

Simulating PEO melts using connectivity-altering Monte Carlo

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Acknowledgements:

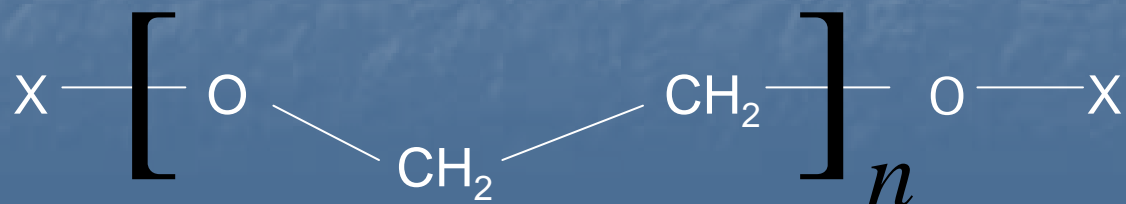
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Introduction

Poly(ethylene glycol) ($X=H$) and poly(ethylene oxide) dimethyl ether ($X=CH_3$) have the same interior segments, but different endpoints.

The volumetric properties of the two systems as a function of chain length behave quite differently.



Molecular Simulation Techniques

- Two predominate simulation techniques are used.
- Molecular Dynamics: the system follows Newton's equations of motion, following their real dynamical trajectory.
- Monte Carlo: the system randomly moves from one state to another with no set trajectory.
- The technique we use is Monte Carlo.

Designing a Monte Carlo Move

$$\rho_{\alpha} T_{\alpha \rightarrow \beta} P_{\alpha \rightarrow \beta} = \rho_{\beta} T_{\beta \rightarrow \alpha} P_{\beta \rightarrow \alpha}$$

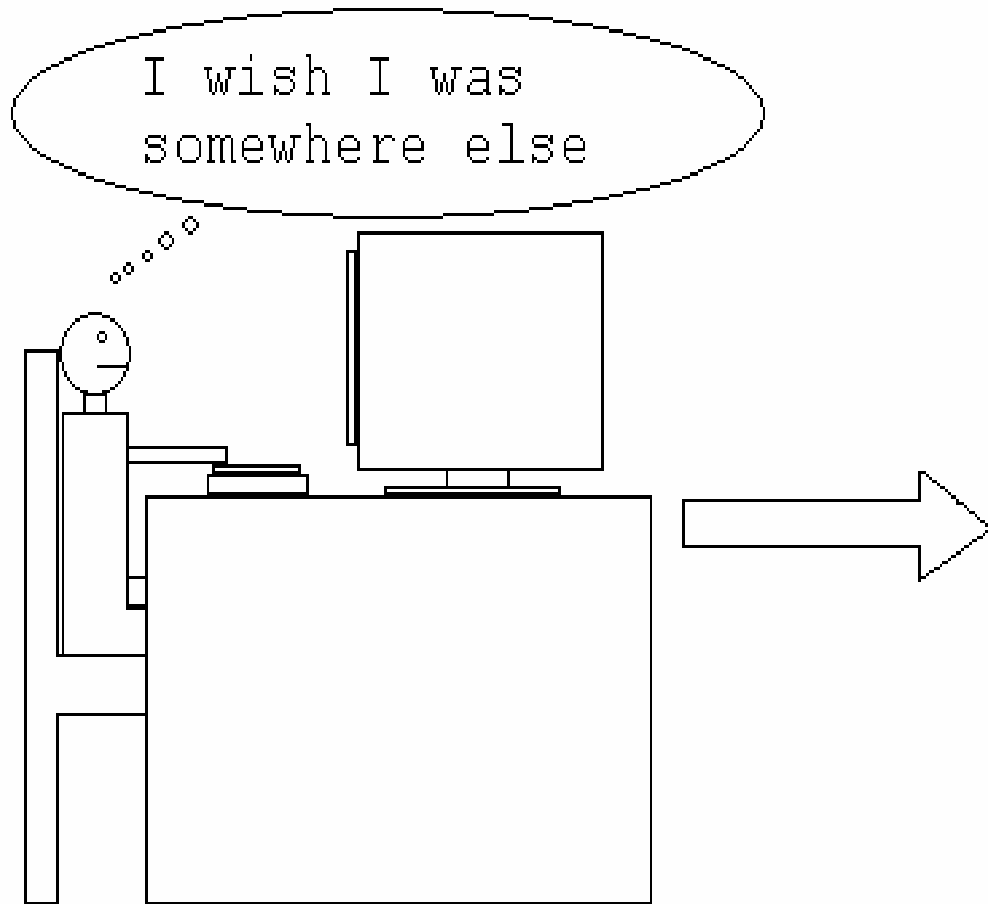
ρ_{α} = prob. density to be in state α

$T_{\alpha \rightarrow \beta}$ = transition prob. for the transfer
from state α to β .

$P_{\alpha \rightarrow \beta}$ = acceptance prob. for the transfer
from state α to β .

$$P_{\alpha \rightarrow \beta} = \min[1, (T_{\beta \rightarrow \alpha} / T_{\alpha \rightarrow \beta})(\rho_{\beta} / \rho_{\alpha})]$$

The Benefit of Monte Carlo



Metropolis Acceptance

$$T_{\alpha \rightarrow \beta} = T_{\beta \rightarrow \alpha}$$

$$P_{\alpha \rightarrow \beta} = \min[1, \rho_{\beta} / \rho_{\alpha}]$$

Translation and rotation moves :

$$\rho_{\beta} / \rho_{\alpha} = \Delta B = \exp[-(u_{\beta} - u_{\alpha}) / k_{\text{B}}T]$$

Volume Fluctuations with outside pressure bath.

Configurational-bias Monte Carlo

$$T_{\alpha \rightarrow \beta} \neq T_{\beta \rightarrow \alpha}$$

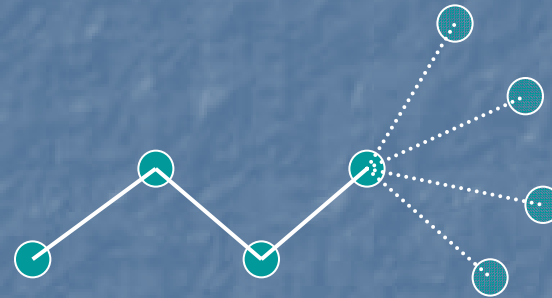
$$T_{\alpha \rightarrow \beta} = \prod_{n=1}^{nstep} (B_i / W)_n$$

$$B_i = \exp(-u_i / k_B T)$$

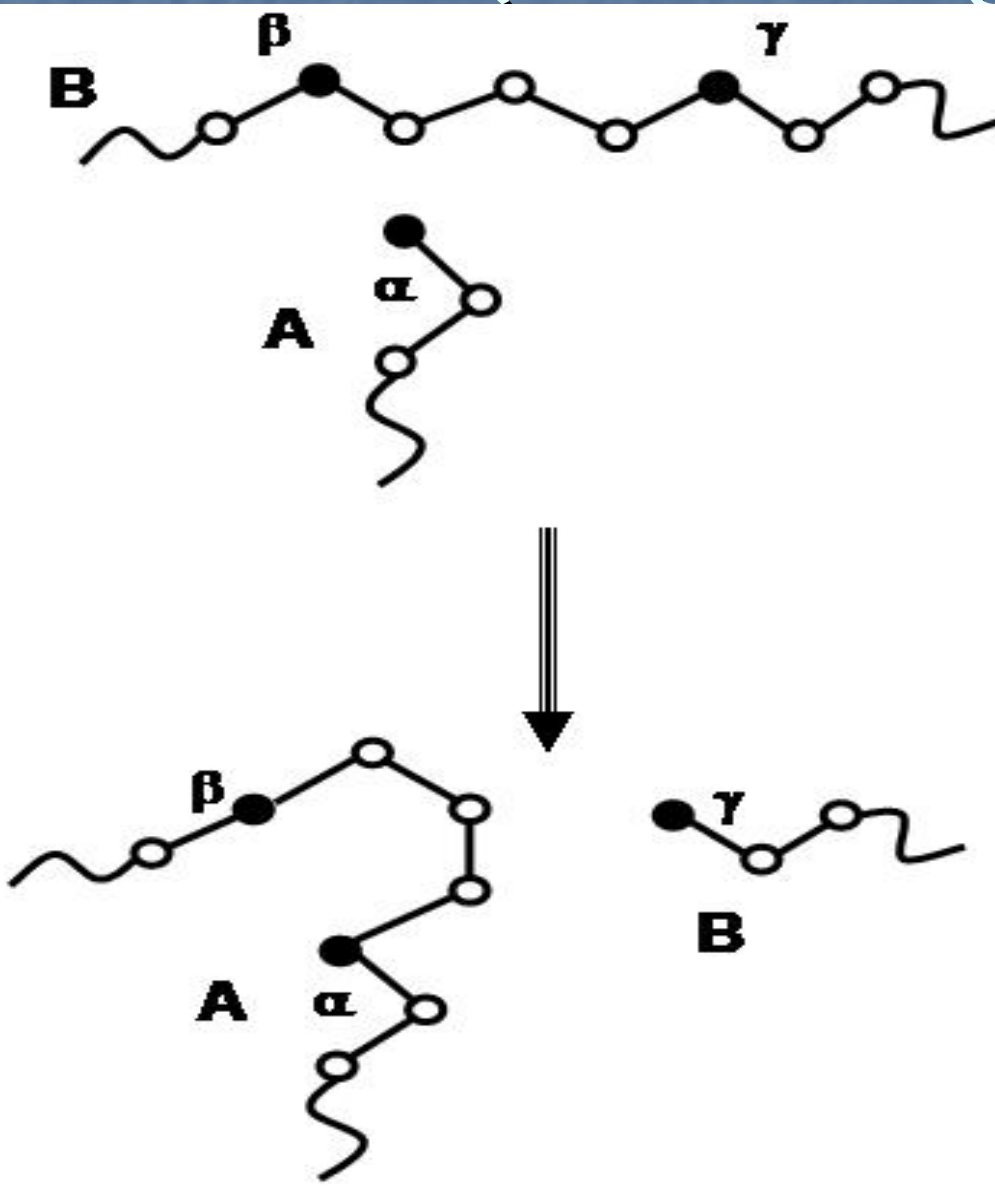
$$W = \sum_{j=1}^{nchoi} B_j$$

$$\rho_\alpha \propto \prod_{n=1}^{nstep} (B_i)_n$$

$$P_{\alpha \rightarrow \beta} = \left[\prod_{n=1}^{nstep} (W)_n \right]_{\alpha \rightarrow \beta} / \left[\prod_{n=1}^{nstep} (W)_n \right]_{\beta \rightarrow \alpha}$$



Connectivity-Altering MC (End-Bridging Move)



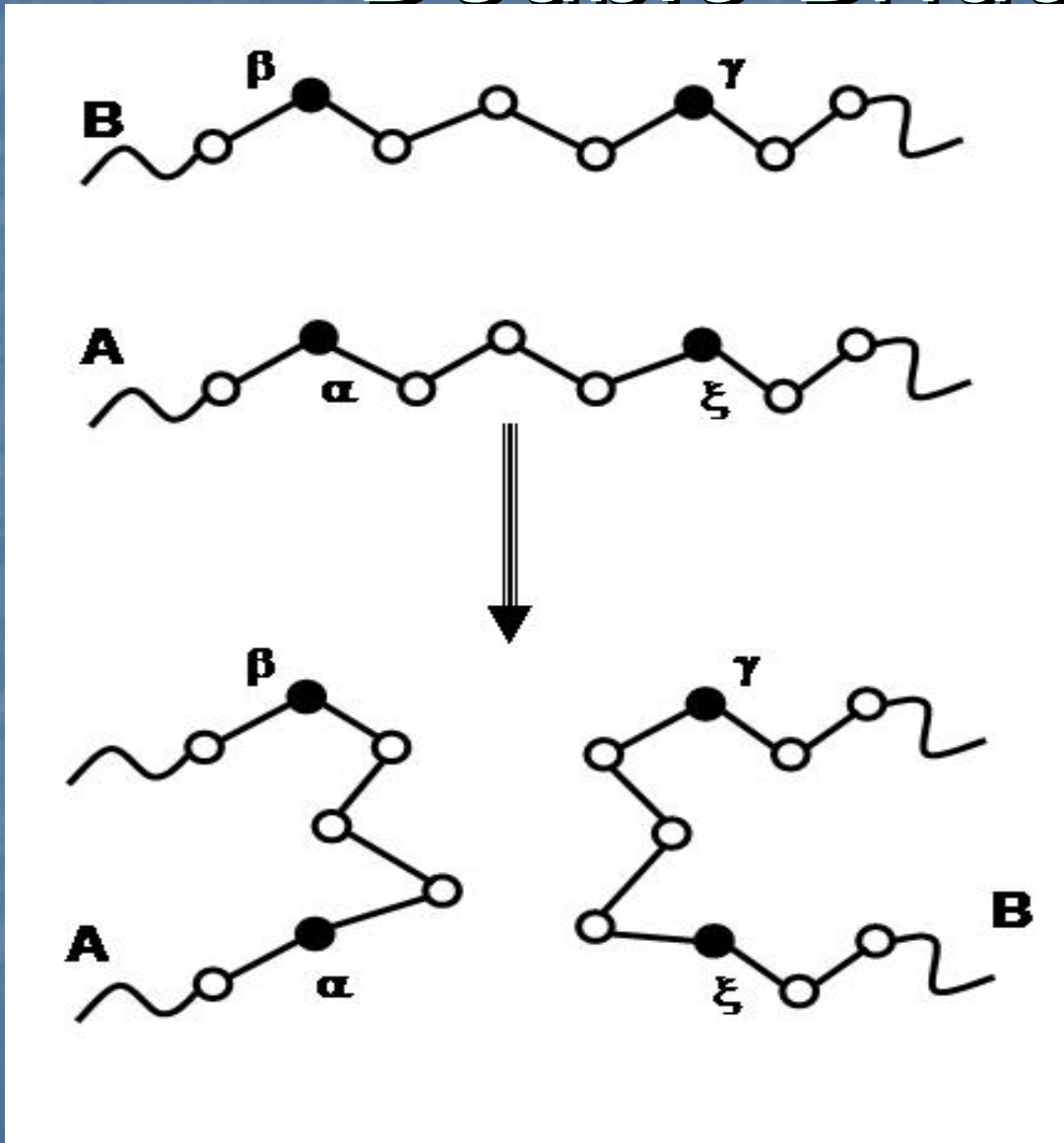
End-bridging (EB)
move from α to β

Use SAFE-CBMC to
regrow the
segments

For PEG, regrow OH
group from γ .

Repeat for reverse
move

Double Bridging Move



Double-bridging (DB) move from α to β , and from γ to ξ . Use SAFE-CBMC to regrow the segments. Repeat for reverse move.

TraPPE-UA Force Field

- Transferable potentials for phase equilibria-united atom form.
- Enforces transferability in the fitting of new groups.
- Utilizes pseudo-atoms for alkyl groups located at carbon centers, and treats all non-alkyl atoms explicitly.
- Fixed bond lengths

Potential Form

Harmonic bond bending potential

$$u_{\text{bend}}(\theta) = \frac{k_0}{2}(\theta - \theta_0)^2$$

Cosine series for dihedral interactions

$$u_{\text{torsion}}(\phi) = c_0 + c_1(1 + \cos(\phi)) + c_2(1 - \cos^2(\phi)) \\ + c_3(1 + \cos^3(\phi))$$

LJ + coulombic terms for non - bonded interactions

$$u_{\text{NB}}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

Parameterizing TraPPE-UA

- Bonded interactions are taken from existing force fields.
- Lennard-Jones and Coulombic interactions are fit to reproduce vapor-liquid coexistence curves.
- For PEODME, all nonbonded parameters were fit to small ether molecules.
- For PEG, all nonbonded parameters were fit to small alkanol and glycol molecules.
- Oxygens have negative charges, and methyl, methylene, and hydrogens have positive charges.

Simulation Details

- Polydisperse melts of PEG and PEODME were simulated with chain length evenly distributed over a selected range.
- Simulation runs consisted of four runs of 200,000 MC cycles (one MC cycle is N MC moves).
- Periodic boundary conditions were used.
- Pressure and temperature were set for each simulation run.

Number, molecular weight, and polydispersity of polymers

Name	N	M_n (g/mol)	M_w/M_n
PEG-600	30	723	1.05
PEG-1540	20	1560	1.08
PEG-3000	12	3014	1.08
PEG-4500	9	4467	1.08
PEG-6000	6	5921	1.08
PEG-18500	2	18520	1.08
PEODME-600	40	619	1.02
PEODME-1000	30	1015	1.03
PEODME-3000	12	2998	1.07
PEODME-4300	8	4319	1.08
PEODME-6000	5	5993	1.08

Percentage and acceptance of select MC moves

	rep	EB	DB
PEODME	(20%)	(20%)	(20%)
	1.5	0.08	0.0035
PEG	(0%)	(30%)	(30%)
	N/A	0.025	0.0031

Center of Mass Movement

Top: PEODME-
3000

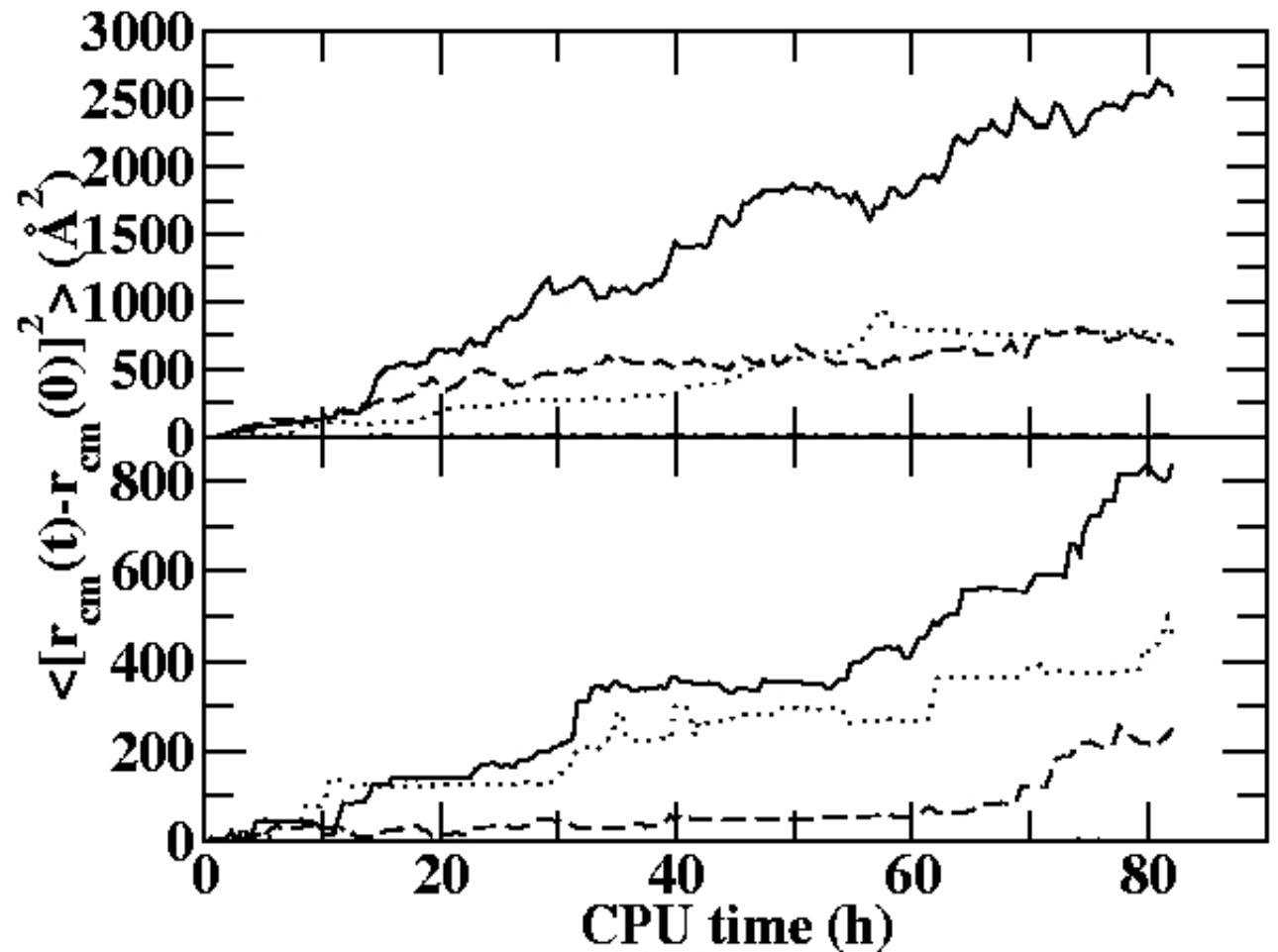
Bottom: PEG-
3000

Solid line: both EB
and DB moves

Dotted line: DB
move only

Dashed line: EB
move only

Dot-dashed line:
neither DB or
EB moves
used



End-Group Movement

Top: PEODME-
3000

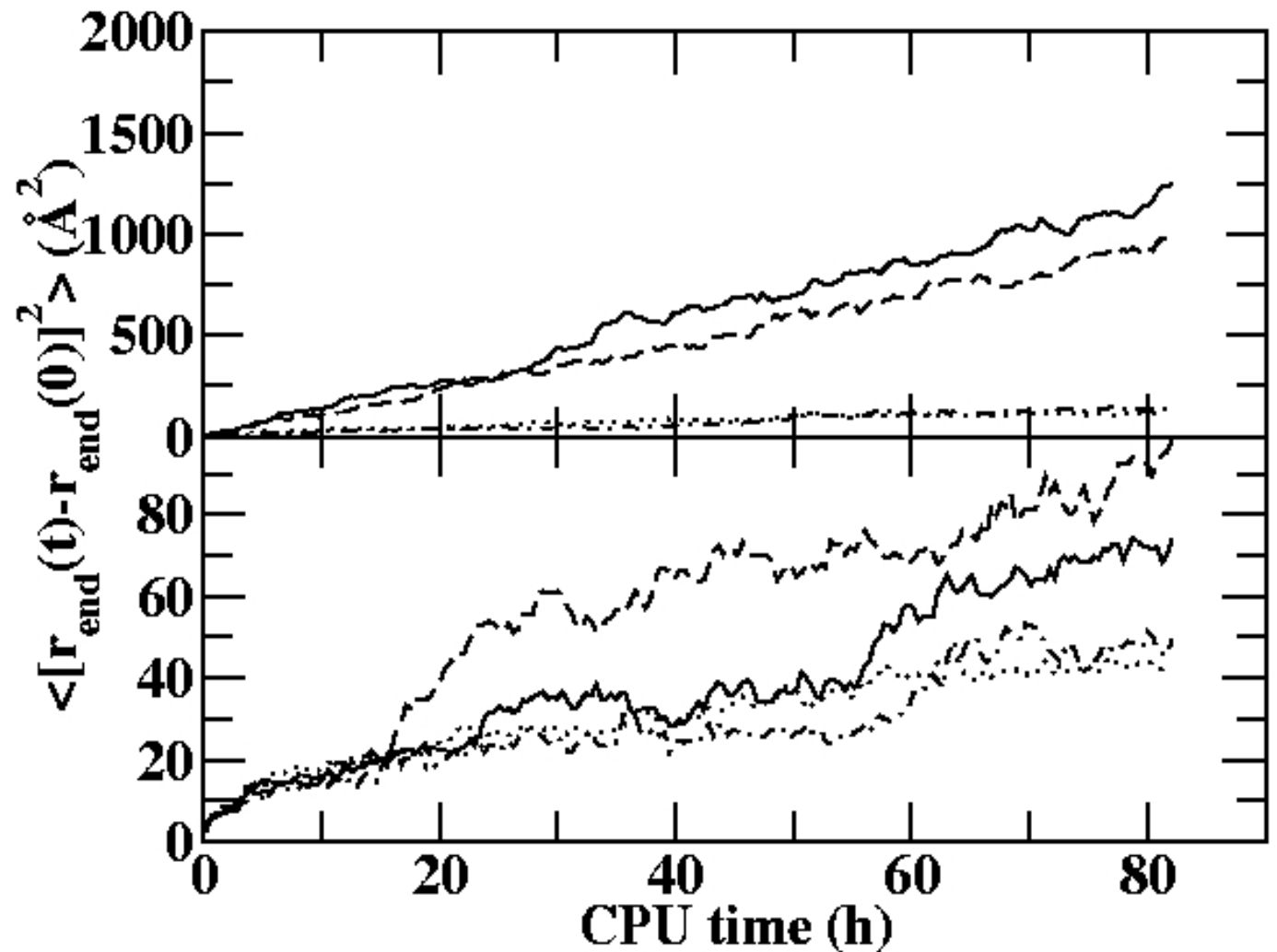
Bottom: PEG-
3000

Solid line: both EB
and DB moves

Dotted line: DB
move only

Dashed line: EB
move only

Dot-dashed line:
neither DB or
EB moves
used



Decay of End-to-End Vector

Top: PEODME-
3000

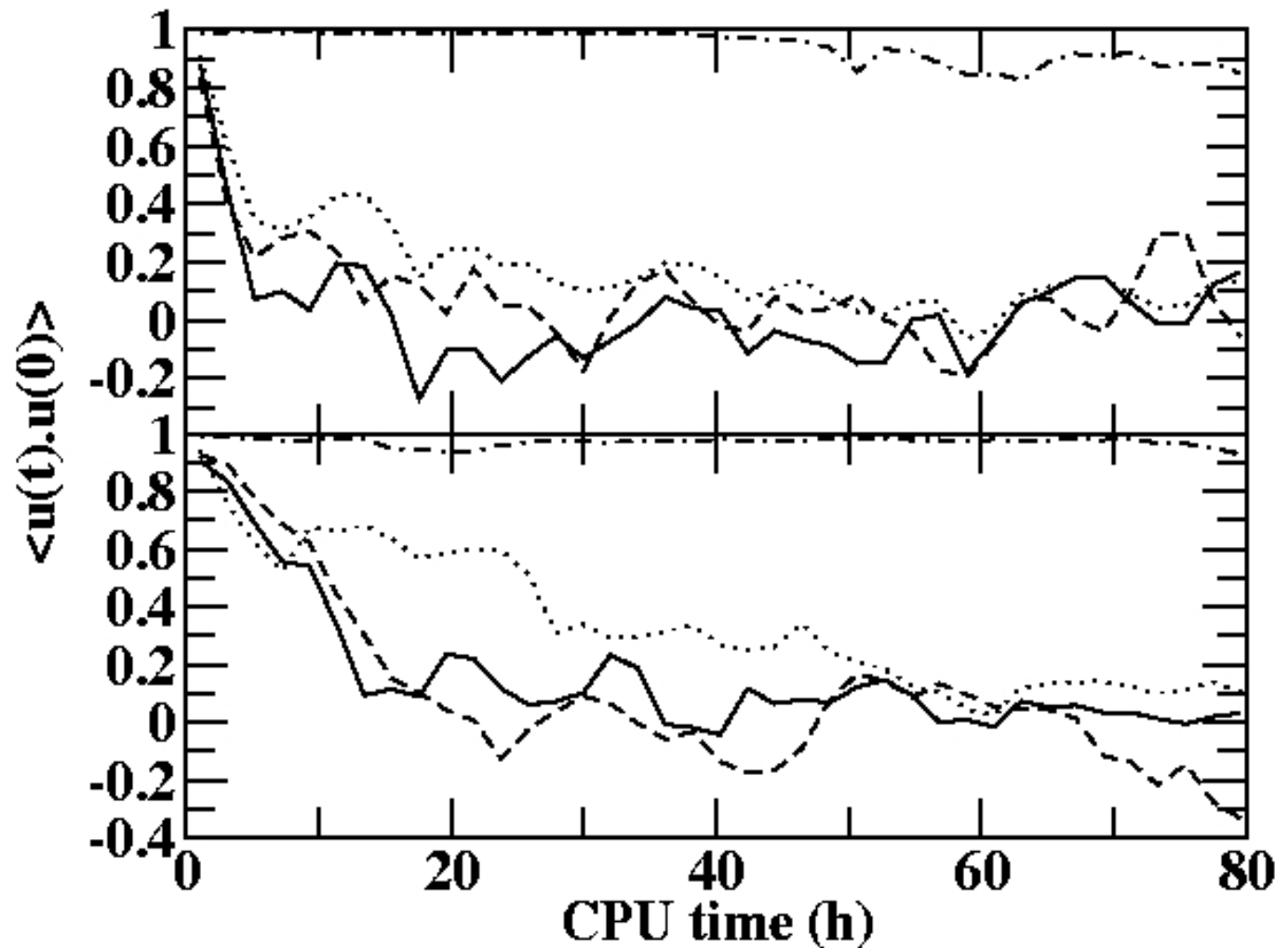
Bottom: PEG-
3000

Solid line: both EB
and DB moves

Dotted line: DB
move only

Dashed line: EB
move only

Dot-dashed line:
neither DB or
EB moves
used



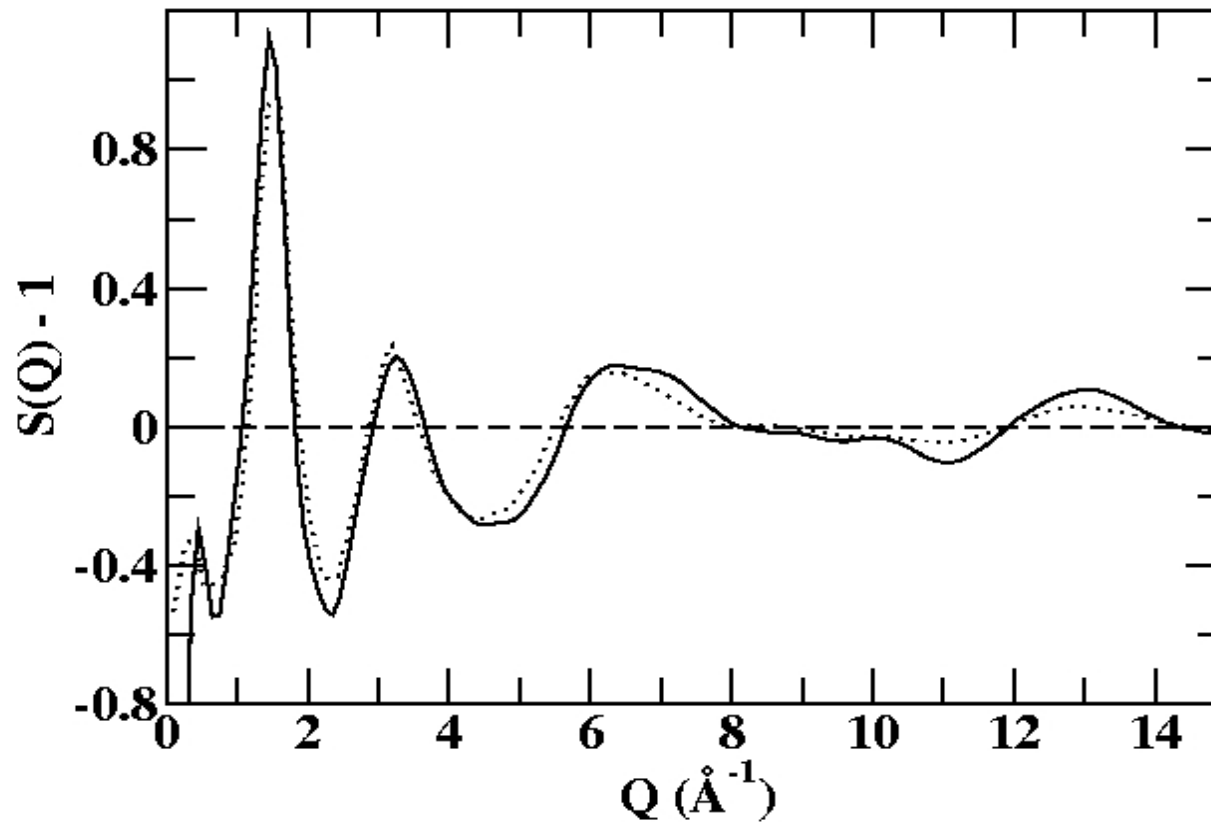
Specific Densities

	T (K)	p (MPa)	density (g/cm ³)	
			sim	exp
PEG-600	383.25	0.1	1.061 ₂	1.059
PEG-600	471.75	0.1	0.990 ₂	0.990
PEG-600	471.75	100.0	1.061 ₄	1.055
PEG-1540	474.65	0.1	0.966 ₅	0.977
PEG-18500	471.75	0.1	0.988 ₂	0.990
PEOMME-750	325.25	0.1	1.086 ₂	1.083
PEODME-600	343.35	0.1	1.042 ₂	1.034
PEODME-600	303.05	0.1	1.064 ₂	1.067
PEODME-600	303.05	100.0	1.111 ₁	1.111
PEODME-1000	343.35	0.1	1.063 _g	1.051

Static Structure Factor ($T=383\text{K}$)

sim, PEODME-3000: solid line

exp, PEG-20000: dotted line



Characteristic Ratio Plot

Top: PEODME

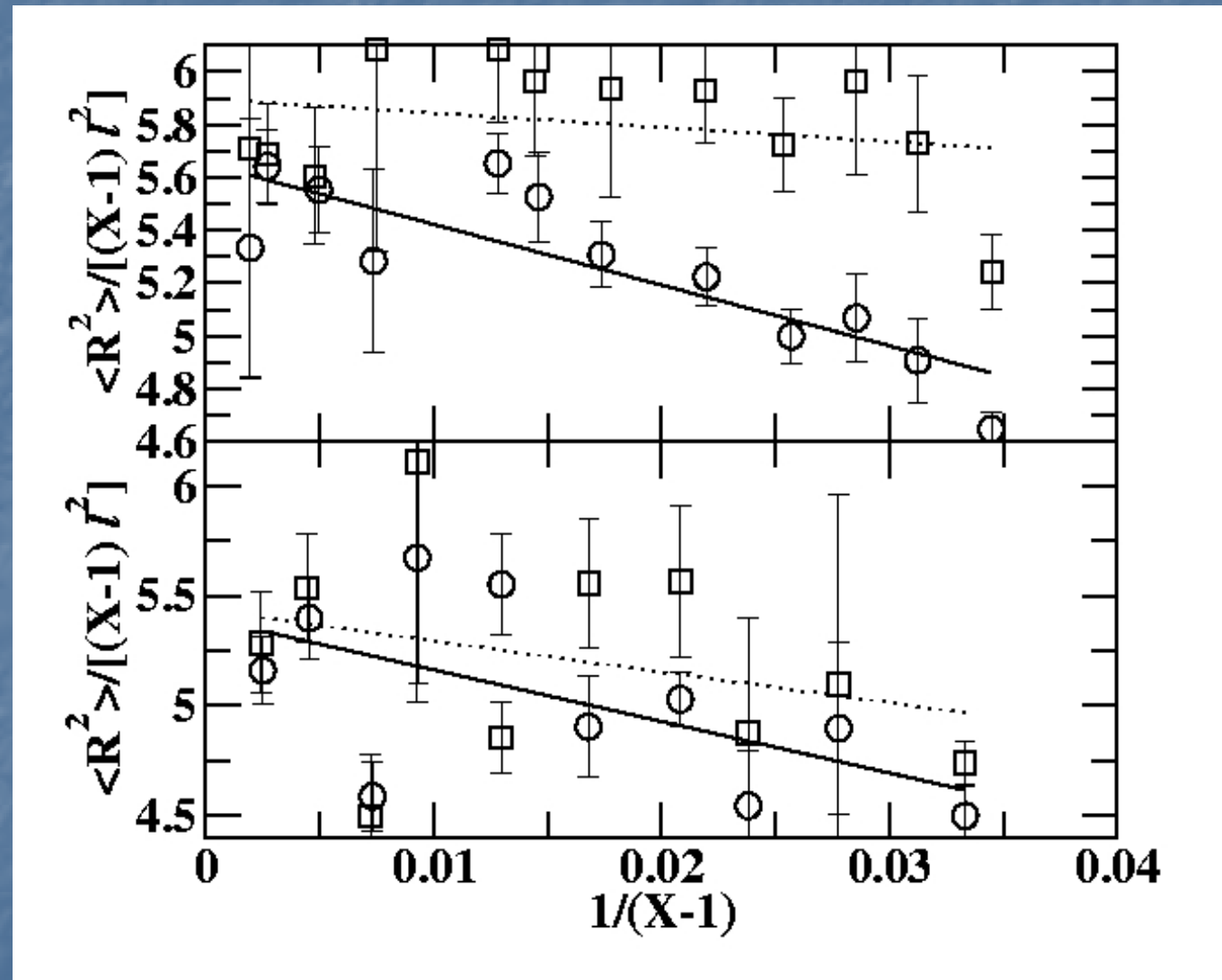
Bottom: PEG

Circles: points
using end-
to-end
distance

Squares: points
using radii of
gyration

Solid lines: fit to
circles

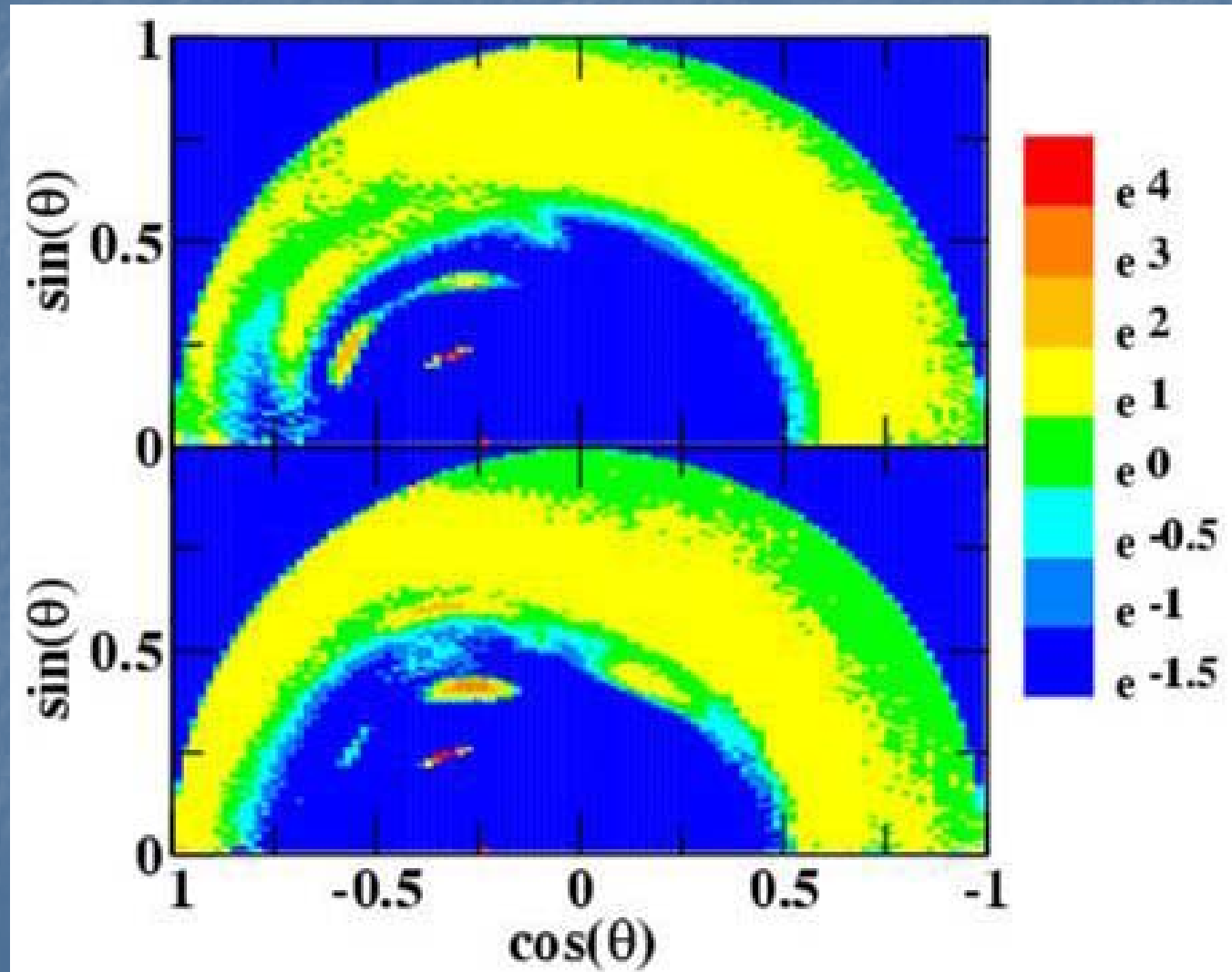
Dotted lines: fit
to squares



Experiment $C_\infty = 5.5$

3-d Radial Distribution Function

3-d radial-angular distribution function: θ =angle for **O-CH₃**—(any other heavy atom) for PEODME (top) and **CH₂-O**—(any other heavy atom) for PEG (bottom).



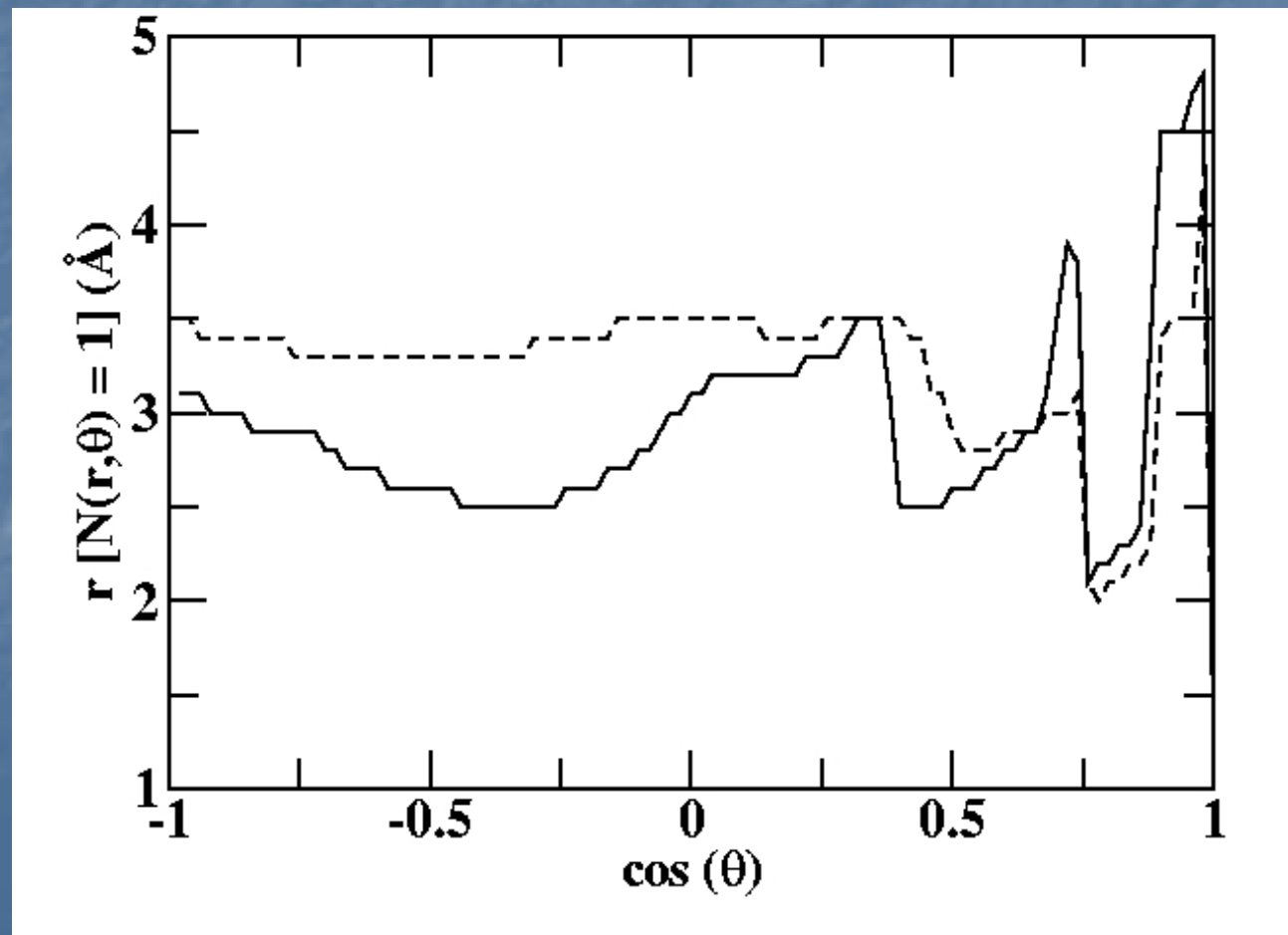
Integral of 3-d RDF

Distance where the integral of the 3-d radial-angular distribution function is unity at fixed θ , or the distance where another heavy atom is most likely present at fixed θ .

Integrating out these curves give a total end-group excluded volume: 162 angstroms for PEODME and 127 angstroms for PEG.

solid line:
PEG

dotted line:
PEODME



Conclusions

- Endbridging and double-bridging do reasonably well in equilibrating the PEO melts, but better for PEODME than for PEG.
- The TraPPE-UA force field does an excellent job of reproducing densities, and a good job of reproducing structural properties of PEO.
- The Molecular weight dependence of the volumetric properties can be related to differences in excluded volume of endgroups.