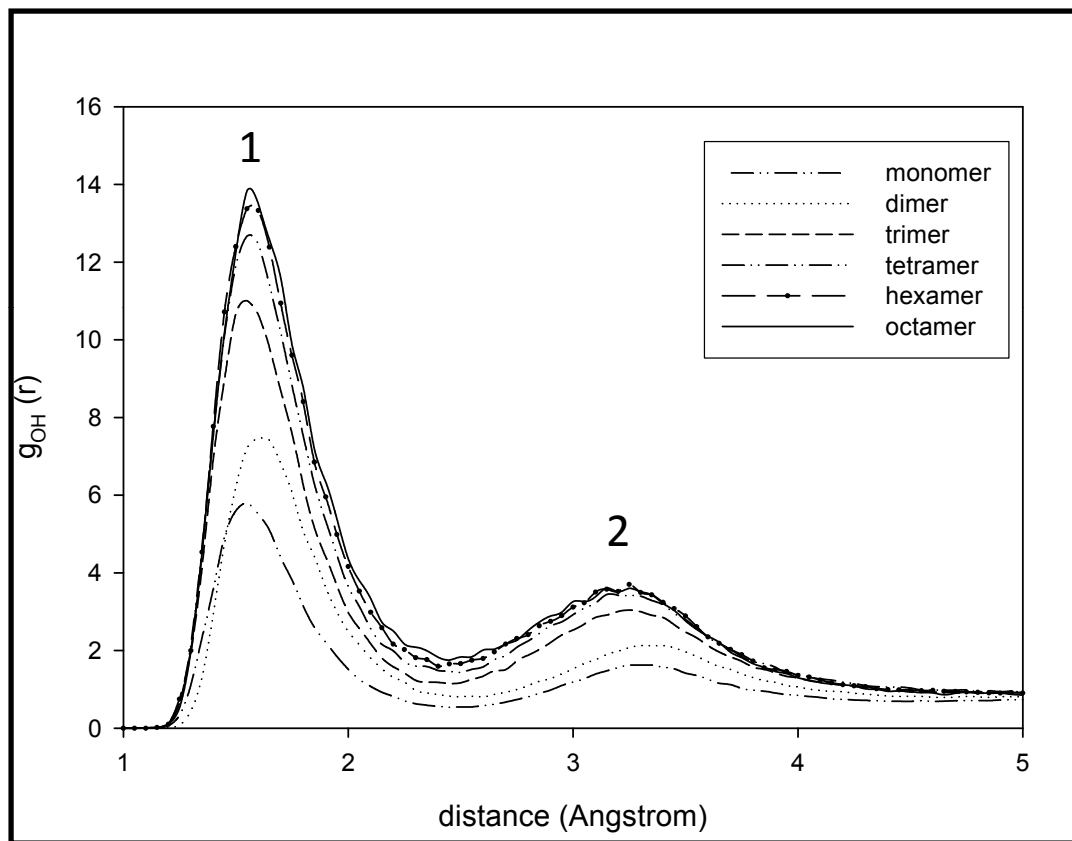
DP	$\langle R_{ete} \rangle$ (Å)
1	9.78±0.99
2	13.57±4.88
3	18.33±6.63
4	21.10±7.49
6	26.81±10.20
8	28.65±11.20

The long tail of end to end pair correlation function is typical for polymer molecules, indicating the complexity of chain molecules.



# Structural properties: Hydrogen Bonding

## Hydrogen Bonding as a function of DP



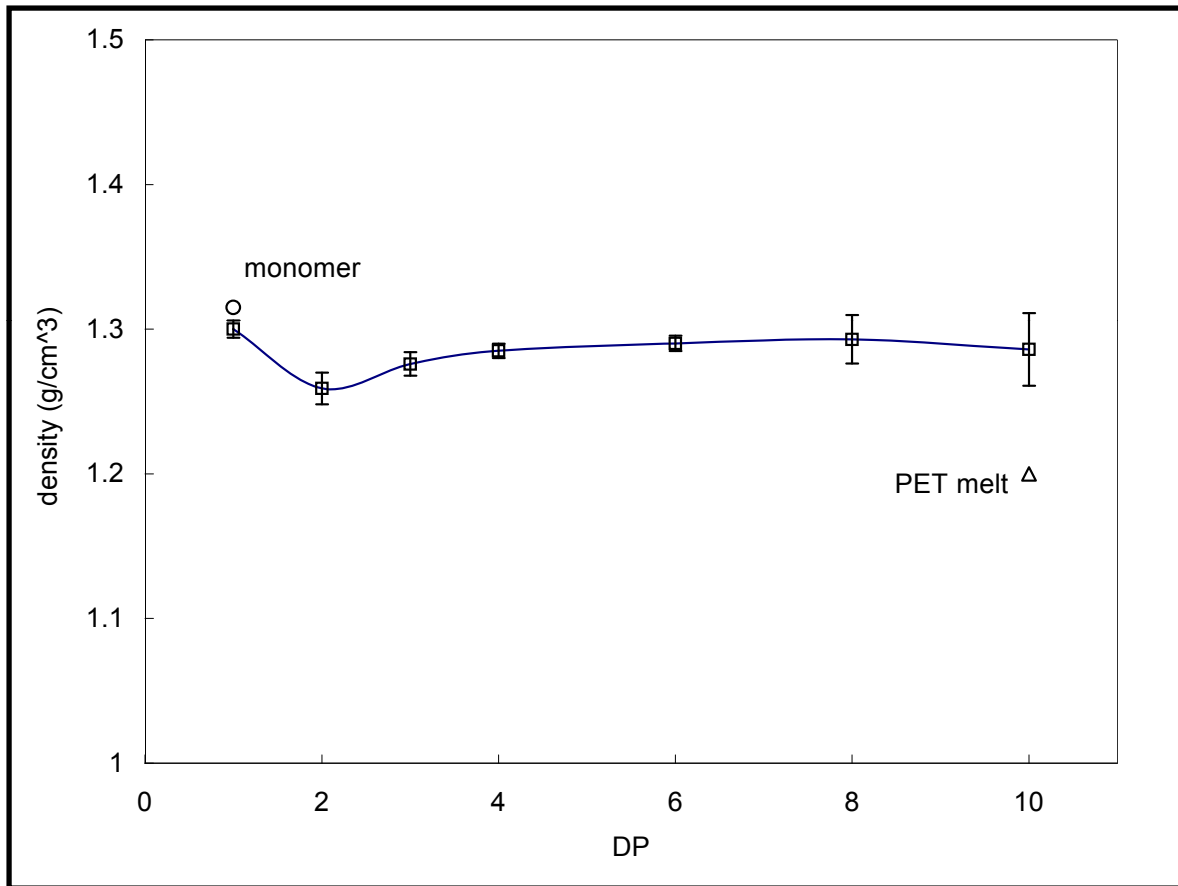
While the number of alcohol end groups decreases with DP, the probability of finding the end groups forming hydrogen-bonds increase with DP.





# Thermodynamic properties: Density

## Melt density as a function of DP



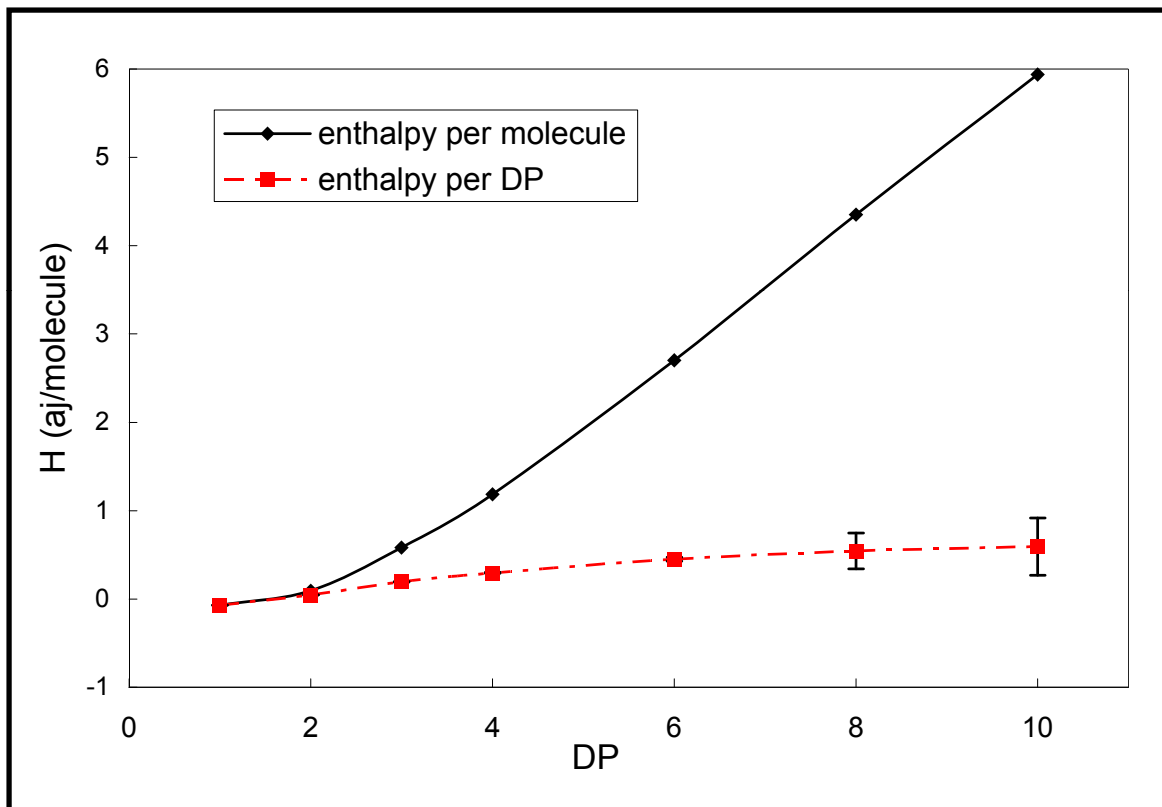
DP	< ρ > (g/cm <sup>3</sup> )
1	1.300±0.006
2	1.259±0.011
3	1.276±0.021
4	1.285±0.005
6	1.291±0.005
8	1.293±0.027
10	1.286±0.034

The density does not change much as DP increases, the melt density of PET is around 1.2 (g/cm<sup>3</sup>) (ASTM D1238,T=285°C), our simulation results are comparable to the experimental data.



# Thermodynamic properties: Enthalpy

## Enthalpy per molecule as a function of DP



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DP	$\langle H \rangle$ (kJ /mole)
1	-42.76±0.84
2	56.62±1.51
3	351.14±8.43
4	710.71±14.45
6	1626.21±84.32
8	2620.01±975.73
10	3577.66±1957.5

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The enthalpy per molecule increases with DP.  
The enthalpy per repeat unit also increases with DP.



Thermodynamic properties: Heat capacity ( $C_p$ ),  
isothermal compressibility ( $\beta$ ), thermal expansion coefficient ( $\alpha$ )

Fluctuations method (one simulation):	Finite difference method: (multiple simulations)
$\beta = \frac{1}{Vk_B T} \langle \sigma_V^2 \rangle$	$\beta = -\frac{1}{V(p,T)} \frac{V(p+\epsilon,T) - V(p-\epsilon,T)}{2\epsilon}$
$\alpha = \frac{1}{Vk_B T^2} \langle \sigma_{(V)(H+PV)} \rangle$	$\alpha = \frac{1}{V(p,T)} \frac{V(p,T+\epsilon) - V(p,T-\epsilon)}{2\epsilon}$
$C_P = \frac{1}{Vk_B T^2} \langle \sigma_{(H+PV)}^2 \rangle$	$C_p = \frac{H(p,T+\epsilon) - H(p,T-\epsilon)}{2\epsilon}$



**Give** a small perturbation of density and temperature.  
**Calculate** changes of pressure, volume, and enthalpy.  
**Derivative** is the corresponding thermodynamic property.



The fluctuation method for these thermodynamic properties is based on the variance of volume, enthalpy and covariance of volume and enthalpy of the system, which can be obtained from one MD simulation.



Thermodynamic properties: Heat capacity ( $C_p$ ), isothermal compressibility( $\beta$ ), thermal expansion coefficient ( $\alpha$ )

Thermodynamic properties	MD (fluctuation)	MD (finite difference)	Experimental data (PET)
Heat capacity ( $J K^{-1} kg^{-1}$ )	$(1.41 \pm 1.38) \times 10^3$	$(2.68 \pm 0.08) \times 10^3$	$2.66 \times 10^3$
Isothermal compressibility ( $GPa^{-1}$ )	$1.76 \pm 1.02$	$(3.14 \pm 0.06) \times 10^{-1}$	$(2.0 \sim 6.0) \times 10^{-1}$
Thermal expansion coefficient ( $K^{-1}$ )	$(2.14 \pm 1.97) \times 10^{-3}$	$(6.42 \pm 0.96) \times 10^{-4}$	$6.55 \times 10^{-4}$

Finite difference : very close to the experimental data

Fluctuation: too much uncertainty.

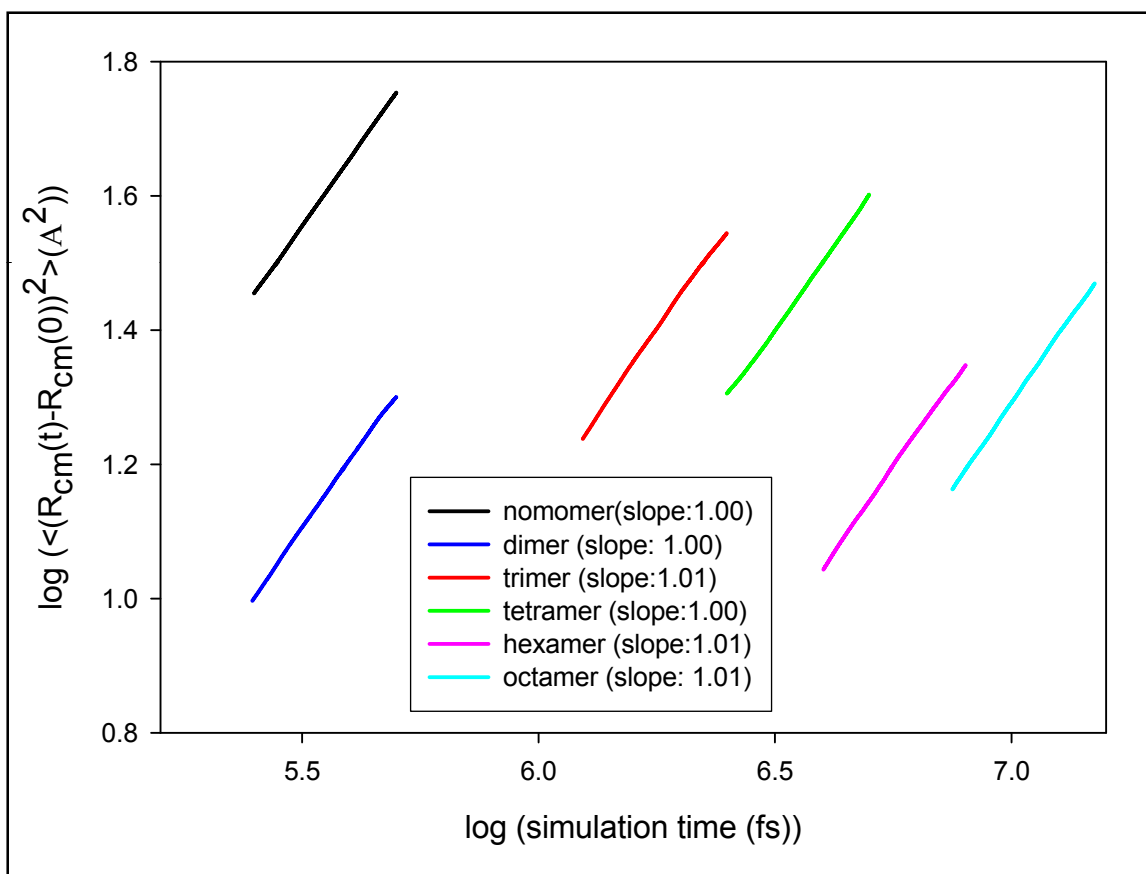
Note: experimental data is taken from "Polymer Handbook" written by J. Brandrup, E.H. Immergut, and E.A. Gulke 1999.

DP	1	2	3	4	6	8	10
$C_p$ (J/K/kg)	$(2.73 \pm 0.089) \times 10^3$	$(2.56 \pm 0.06) \times 10^3$	$(2.47 \pm 0.055) \times 10^3$	$(2.45 \pm 0.067) \times 10^3$	$(2.35 \pm 0.048) \times 10^3$	$(2.29 \pm 0.043) \times 10^3$	$(2.25 \pm 0.046) \times 10^3$
$\beta$ ( $GPa^{-1}$ )	$(2.17 \pm 0.77) \times 10^{-1}$	$(3.02 \pm 1.12) \times 10^{-1}$	$(4.70 \pm 3.27) \times 10^{-1}$	$(4.51 \pm 1.65) \times 10^{-1}$	$(3.44 \pm 0.44) \times 10^{-1}$	$(6.40 \pm 3.06) \times 10^{-1}$	$(6.87 \pm 2.23) \times 10^{-1}$
$\alpha$ ( $K^{-1}$ )	$(6.73 \pm 1.02) \times 10^{-4}$	$(5.26 \pm 0.38) \times 10^{-4}$	$(4.81 \pm 0.55) \times 10^{-4}$	$(4.80 \pm 0.17) \times 10^{-4}$	$(4.53 \pm 0.27) \times 10^{-4}$	$(4.28 \pm 0.16) \times 10^{-4}$	$(3.75 \pm 0.79) \times 10^{-4}$



## Transport properties: Diffusivity

Diffusion coefficient is calculated from the center of mass mean square displacement



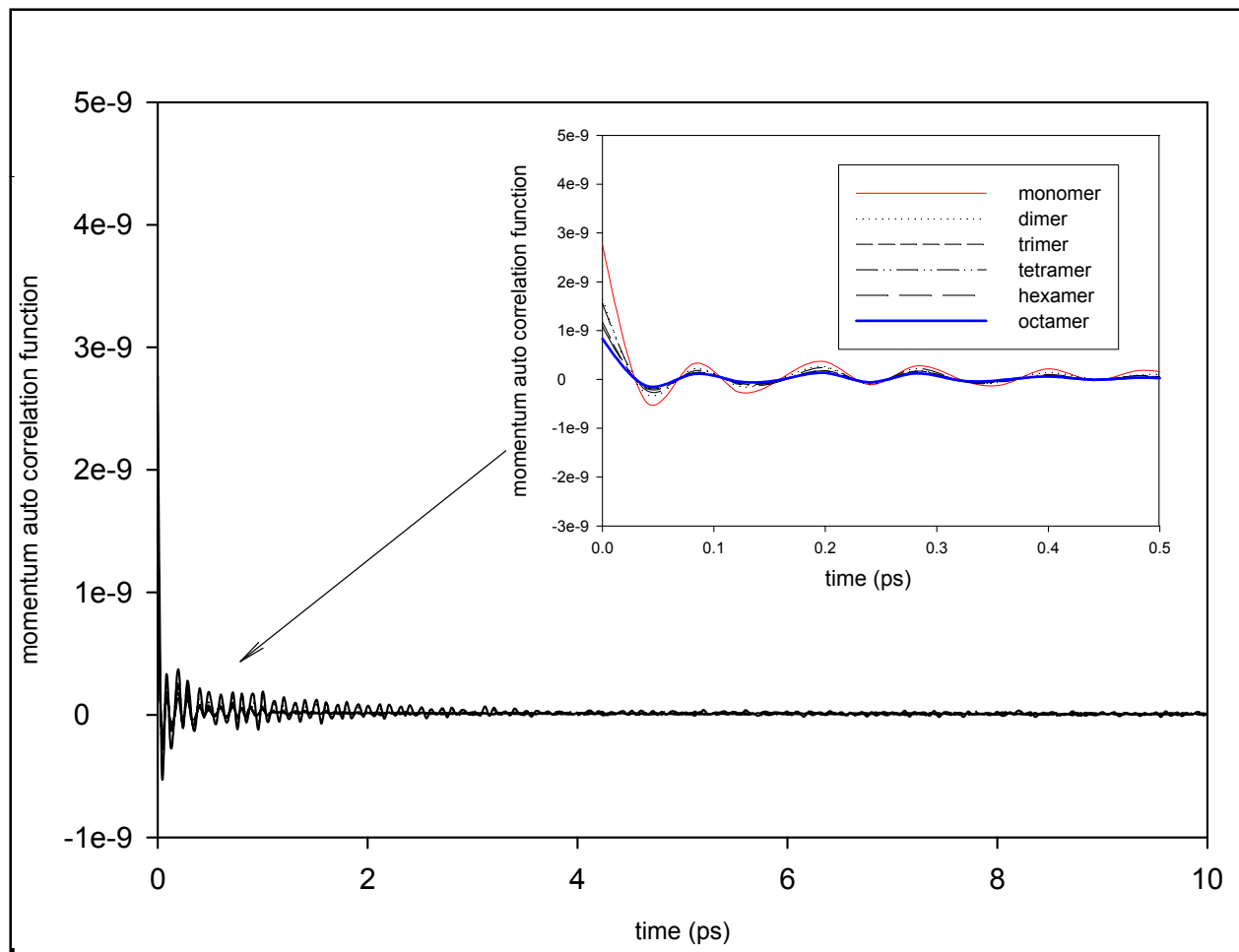
DP	D (m <sup>2</sup> /sec) × 10 <sup>11</sup>
1	56.8 ± 11.4
2	20.5 ± 2.3
3	7.09 ± 1.41
4	4.01 ± 0.95
6	1.65 ± 0.16
8	0.99 ± 0.27
10	1.45 ± 0.60

The slope of the curve equal to 1 means our simulations are long enough to guarantee a good diffusivity. The self diffusion coefficient decreases with DP as the diffusion process becomes harder for longer molecules.



## Transport properties: Viscosity

Zero shear-rate viscosity is obtained by integrating momentum auto-correlation function over time, by following Green-Kubo relations.

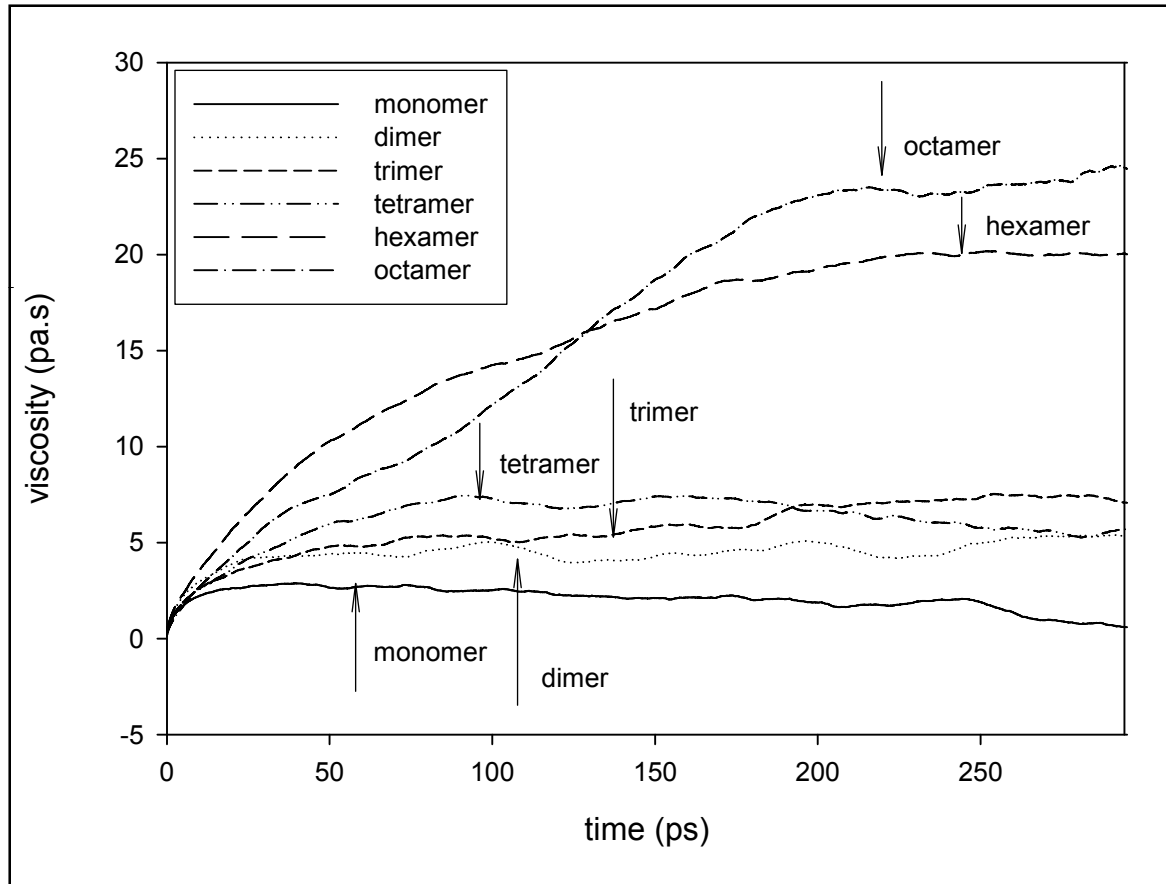


The decay to zero ensures convergence of the integration.



# Transport properties:Viscosity

Zero shear viscosity as a function of DP.



DP	$\eta(\text{Pa.s}) \times 10^3$
1	$2.68 \pm 0.13$
2	$5.45 \pm 0.83$
3	$5.83 \pm 0.96$
4	$6.51 \pm 0.66$
6	$19.5 \pm 6.5$
8	$22.3 \pm 6.0$
10	$30.3 \pm 8.0$

The viscosity increases with DP, this is true based on polymer physics.

We measured the viscosity of the monomer using a rheometer at UT.

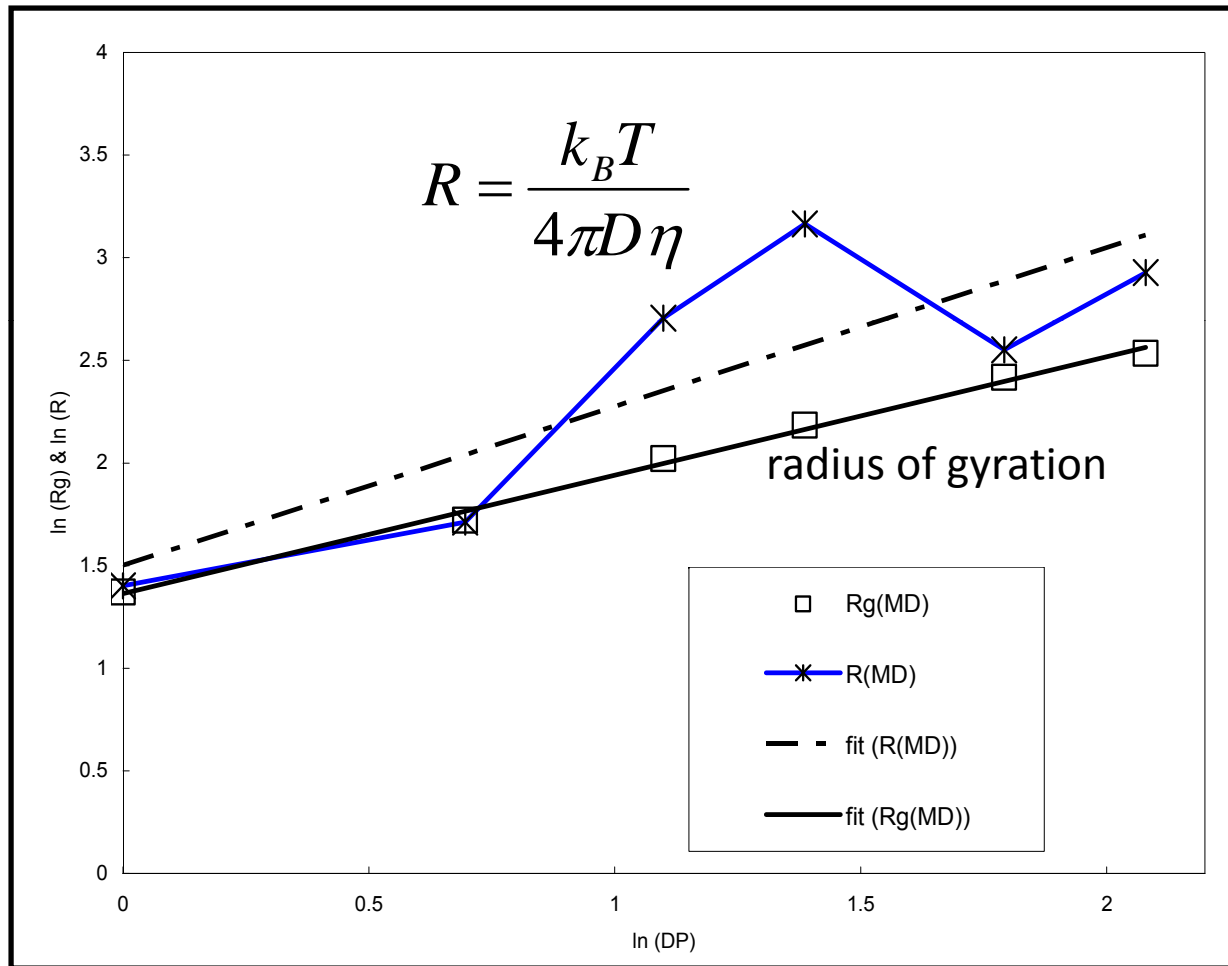
The experimental viscosity of the monomer at  $T=533\text{ K}$  and  $1\text{ atm}$  is  $3.8 \times 10^{-3}\text{ Pa.s}$ .

Compare to a simulated viscosity at  $T=563\text{ K}$  and  $1\text{ atm}$  of  $3.83 \times 10^{-3}\text{ Pa.s}$ .



# Transport properties: Stokes-Einstein equation

## Relationship between diffusion coefficient and viscosity



$$\frac{D\eta}{k_B T} = \frac{1}{4\pi R}$$

Once we know R, either D or  $\eta$  as a function of DP, we can calculate the other by using above equation.

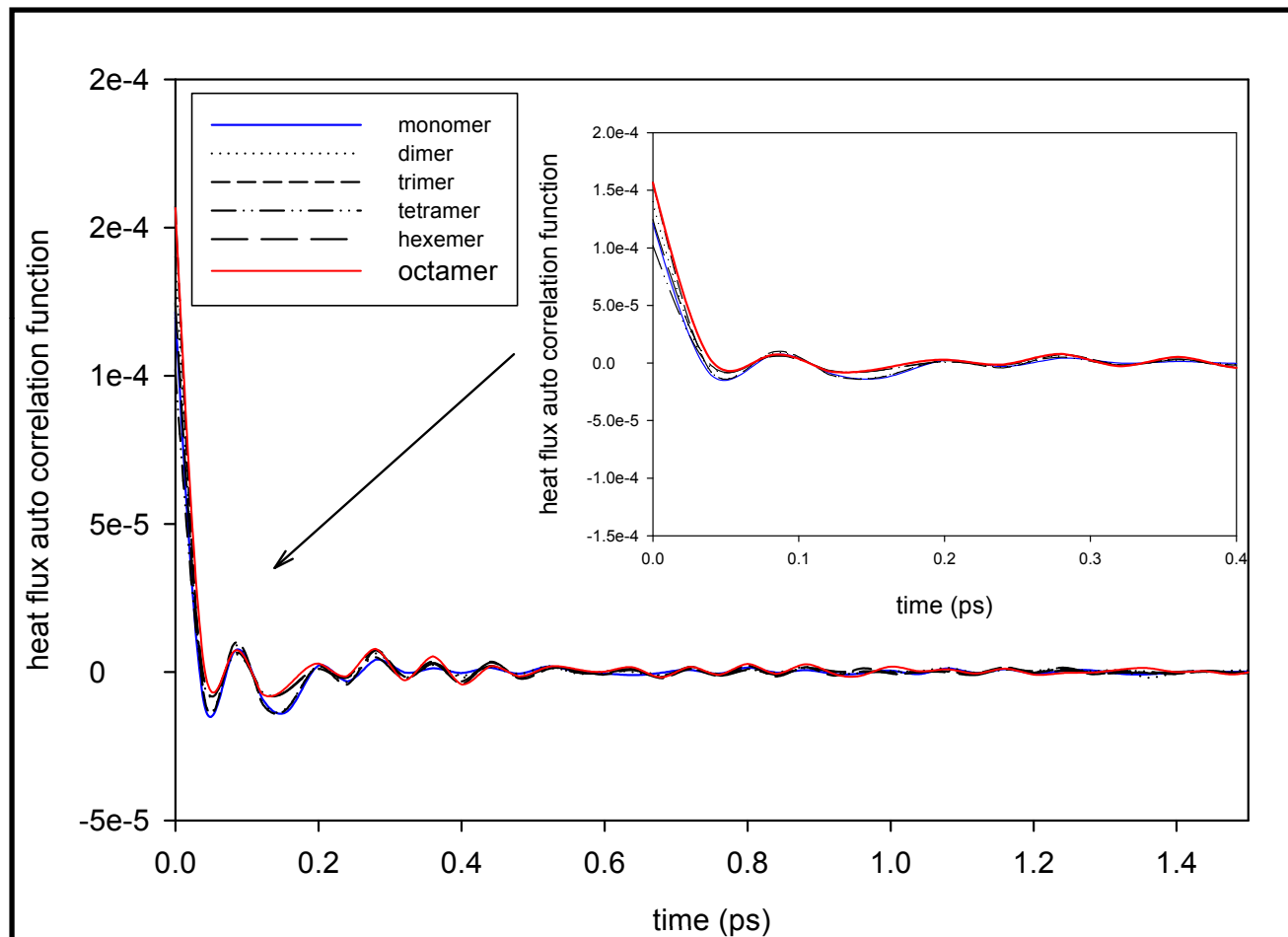
For monomer and dimer, R agrees with  $R_g$ , R increases with DP, fluctuating around its trend line with slope equals to 1. This is governed by scaling behavior of D and  $\eta$ .





## Transport properties: Thermal conductivity

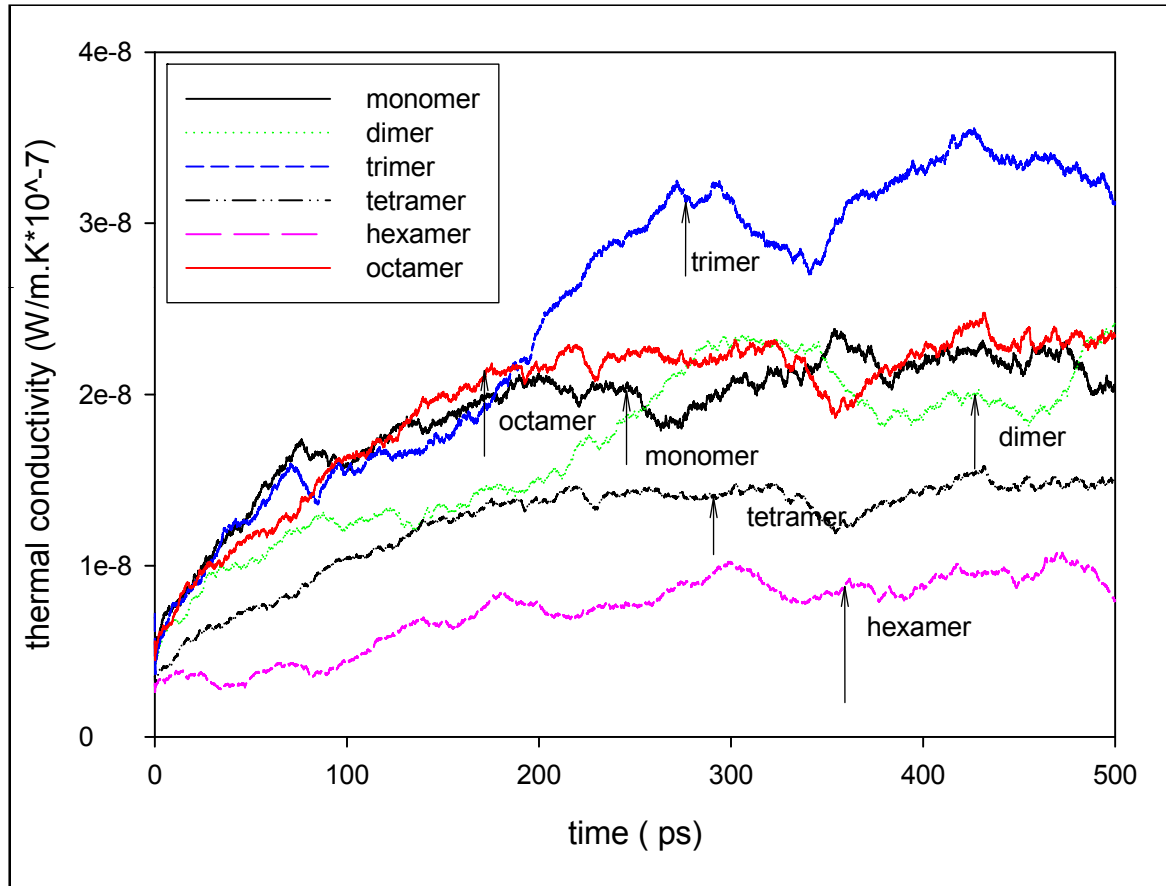
Based on integration of heat flux auto correlation function over time.



The heat flux auto correlation function has a faster decay compared with the momentum auto correlation function.



# Transport Properties: Thermal Conductivity



DP	$\lambda$ (W/m.K)
1	$0.19 \pm 0.02$
2	$0.20 \pm 0.05$
3	$0.31 \pm 0.02$
4	$0.13 \pm 0.01$
6	$0.12 \pm 0.01$
8	$0.22 \pm 0.03$
10	$0.18 \pm 0.01$

The thermal conductivity obtained from simulation is between 0.1 and 0.3(W/m.K), consistent with the experimental data (0.24 from polymer handbook).



## Scaling Analysis

**Objectives:** The structural, thermodynamic and transport properties all scale with DP according to polymer dynamic theory, these scaling behaviors enable us to verify our simulation results and give predictions to the properties of longer chains, such as DP=10, which is difficult to obtain from MD simulation.

**Principles:** Study how the physical quantities change when DP is changed. Properties such as  $R_g$ ,  $R_{ete}$ ,  $\tau_{kww}$ ,  $C_p$ ,  $D$  are all  $\approx a(DP)^b$ , The scaling exponent  $b$  is the constant we are interested in and different from property to property

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

**Method:** By fitting our simulation data to  $a(DP)^b$  in log-log plots, the slope of the curve is  $b$ . The literature reported values of  $b$  for polymer melts are as follows:

$b = -2.1$  for  $D$  (reptation model)

$b = 0.589$  for  $R_g$ ,  $R_{ete}$

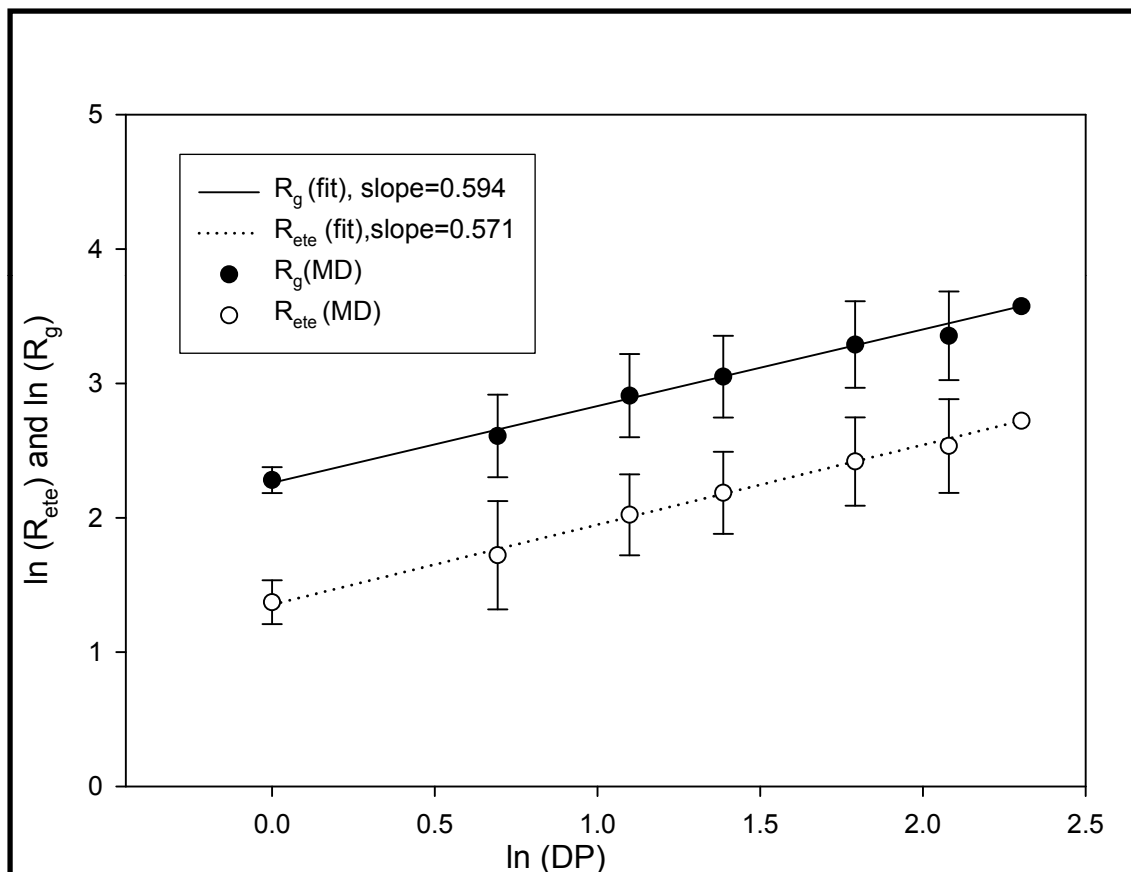
$b = 1$  for  $\eta$  (below critical molecular weight)

M. Doi and S.F. Edwards, "The Theory of Polymer Dynamics", 1986.

G. Tsolou, V.G. Mavrantzas, D.N. Theodourou, Macromolecules, 2005.



# Scaling Analysis: Chain radius of gyration ( $R_g$ ) and average end to end distance ( $R_{ete}$ )



Estimated value for decamer:

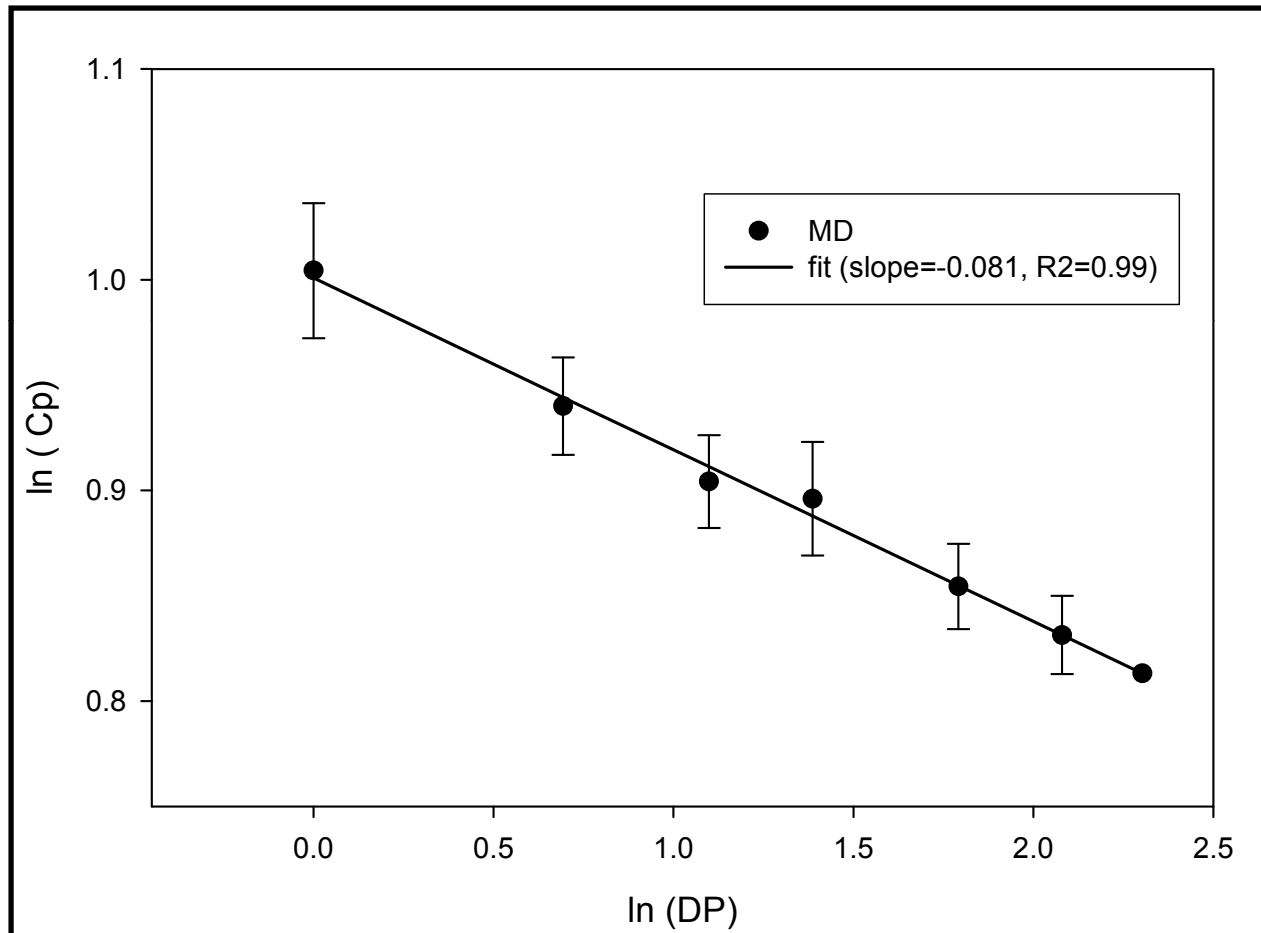
$$\langle R_g \rangle = 15.19 \text{ (\AA)}$$

$$\langle R_{ete} \rangle = 35.65 \text{ (\AA)}$$

The scaling exponent for  $R_g$  and  $R_{ete}$  is 0.594 and 0.571 separately, very close to theoretical prediction of 0.589. Our result is valid and we also give the prediction of the value of  $R_g$  and  $R_{ete}$  for decamer.



# Scaling Analysis: Heat Capacity ( $C_p$ )



$b=0.081$   
from MD

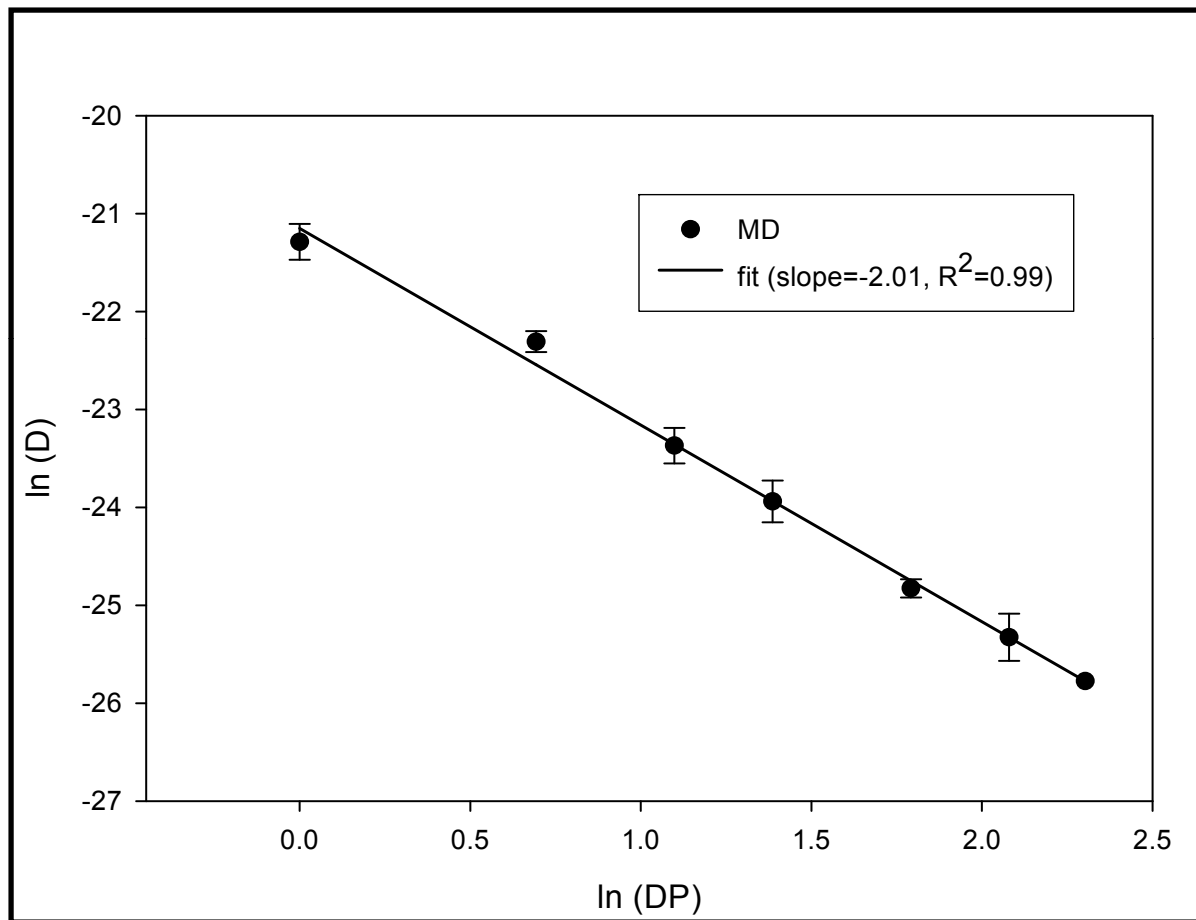
no reported  
literature  
value

Estimated value for  
decamer:

$$C_n = 2250 \text{ (J K}^{-1} \text{ kg}^{-1}\text{)}$$



# Scaling Analysis: Diffusion Coefficient (D)



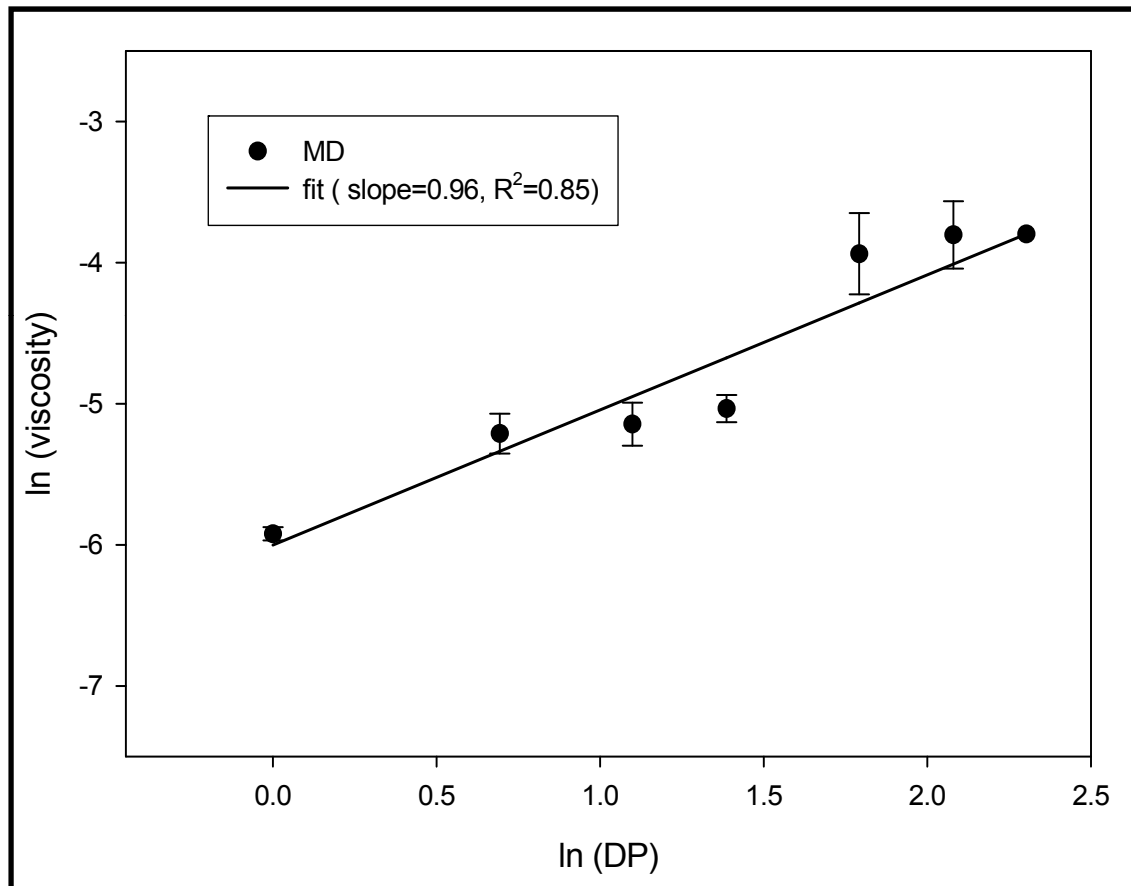
MD simulation  
b = -2.01

theoretical value:  
b = -2.1

Estimated value for  
decamer:  
 $D = 6.40 \times 10^{-12} \text{ (m}^2\text{/sec)}$



## Scaling Analysis: Zero Shear-Rate Viscosity ( $\eta$ ).



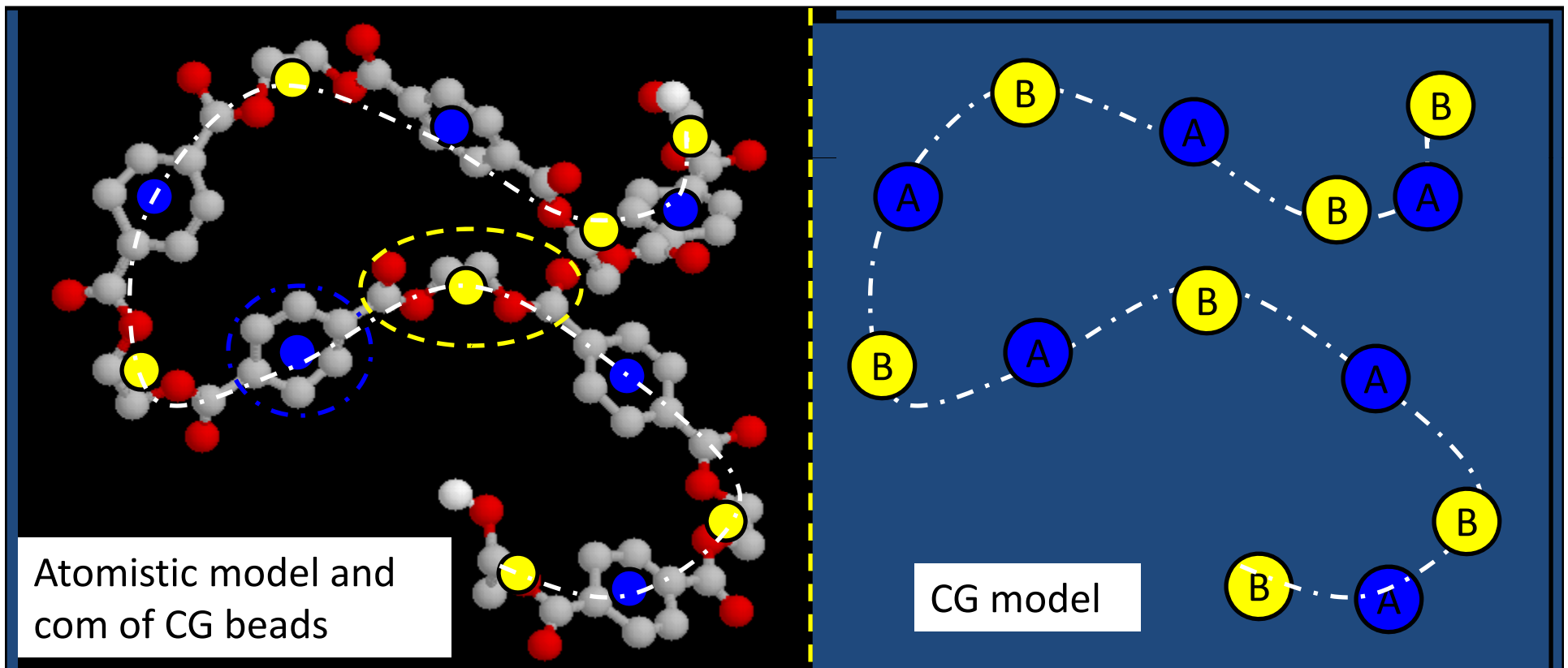
MD value  
 $b = 0.96$

Literature reported value is 1 (for PET with molecular weight under critical point).

Estimated value for decamer:  
 $\eta = 2.24 \times 10^{-2}$  (pa.s)



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.



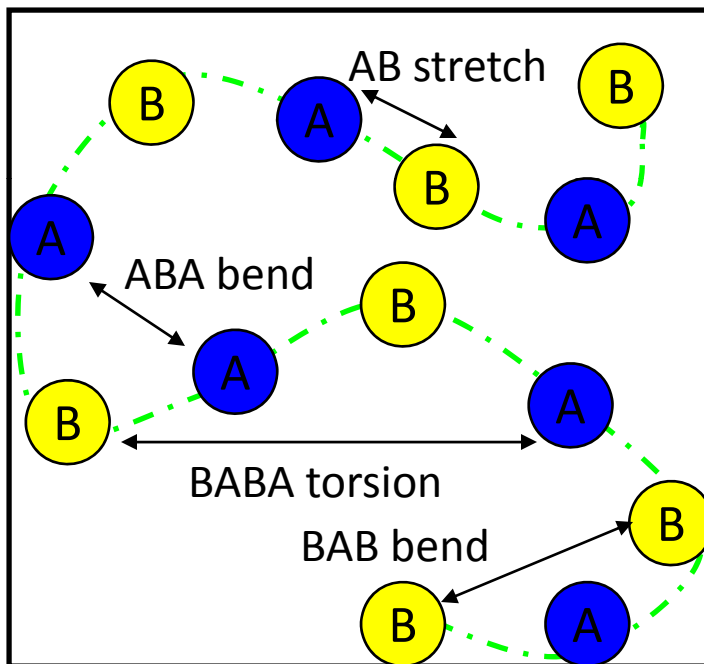
CG model on top of atomistic model for hexamer (DP=6)

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)

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

$$U_{stretch}^{CG}(r, T) = -k_B T \ln P_{stretch}^{CG}(r, T) + C_r$$

$$U_{bend}^{CG}(\theta, T) = -k_B T \ln P_{bend}^{CG}(\theta, T) + C_\theta$$

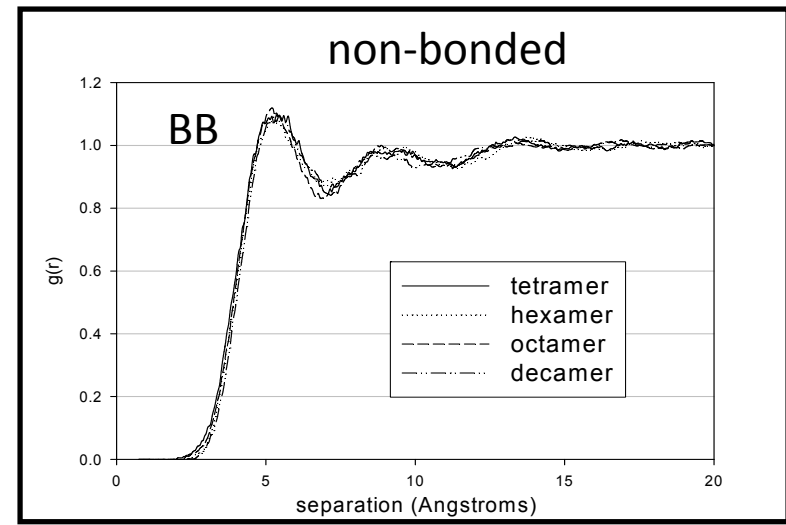
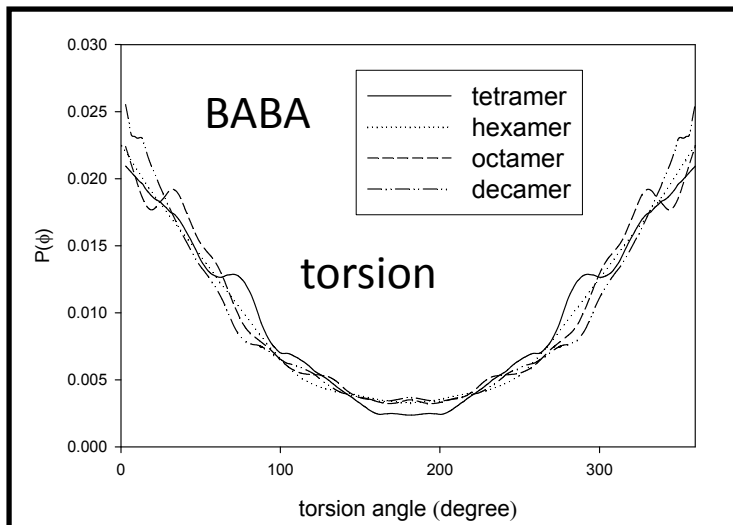
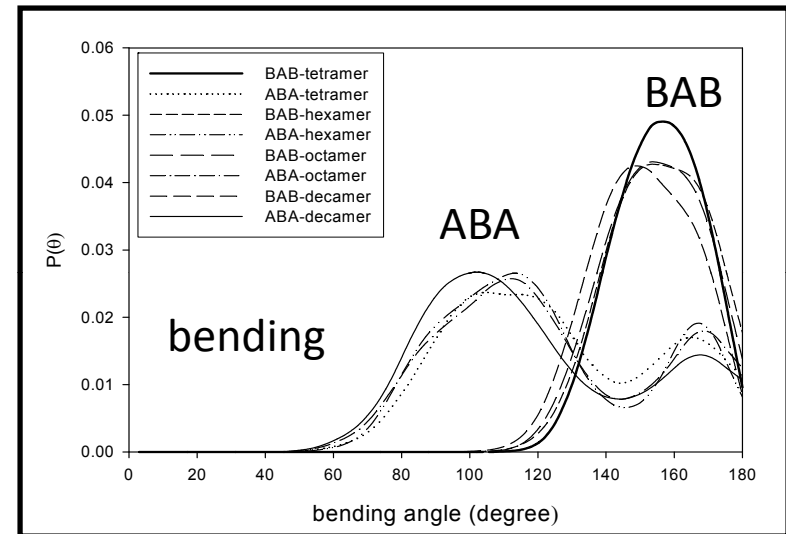
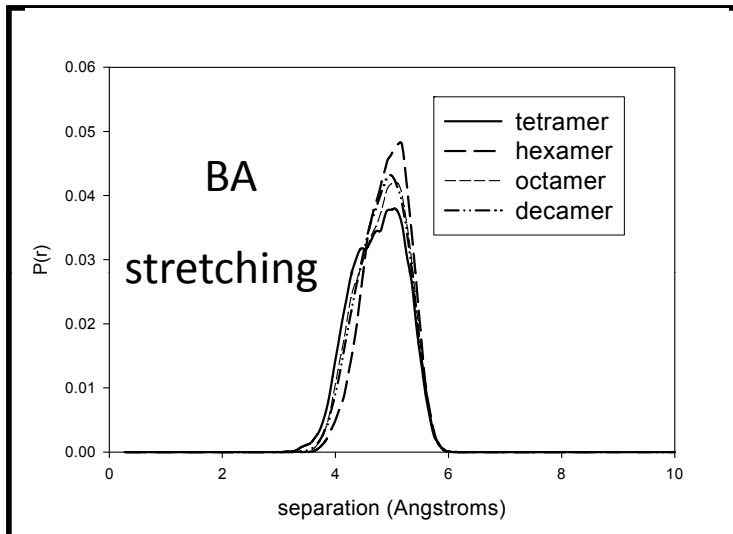
$$U_{torsion}^{CG}(\phi, T) = -k_B T \ln P_{torsion}^{CG}(\phi, T) + C_\phi$$

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

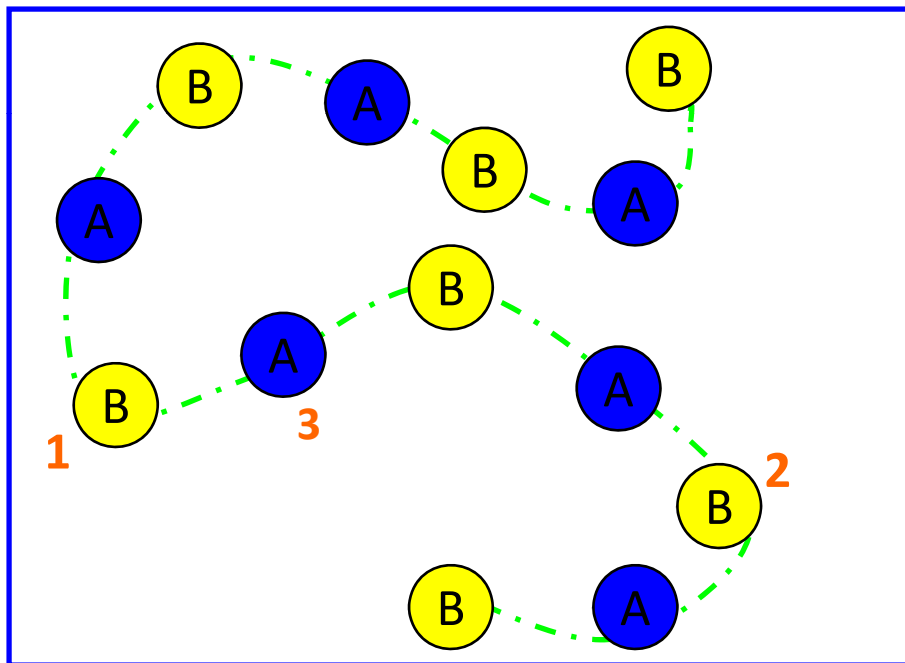
We obtained  $P(r)$ ,  $P(\theta)$ ,  $P(\phi)$ ,  $g(r)$  based on atomistic MD simulation configurations.



Coarse-Grained potentials: OZPY<sup>-1</sup> 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<sup>-1</sup>: given PCF, find U

need to know:

- PCFs
- allowable combinations

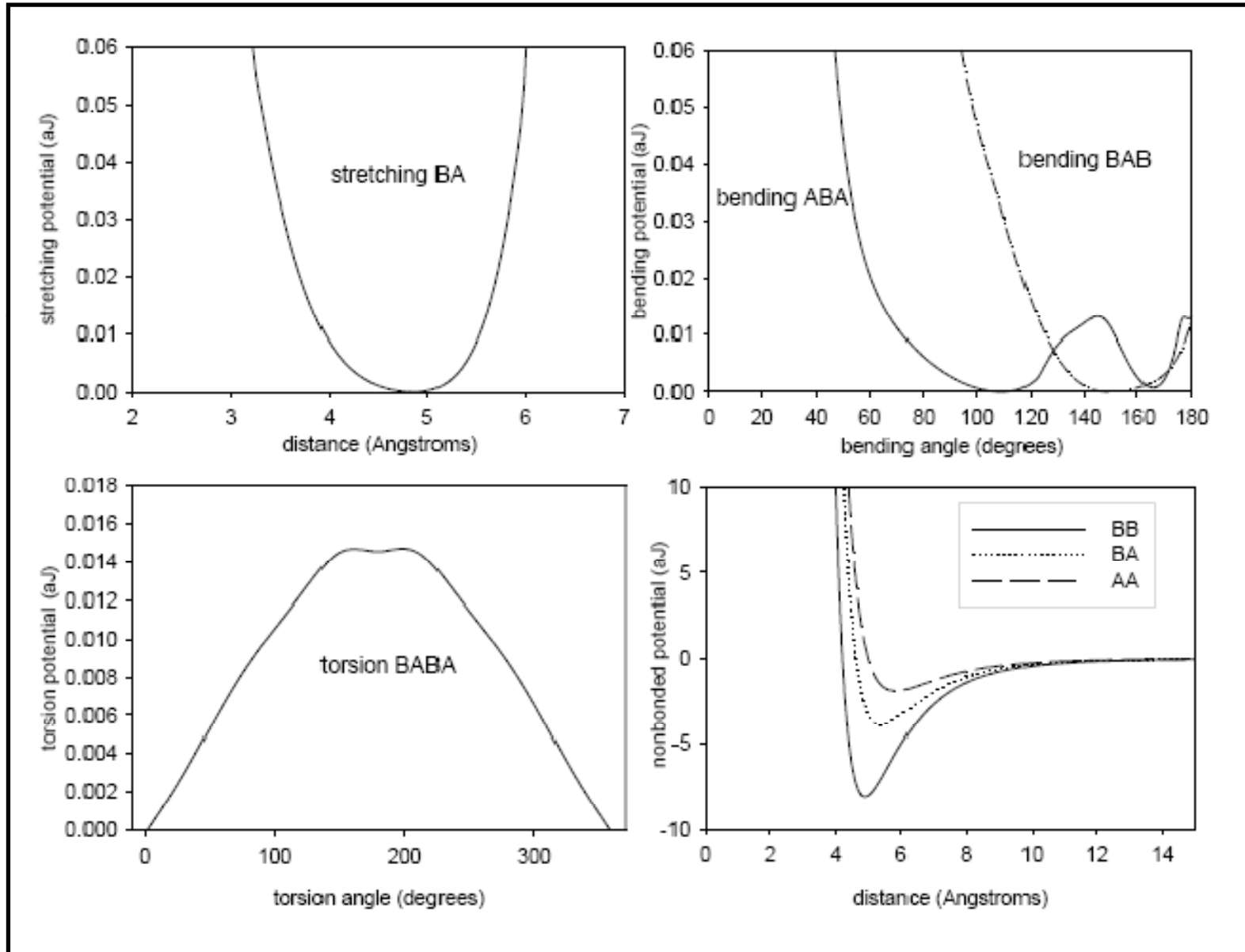
(BA)<sub>n</sub>B linear chain

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.



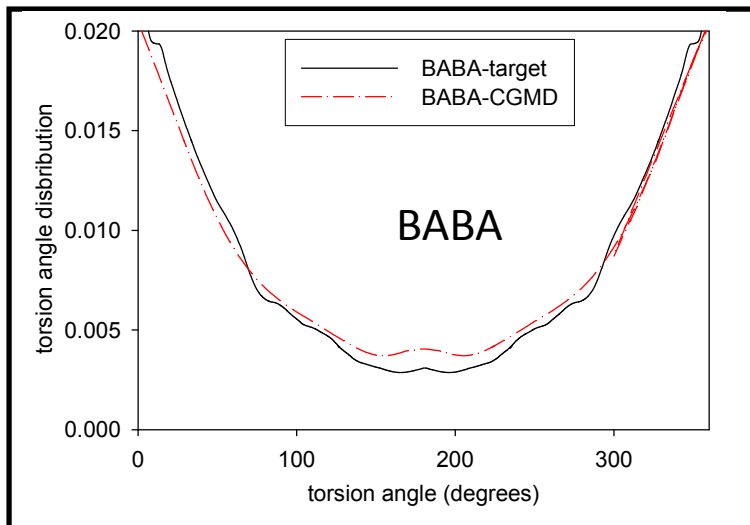
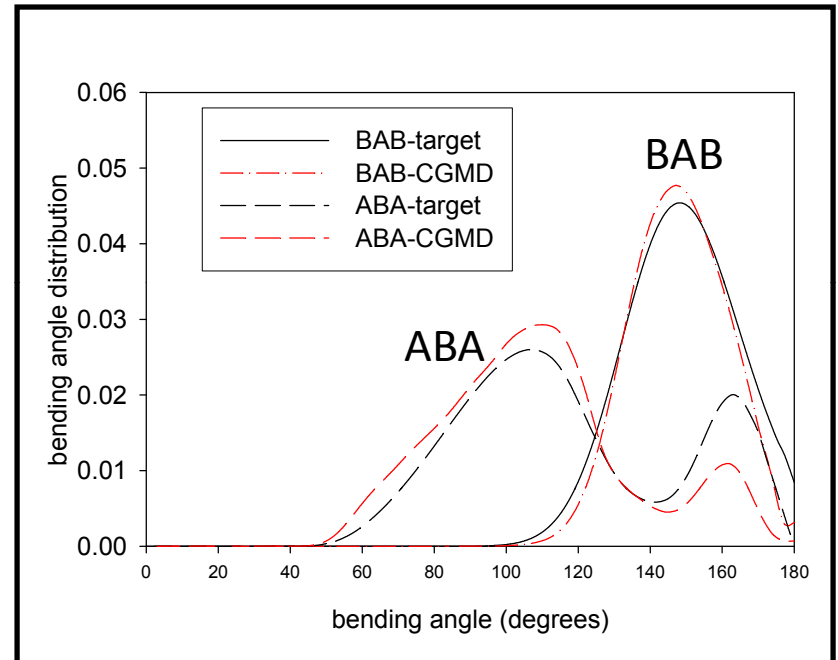
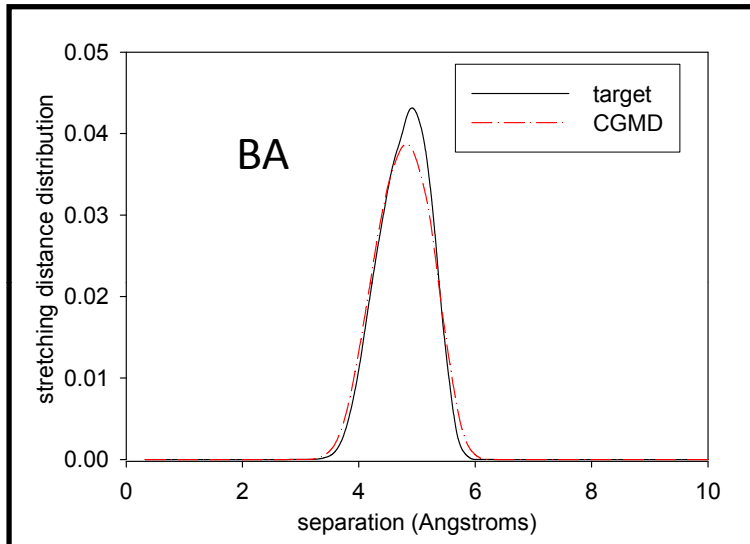
Coarse-Grained potentials: bonded and non-bonded.





## Coarse-Grained MD simulation: comparison of structures.

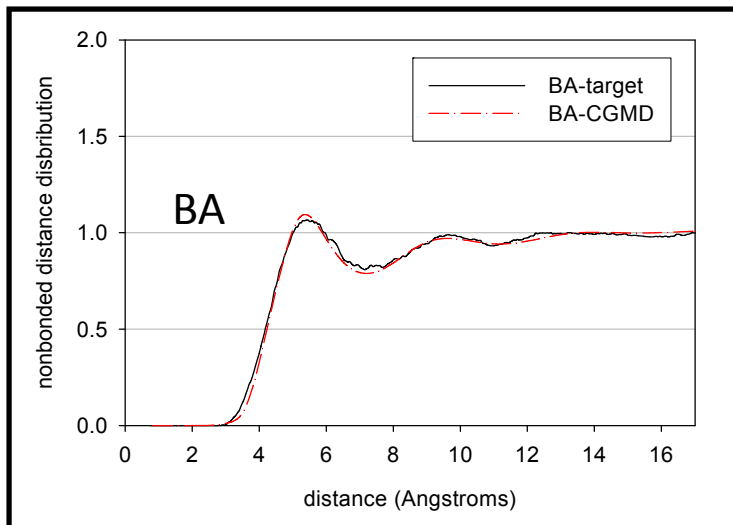
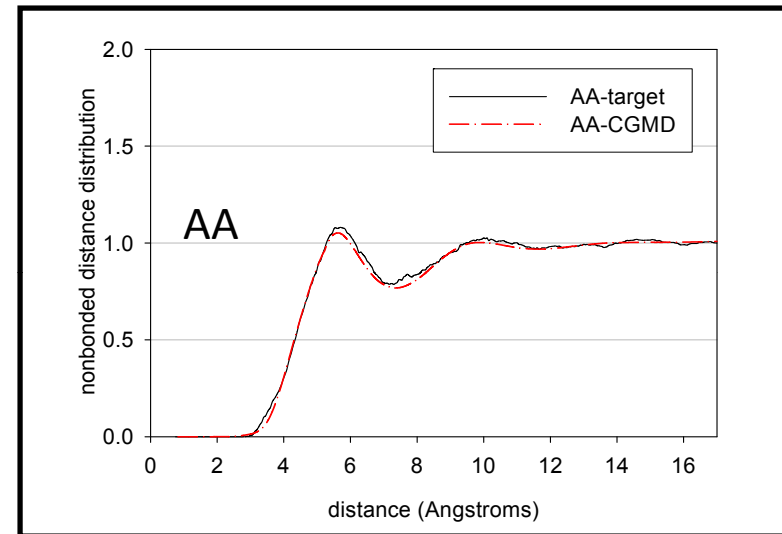
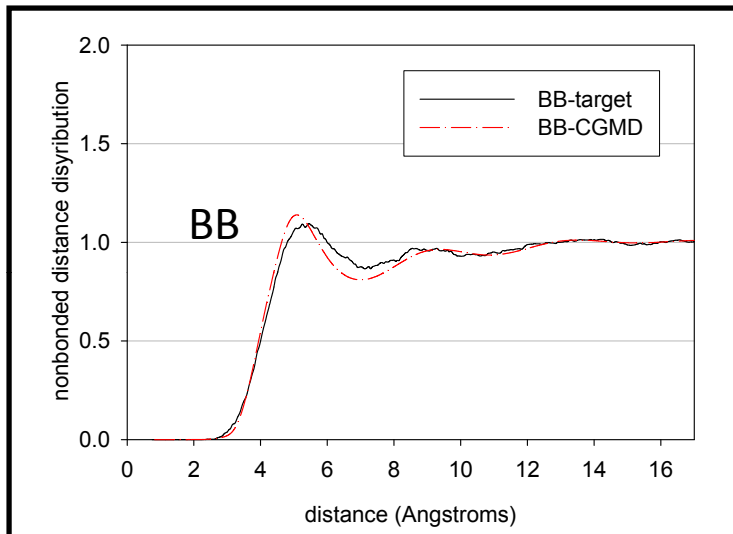
We compared the  $P(r)$ ,  $P(\theta)$  and  $P(\phi)$  from CG and atomistic MD simulation.



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.

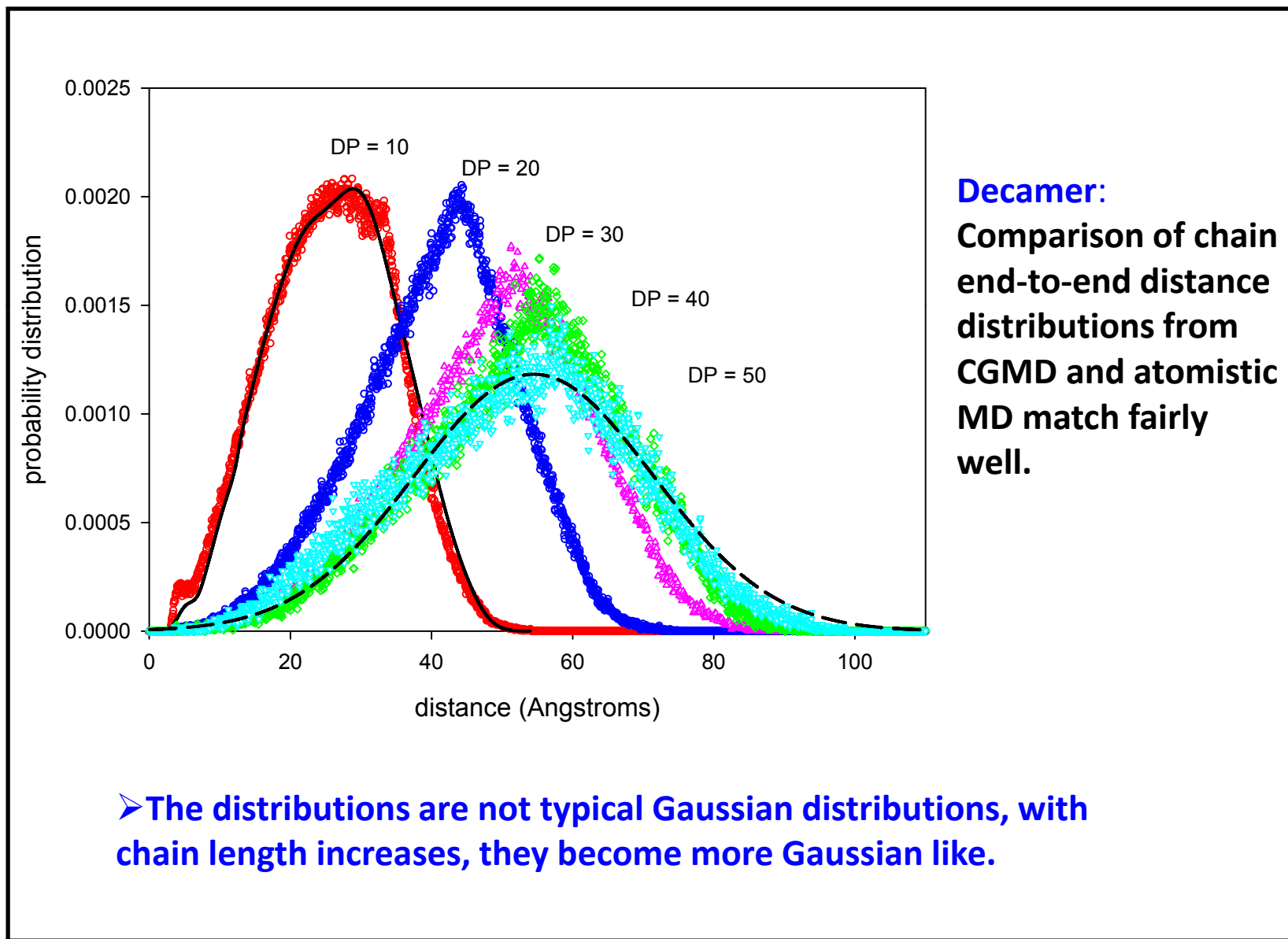


The non-bonded PCFs from CGMD and atomistic MD simulations match fairly well.

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

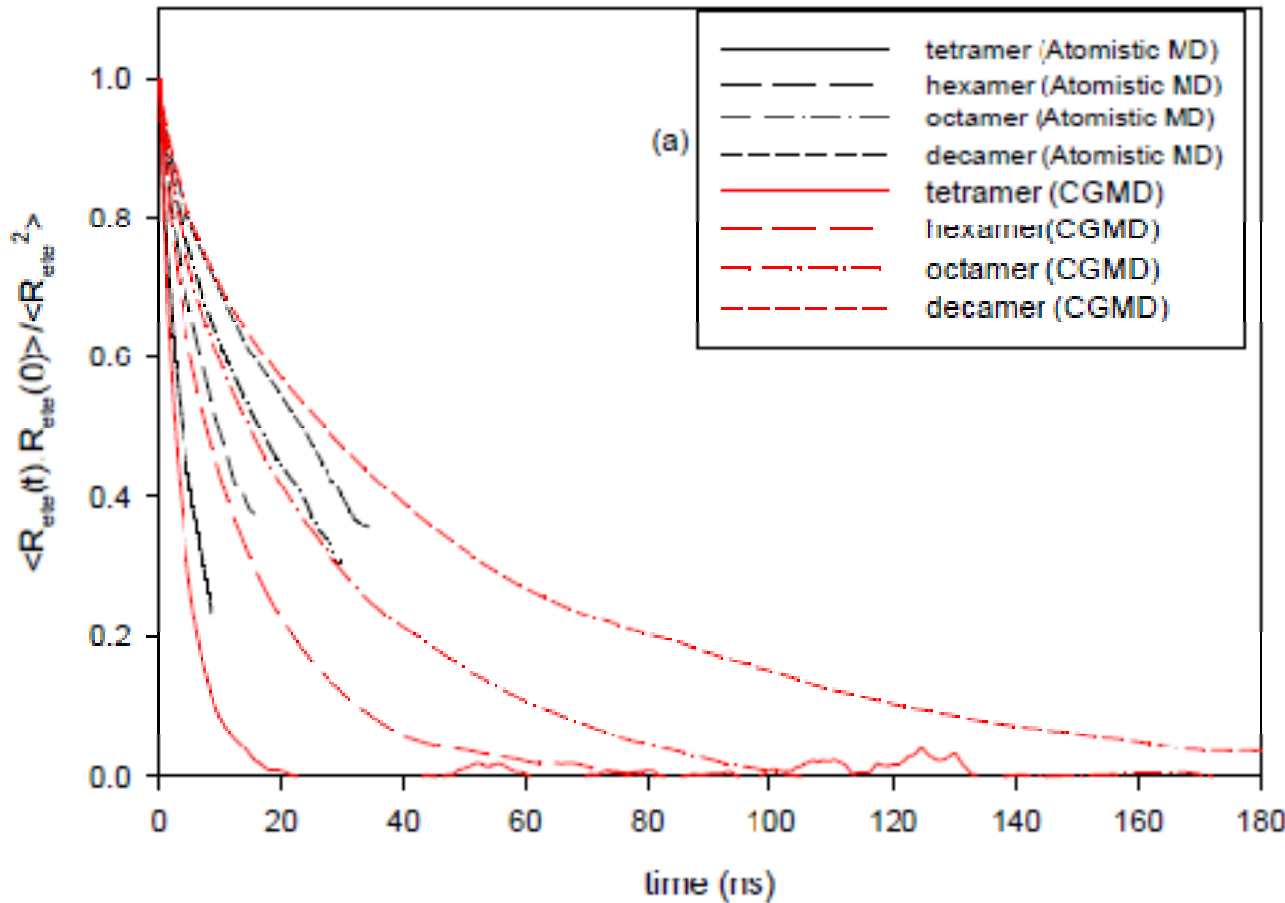


**Decamer:**  
Comparison of chain end-to-end distance distributions from CGMD and atomistic MD match fairly well.

➤ 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 systems 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.

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

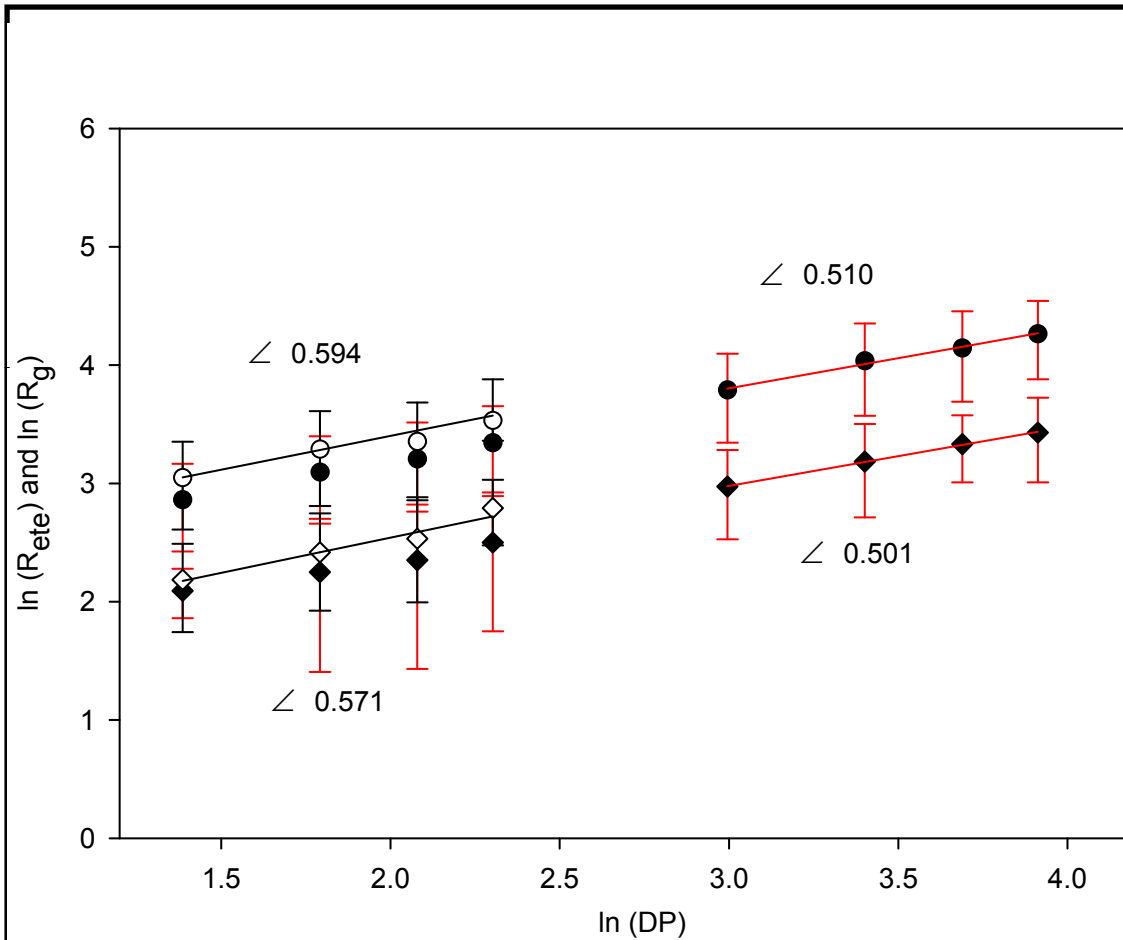
DP	Simulation method	$D$	$\eta$	$\tau_{KWW}$	$\langle R_{ete} \rangle$	$\langle R_g \rangle$
1~10	Atomistic MD	-2.01	0.96	2.78	0.594	0.571
4~10	CGMD	-1.91	1.6	2.81	0.59	0.57
20~50	CGMD	-2.0	2.0	3.7	0.51	0.50
<b>Rouse Model (1, 2)</b>	N/A	-1	1	2	0.59	0.59
<b>Reptation Model (1, 2)</b>	N/A	-2	3	3	0.50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

1 Tzoumanekas *et al.* Macromolecules 2009

2 Lahmar *et al.* Macromolecules 2009



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



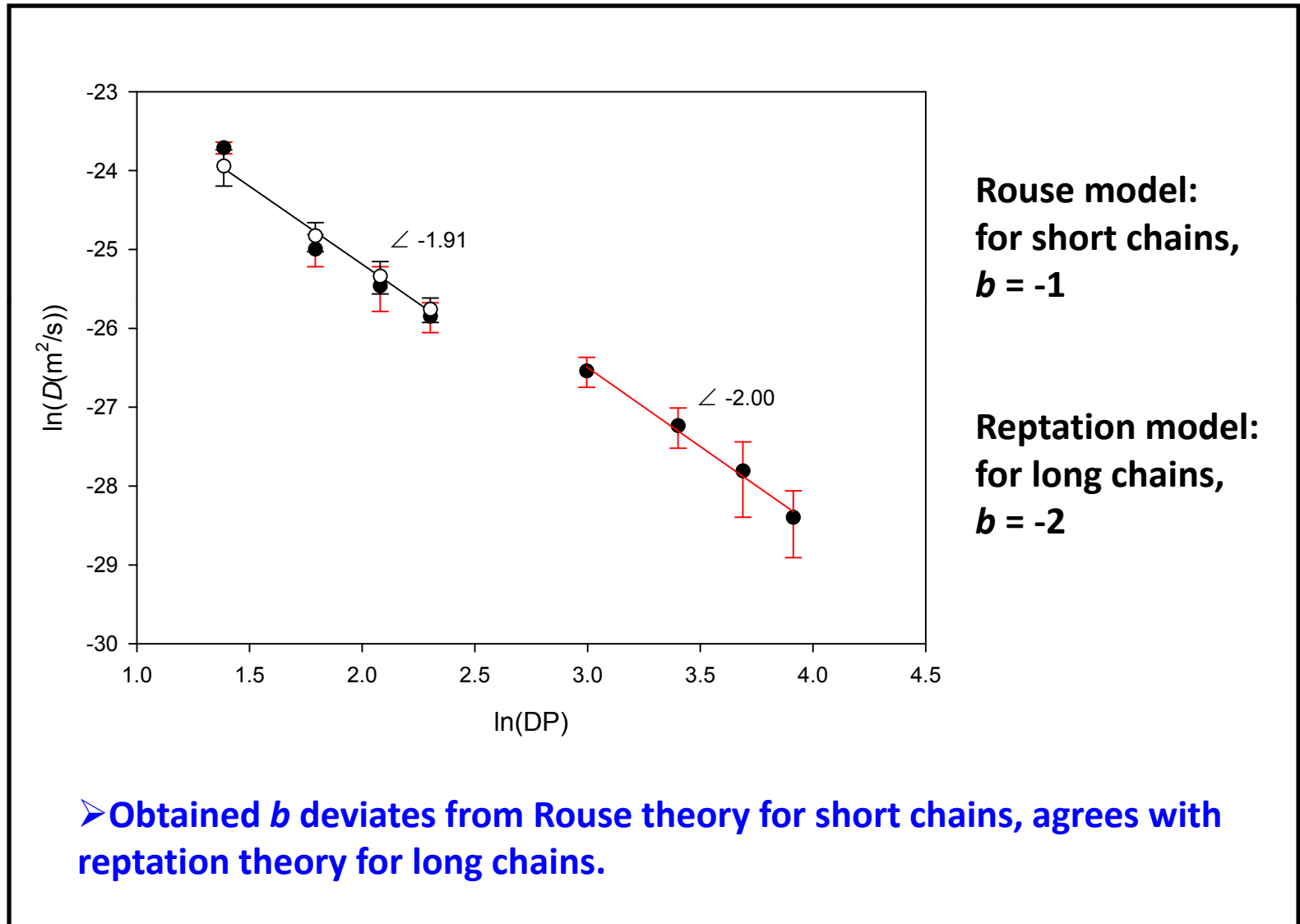
for Long chains:  
obtained  $b$  is  
close to 0.5

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





## 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.

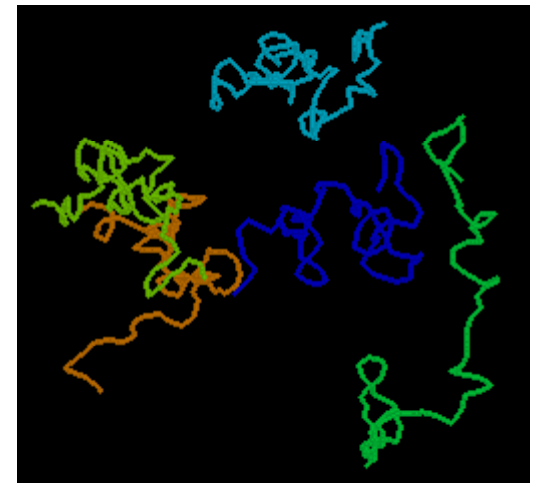
The Z-code: A common algorithm to study the entanglements in polymeric systems (Kroger, M. *Comput. Phys. Commun.* **2005** )

What can we get from Z-code?

mean contour length of primitive path ( $\langle L_{pp} \rangle$ ), 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 <sup>a</sup> , 38-43 <sup>b</sup>	30.2 <sup>a</sup> , 24.2 <sup>b</sup> , 25.0 <sup>c</sup>	N/A	14.9 <sup>d</sup>

➤ For DP = 10, unentangled system. for DP = 20 to 50, ( $d$ ), ( $N_e$ ) 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:



- Atomistic simulations of PET from DP = 1 to 10 yield a variety of structural, thermodynamic and transport properties that compare well with experimental data.
- CG model of PET was implemented in CGMD simulations of PET chains with DP up to 50. This allows simulation up to 1000 ns. The CG potential is parameterized to structural distribution functions obtained from atomistic simulations using OZPY<sup>-1</sup>.
- The CGMD simulation of PET chains satisfactorily reproduces the structural and dynamic properties from atomistic MD simulation of the same systems.
- For the long 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 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.