Simulating PEO melts using connectivity-altering Monte Carlo

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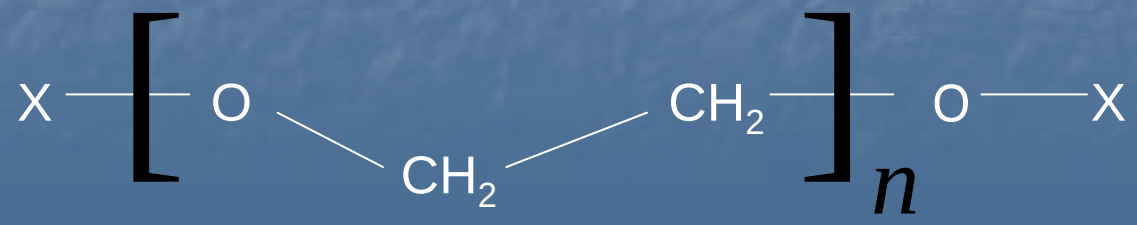
Introduction

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

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

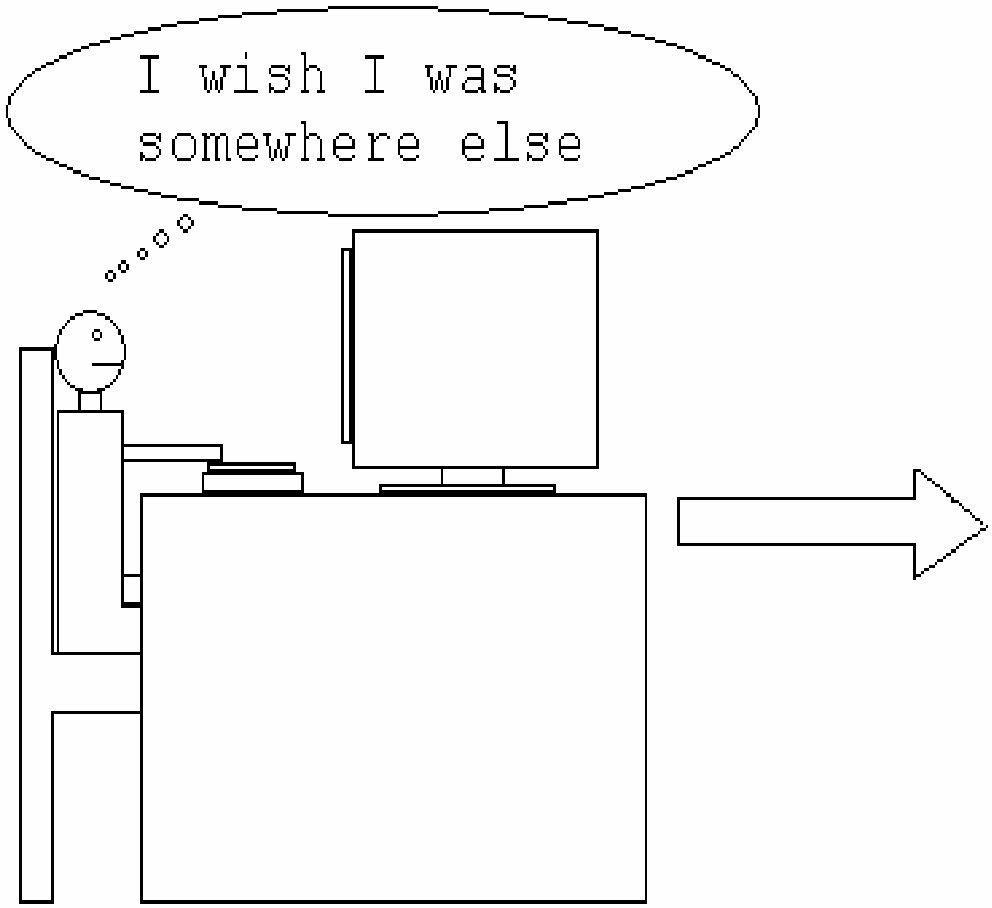
ρ_α = prob. density to be in state α

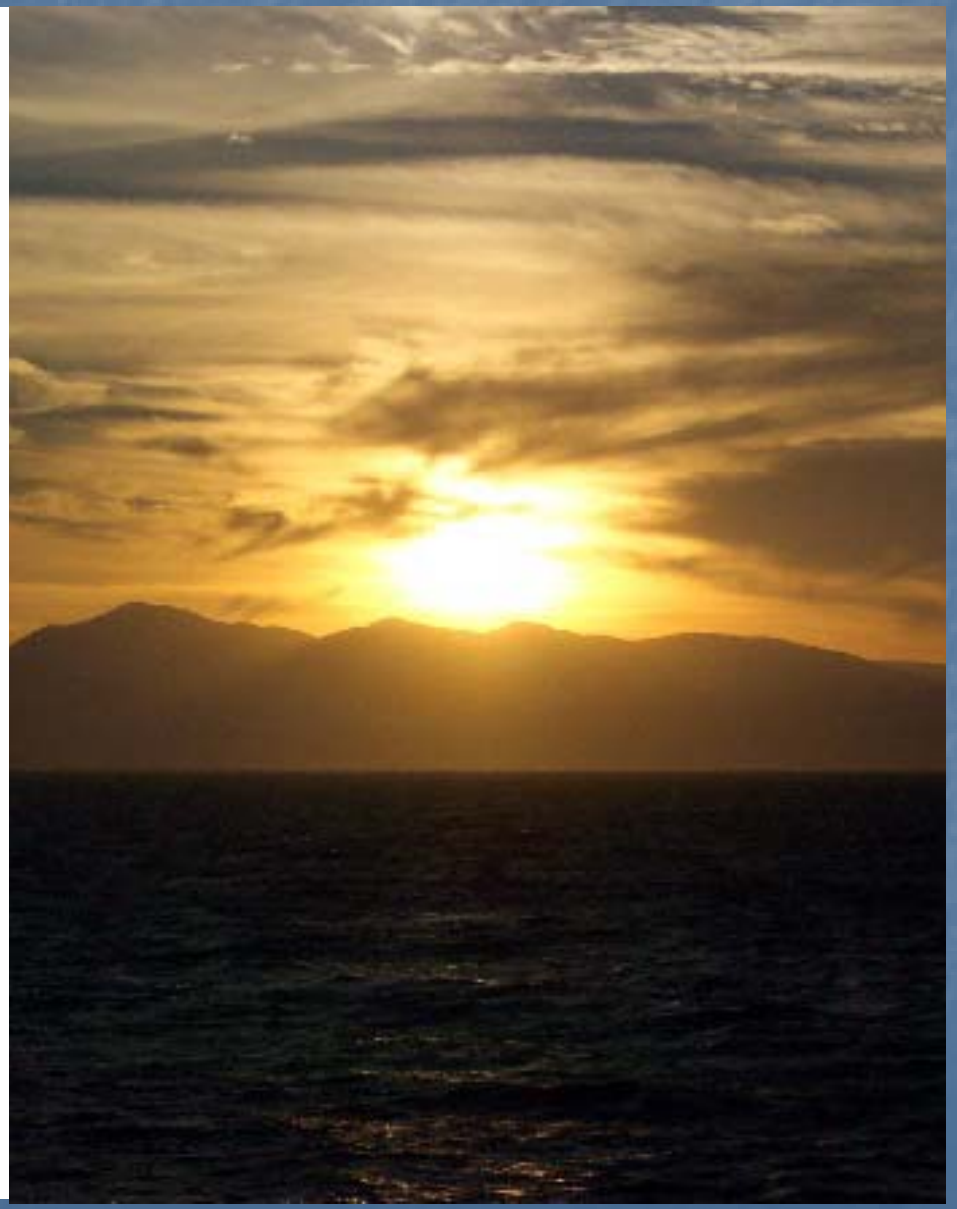
$T_{\alpha\to\beta}$ = transition prob. for the transfer from state α to β.

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

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

The Benefit of Monte Carlo





Metropolis Acceptance

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

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

Translation and rotation moves :

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

Volume Fluctuations with outside pressure bath.

Configurational-bias Monte Carlo

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

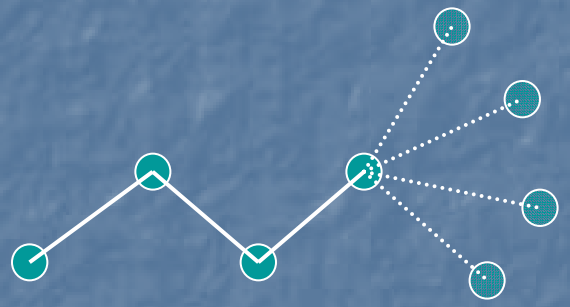
$$T_{\alpha\to\beta} = \prod_{n=1}^{nstep} (B_i / W)_n$$

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

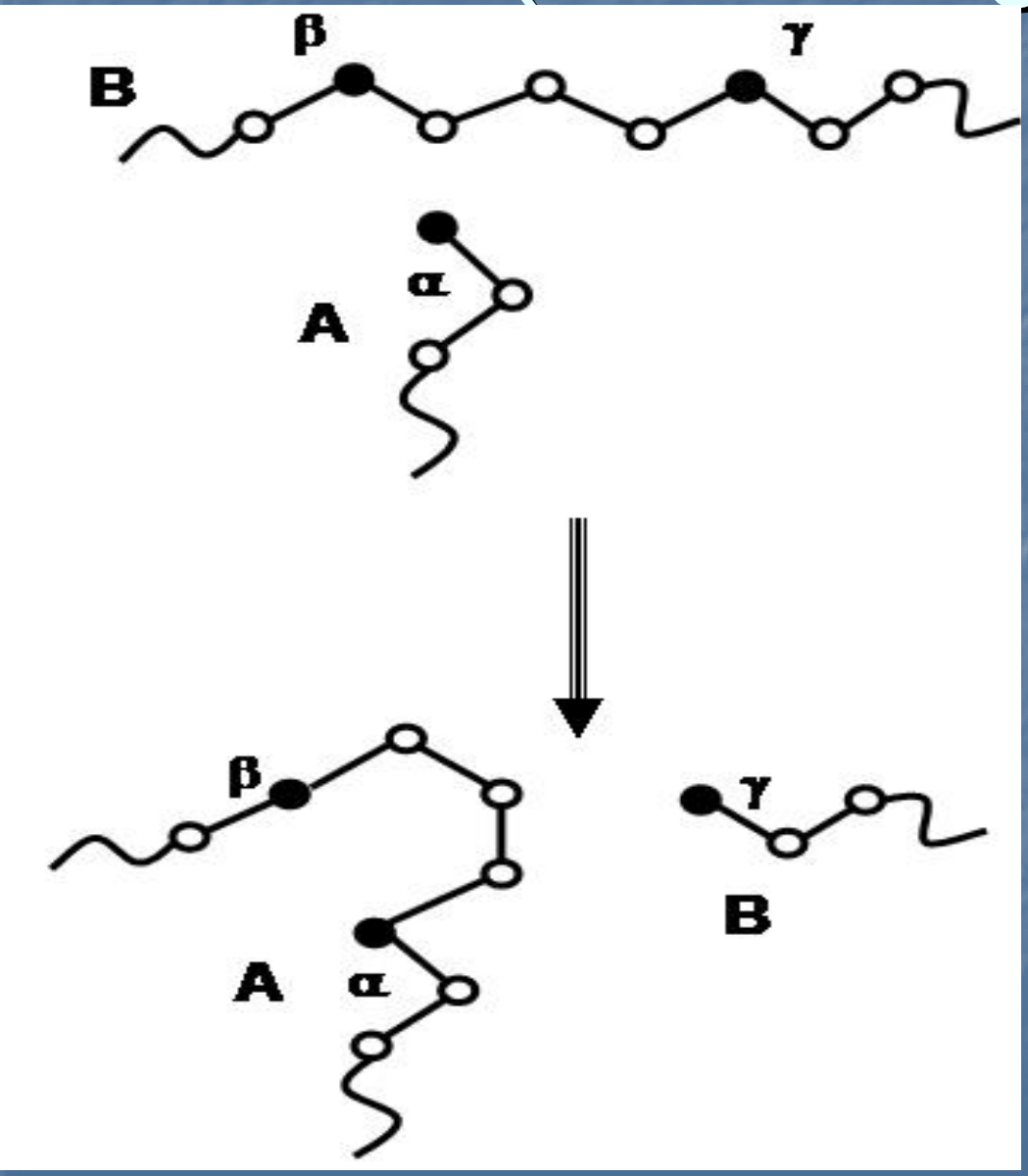
$$W = \sum_{j=1}^{nchoi} B_j$$

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

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

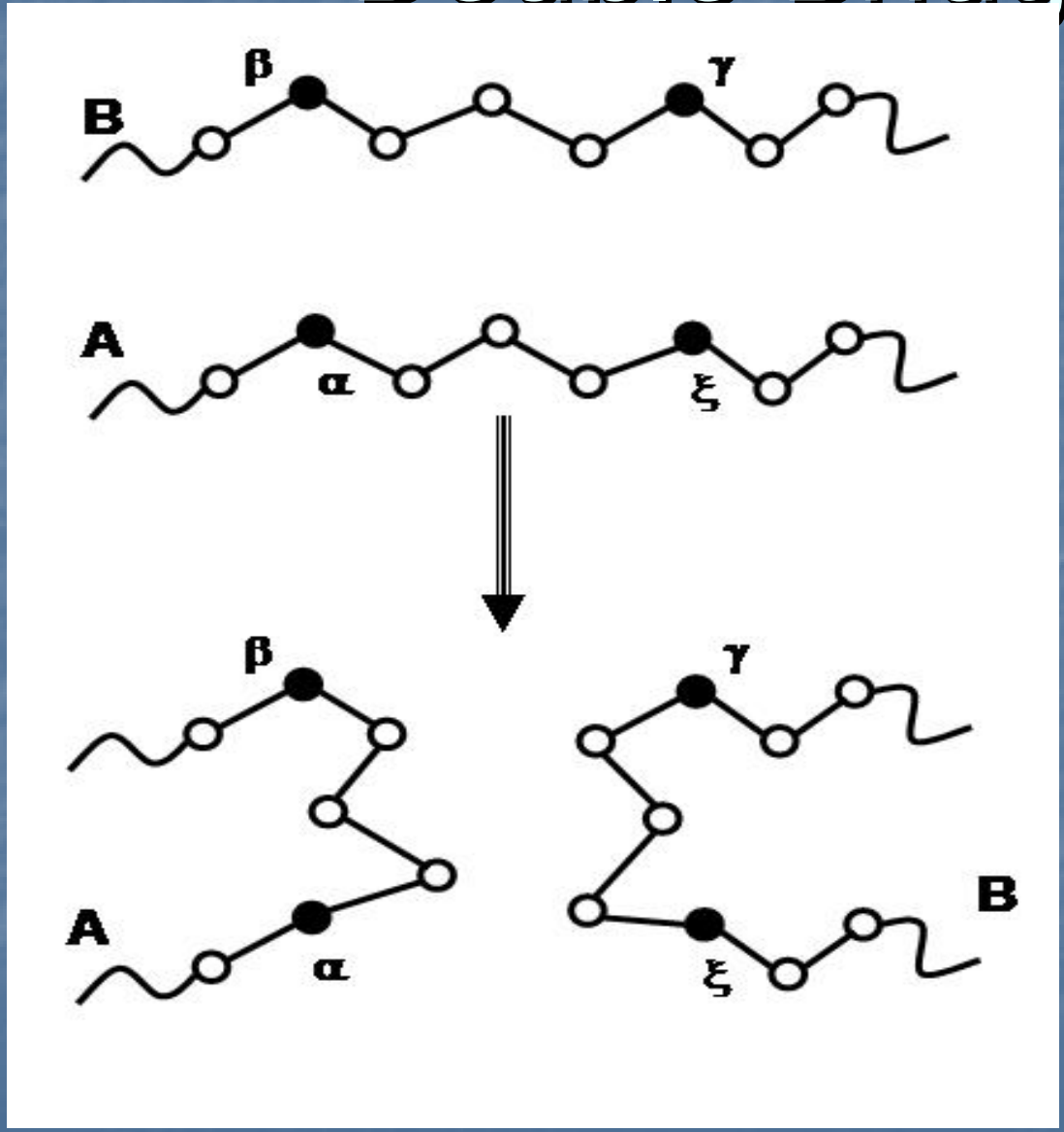


Connectivity-Altering MC (End-Bridging Move)



- 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 τo 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 + couloumbic terms for non - bonded interactions

$$u_{\text{NB}}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

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

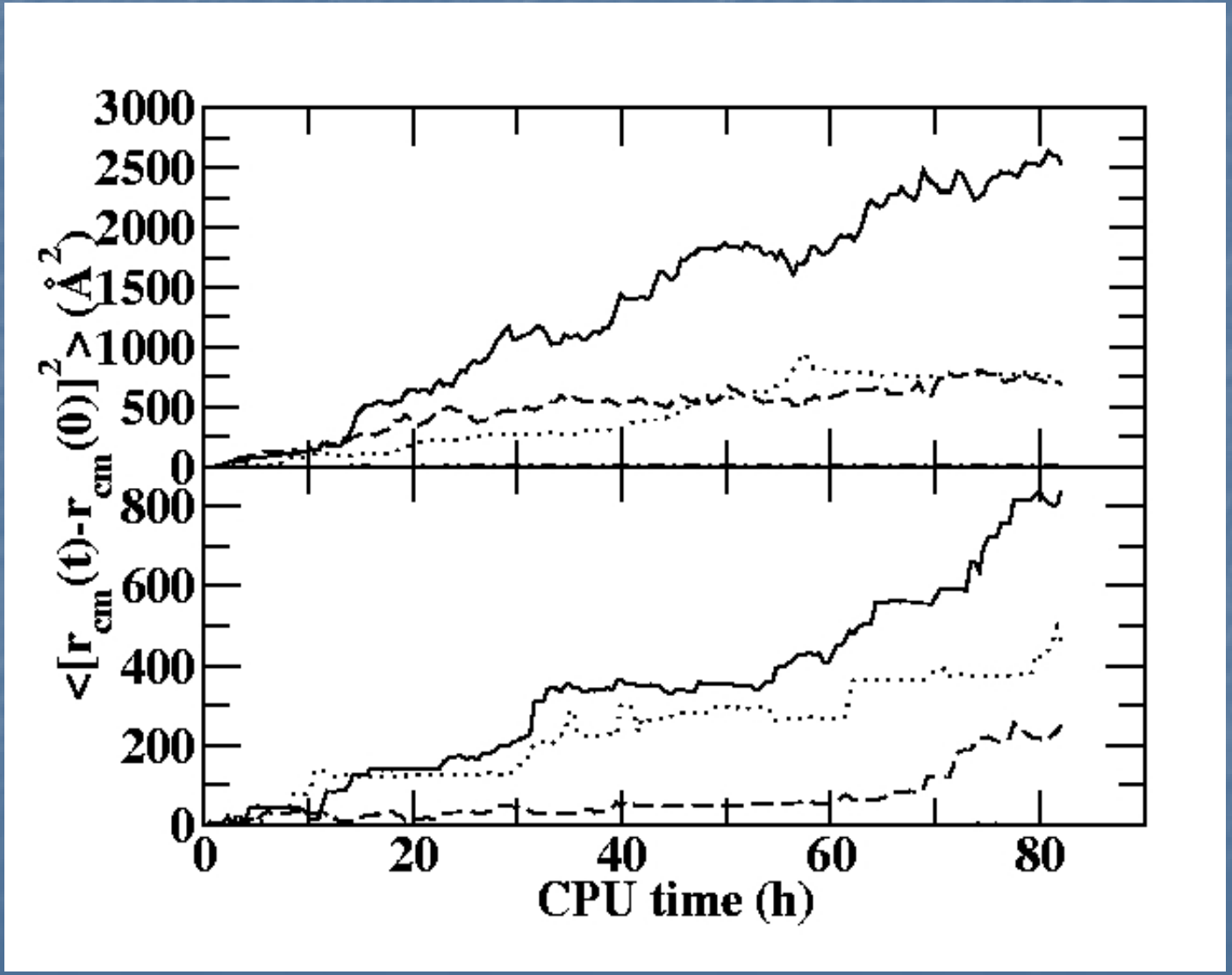
Bottom: PEG-3000

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

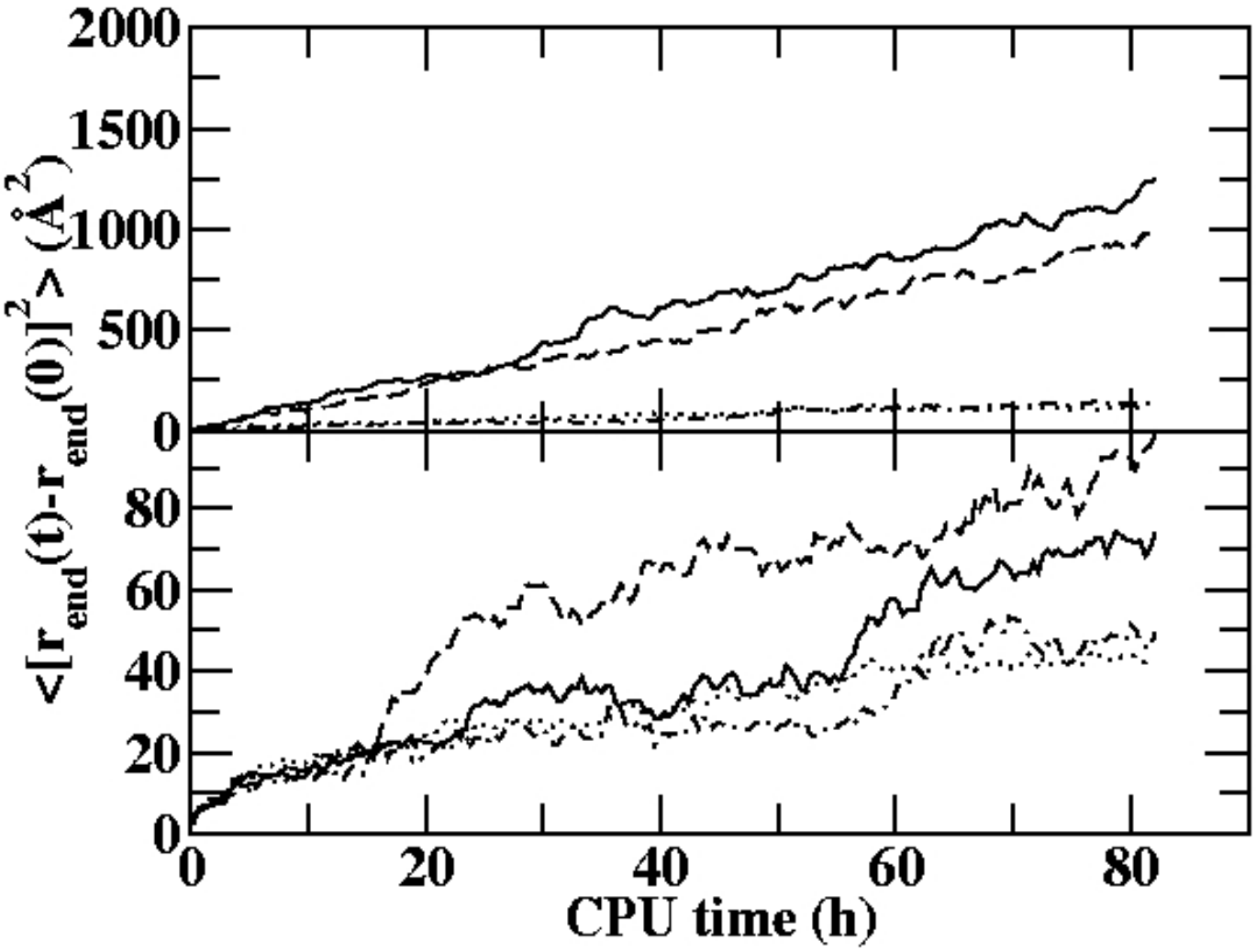
Bottom: PEG-3000

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

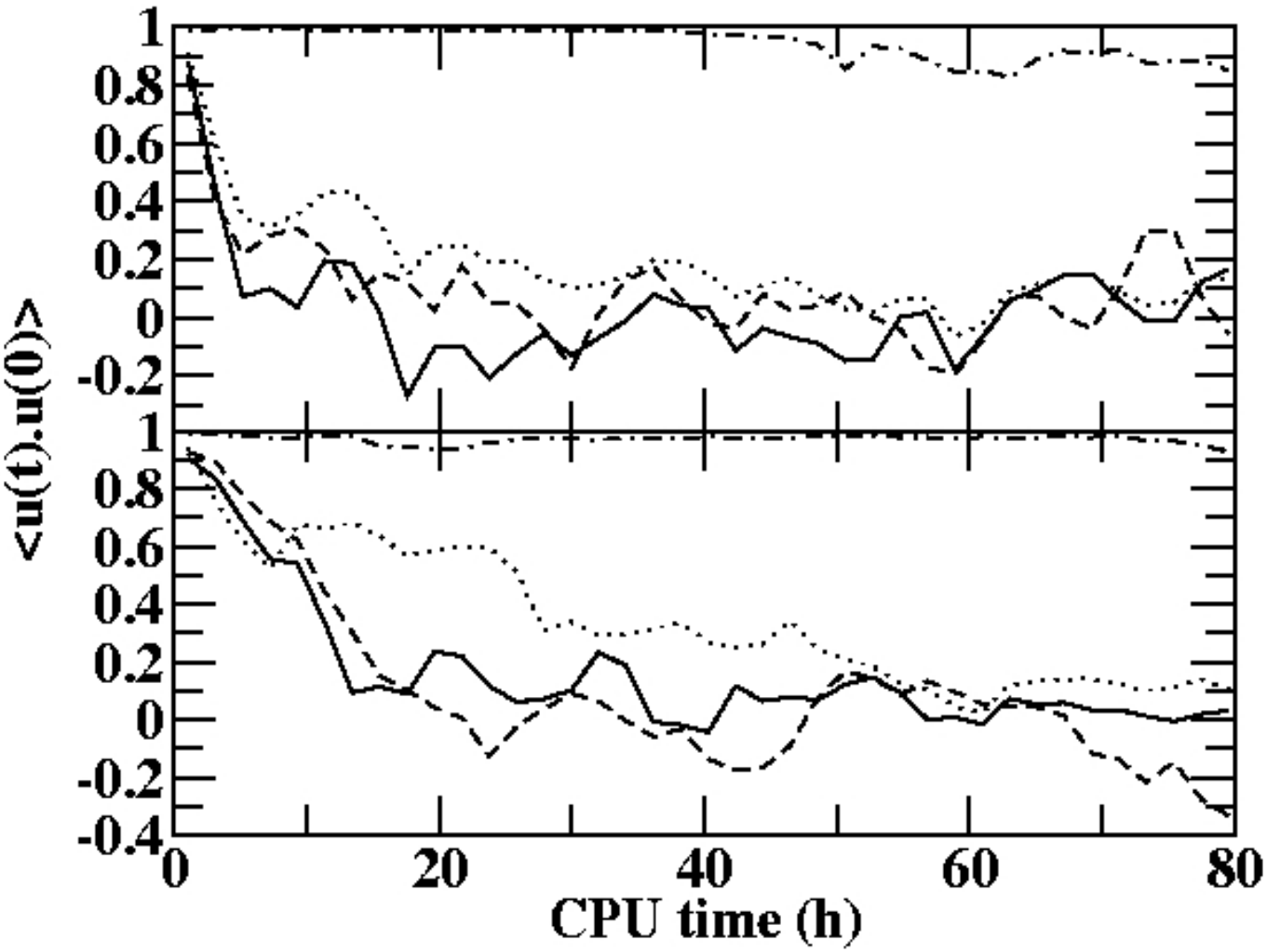
Bottom: PEG-3000

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

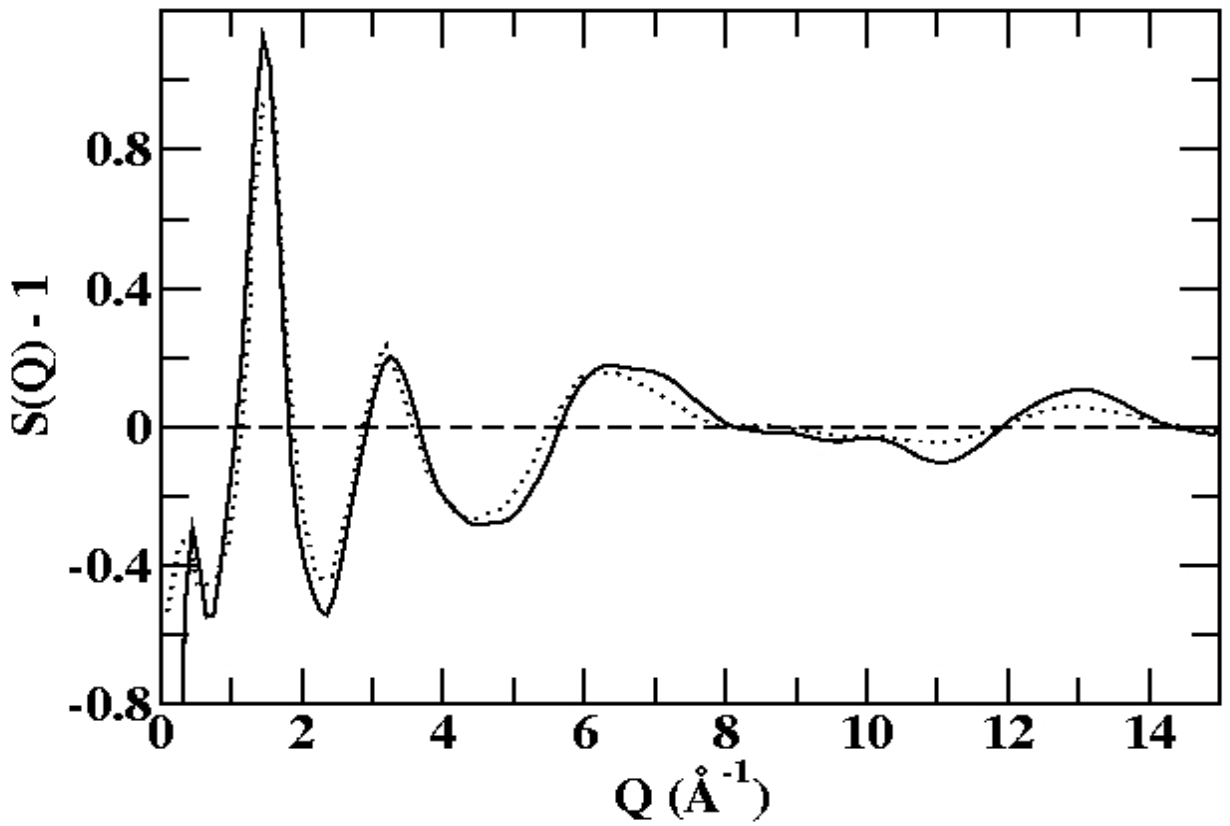


Specific Densities

	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_8	1.051

Static Structure Factor (T=383K)

sim, PEODME-3000: solid line
exp, PEG-20000: dotted line



Characteristic Ratio Plot

Top: PEODME

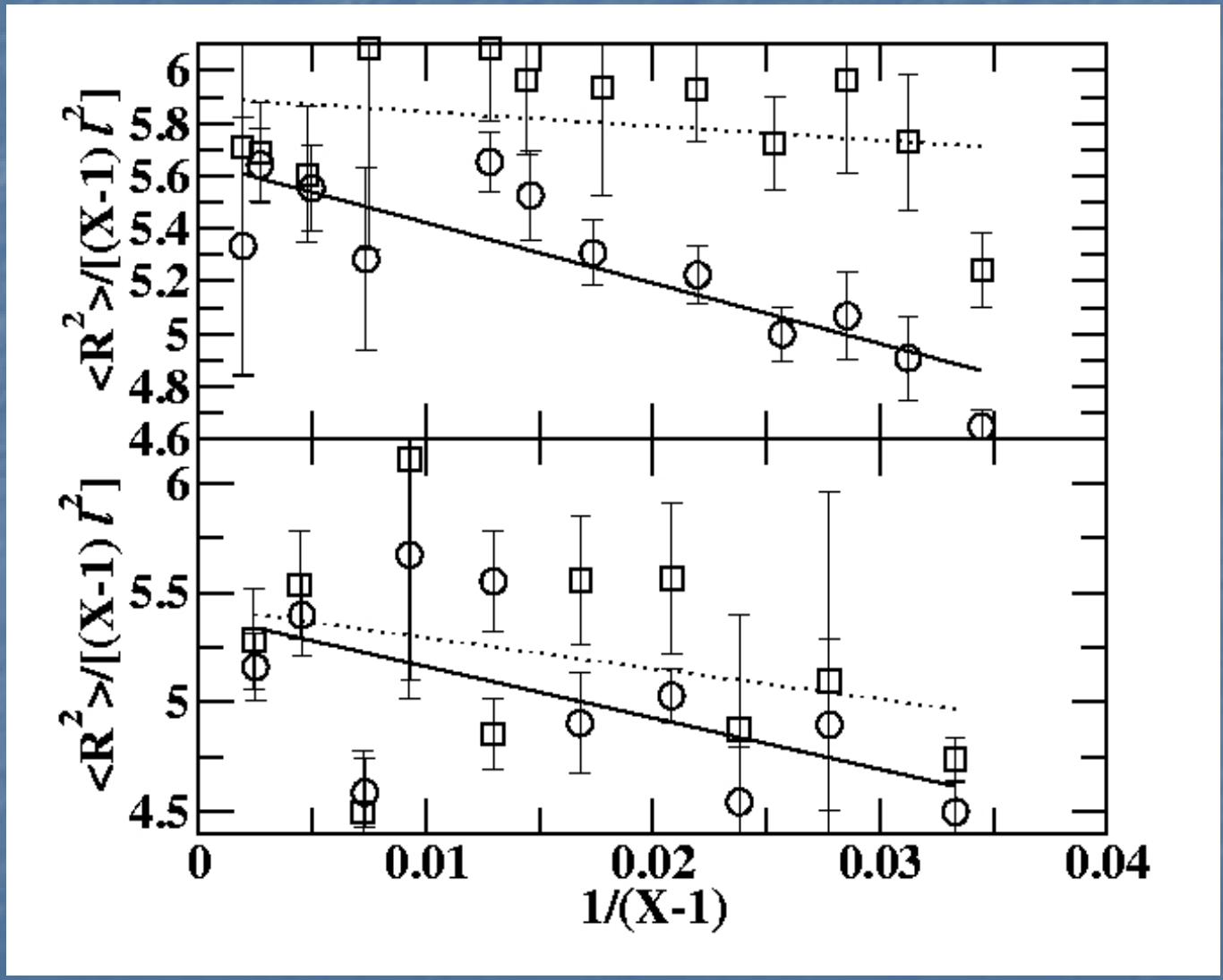
Bottom: PEG

Circles: points using end-to-end distance

Squares: points using radii of gyration

Solid lines: fit to circles

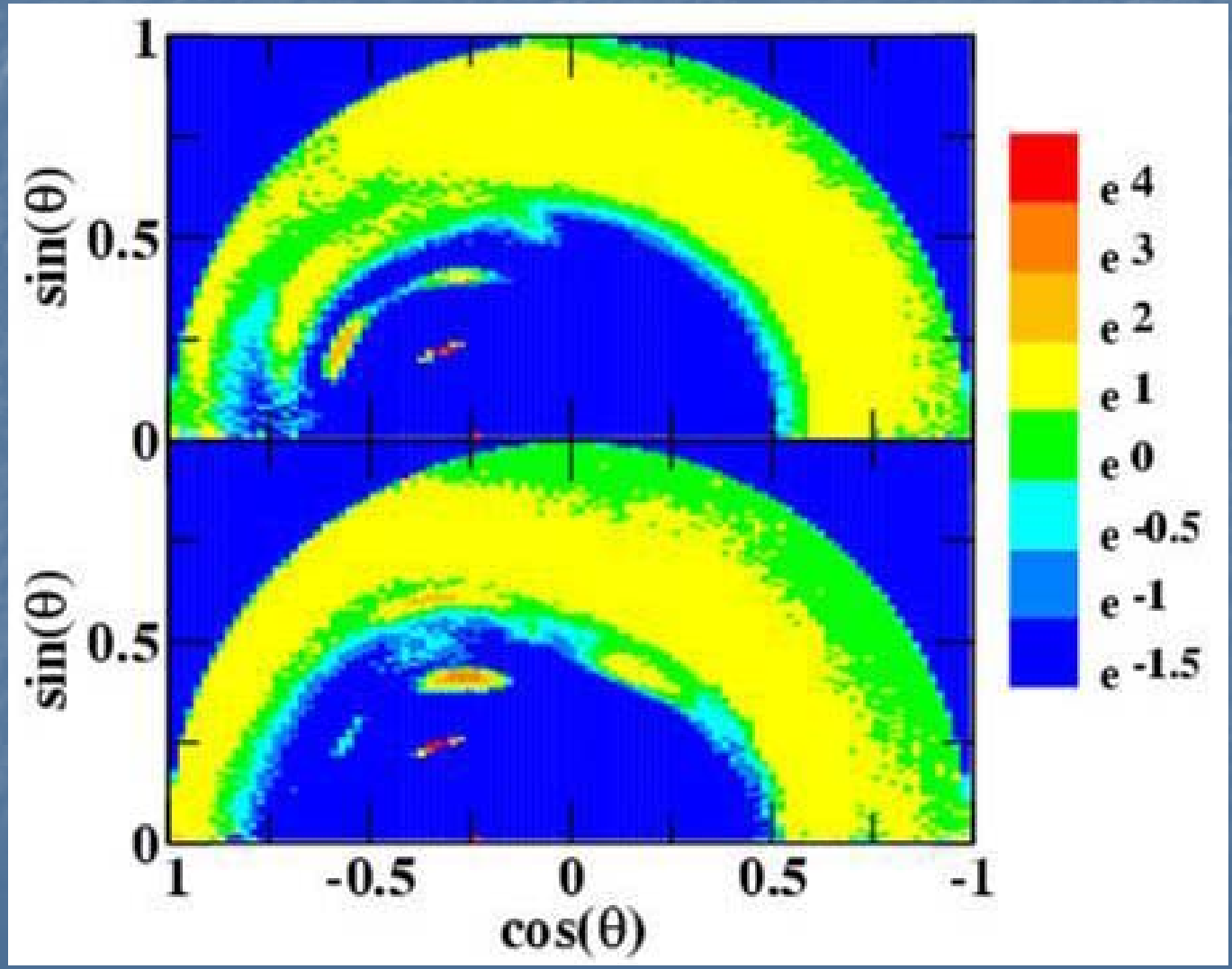
Dotted lines: fit to squares



Experiment $C_\infty = 5.5$

3-d Radial Distribution Function

3-d radial-angular distribution function: θ=angle for **O-CH_3**—(any other heavy atom) for PEODME (top) and **CH_2-O**—(any other heavy atom) for PEG (bottom).



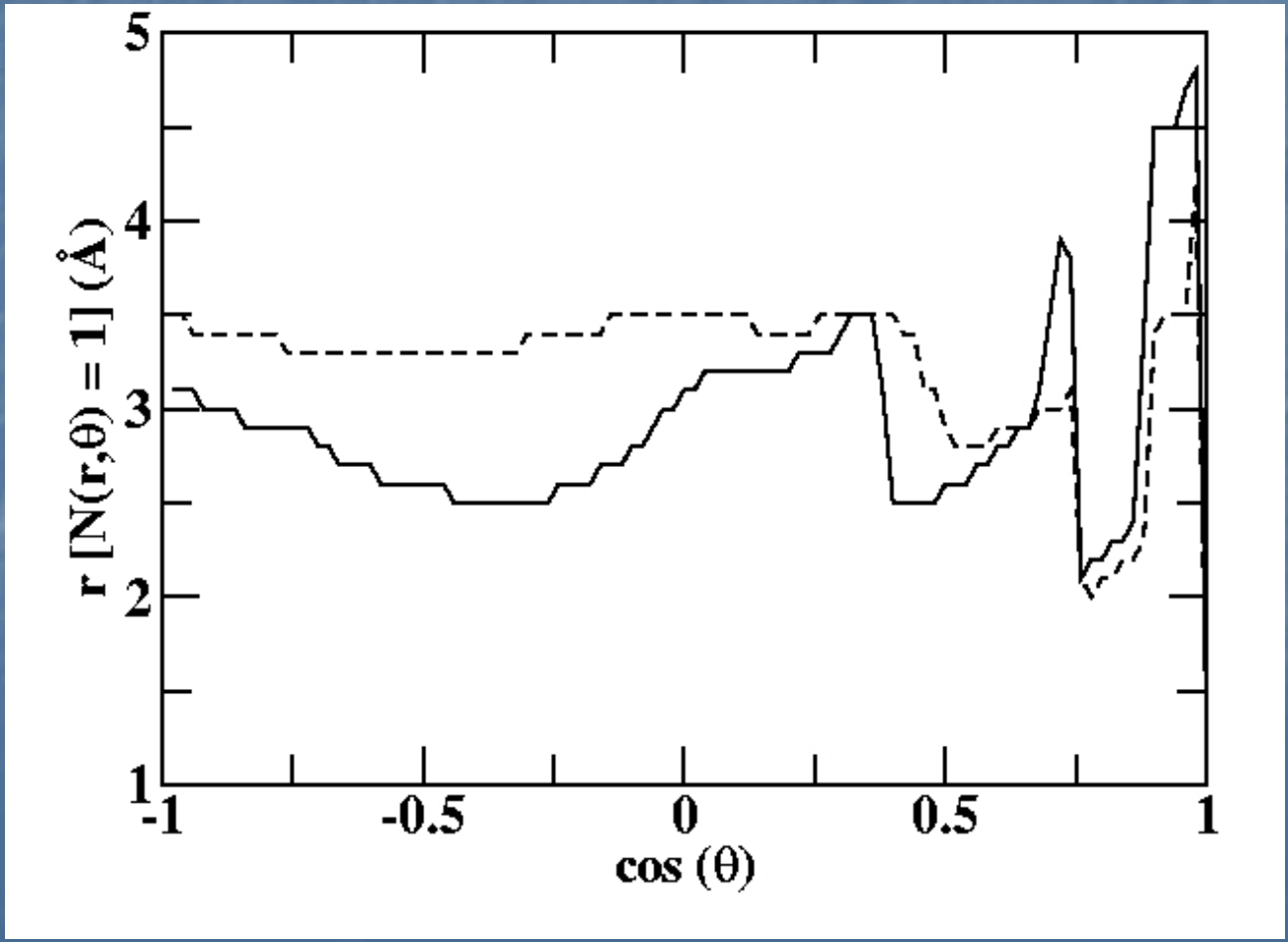
Integral of 3-d RDF

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.