DOW Latex Water ImPermeability Degradation: Coarse Grain Force Field and Models

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Outline

- Recap
- Changed to the CG force field model. Water model (Morse to SW) and 1-3 nonbond UB
- Developed coarse-grain description for water-polymer interactions
- Validated CG force field on hydrophilic and hydrophobic cases
- Built large-scale CG models for hydrophobic and hydrophilic cases
- Work in progress …

RECAP

Polymer Latex Systems studied

1) 60 BA/39 MMA/1 MAA//0.2 nDDM

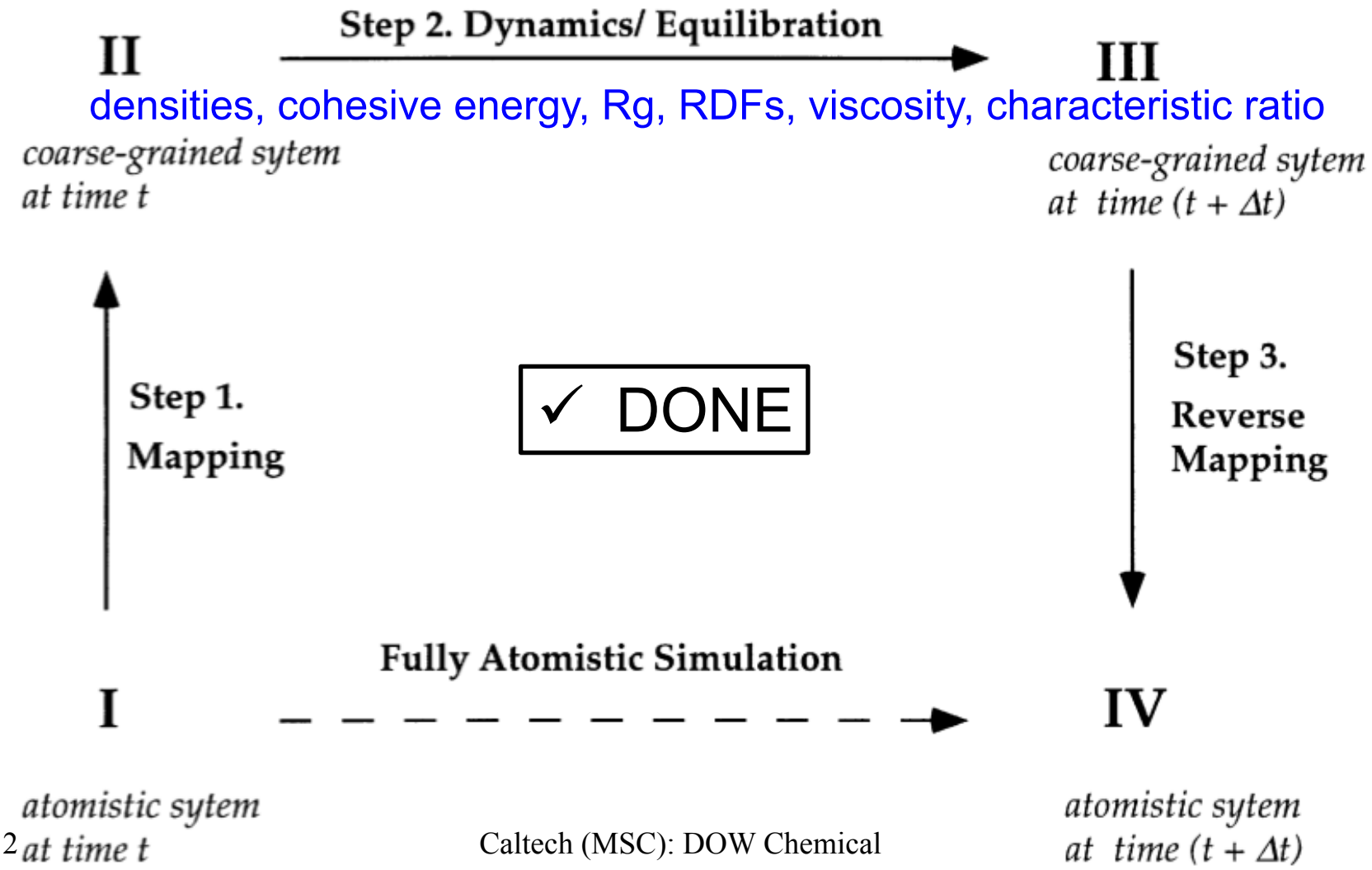
2) 40 BA/20 LMA/39 MMA/1 MAA//0.2 nDDM

3) 20 BA/40 LMA/39 MMA/1 MAA//0.2 nDDM

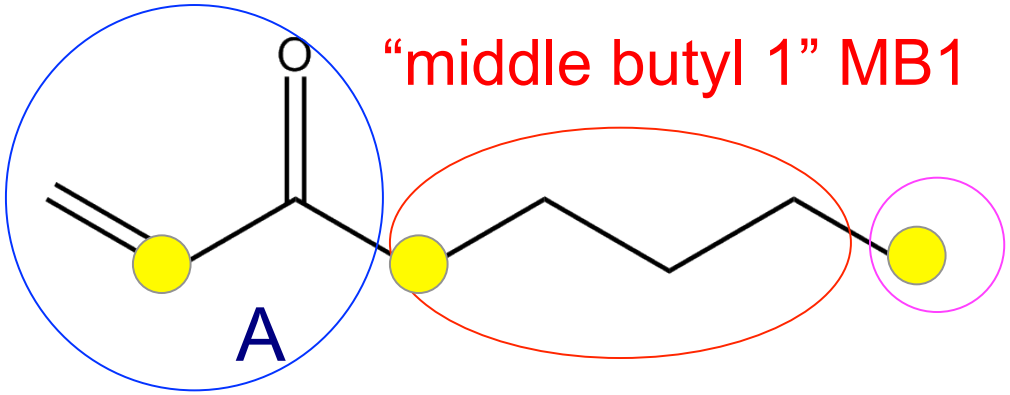
Recap on on why we needed CG model

- Bonds and angles have characteristic time scales $\tau \sim 10^{-13}$s and torsion $\tau \sim 10^{-11}$s
- A polymer coil $n_p < n_e$ (Rouse model) needs at least x n_p^2 to equilibrate, i.e. n_p^2/ω, and $n_p^3/(n_e\omega)$ for $n_p \geq n_e$ (reptation model)
- PE has $n_e \sim 100$, therefore relaxation time for a chain with $10^2 \leq n_p \leq 10^2$ is $\tau \sim 10^7$-10^4s
- For low temperatures (near T_g) relaxation time may be much larger (macroscopic)
- DOW polymers considerably more complicated than PE, may need additional equilibration effort

Atomistic to Coarse-grain forward/reverse mapping

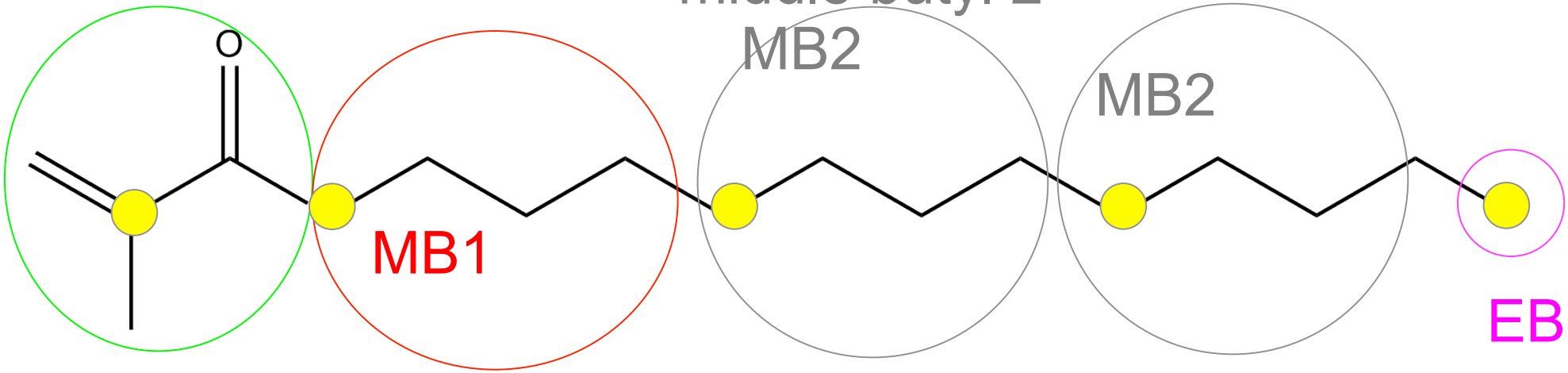


Current Bead Assignments



"middle butyl 1" MB1

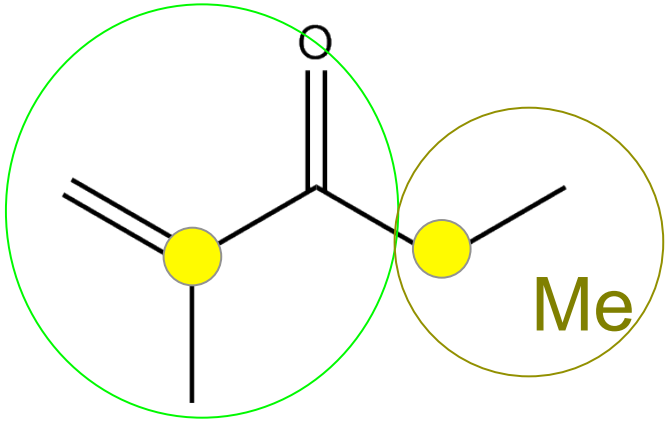
"end bead" EB

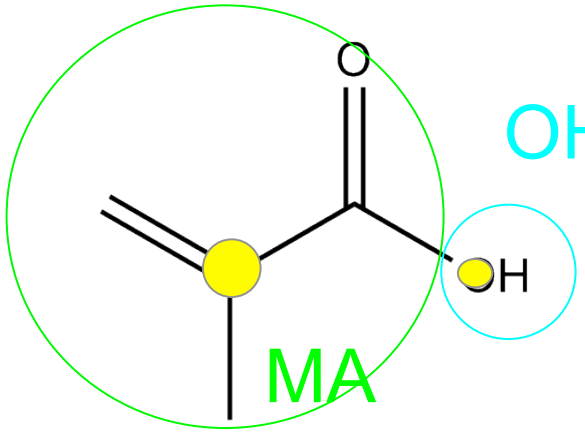


"middle butyl 2"
MB2

MB2

EB





Introduce EB so we have a bead every 4 atoms along the side chains

MA

CG FORCE FIELD AND MODEL UPDATES

Original Molinero-Goddard's coarse-grain water model

- 3 Morse parameters adjusted to reproduce experimental density, intermolecular energy, and diffusion coefficient of water at 300 K and 1 atm. Diffusion coefficient also considered (because of water transport in polymer film).

J. Phys. Chem. B **2004,** *108,* 1414-1427

bead type	R_0 (Å)	D_0 (kcal/mol)	α
W	3.77	1.15	8

water	ρ (g/cm^3)	*E* (kcal/mol)	*D* (10^{-5} cm^2/s)
W	0.97(2)	−10.2(1)	1.7
exptl	0.996[a]	−10.517[a]	2.4[b]

a) CRC Handbook of Chemistry and Physics, 81st ed.; Lide, D. R., *Ed.; CRC Press: Boca Raton, FL, 2000-2001.*
b) CODATA Key Values for Thermodynamics; Cox, J. D., Wagman, D., Medevyer, V., Eds.; Hemisphere Publishing Corp.: NY, 1984.

[1] J. Phys. Chem. B **2009,** *113,* 4008–4016

Changed water model (mW)

- Water and Si are dissimilar chemical substances with common physical properties. Their liquids display a T of maximum density, increased diffusivity on compression, and they form tetrahedral crystals and tetrahedral amorphous phases
- Molinero et al [1] found that it is not the nature of interactions but connectivity of molecules that determines structural and thermodynamic behavior of water
- Prevailing CG models use of long-ranged forces (electrostatics) to produce short-ranged (hydrogen-bonded) structure
- Molinero et al [1] developed a CG water model (mW) that is essentially an atom with intermediate tetrahedrality between C and Si. Showed mW was useful for wetting-drying transitions
- mW mimics the H-bonded structure of water through a nonbond angular dependent term that encourages tetrahedral configurations

mW: a Stillinger-Weber (SW) type monoatomic potential

- To “make water out of silicon”started from SW Si potential, i.e. tetrahedral coordination of atoms favored by a pairwise potential $v_2(r)$, a three- body term $v_3(r,\theta)$ that penalizes configurations with angles that are not tetrahedral, $v=v_2(r)+\lambda\, v_3(r,\theta)$, where λ tunes the strength of the tetrahedral penalty.

$$E = \sum_i \sum_{j>i} \varphi_2(r_{ij}) + \sum_i \sum_{j\neq i} \sum_{k>j} \varphi_3(r_{ij}, r_{ik}, \theta_{ijk})$$

$$\varphi_2(r) = A\varepsilon\left[B\left(\frac{\sigma}{r}\right)^p - \left(\frac{\sigma}{r}\right)^q\right]\exp\left(\frac{\sigma}{r - a\sigma}\right)$$

$$\varphi_3(r, s, \theta) = \lambda\varepsilon[\cos\theta - \cos\theta_o]^2\exp\left(\frac{\gamma\sigma}{r - a\sigma}\right)\exp\left(\frac{\gamma\sigma}{s - a\sigma}\right)$$

λ = 23.15, ε = 6.189 Kcal/mol and σ) 2.3925 Å; all other parameters are identical to silicon

Comparison of mW to other water models

	$T_{m\ HEX.\ ICE}$ (K)	ΔH_m (T_m) (kcal·mol^{-1})	ρ_{liquid} (T_m) (g·cm^{-3})	ρ_{ice} (T_m) (g·cm^{-3})	ρ_{liquid}(298 K) (g·cm^{-3})	ΔH_{vap} (298 K) (kcal·mol^{-1})	D (298 K) (10^{-5} cm^2·s^{-1})	γ_{LV} (300 K) mJ·m^{-2}	*TMD* (K)	$\rho_{liquid,\ MAX}$ (TMD) (g·cm^{-3})
exp	273.15	1.436	0.999	0.917	0.997	10.52	2.3	71.6	277	0.99997
mW	**274.6**	**1.26**	**1.001**	0.978	**0.997**	10.65	6.5	**66.0**	250	**1.003**
SPC	(191)	0.62	0.991	**0.934**	0.977	**10.56**	4.0	53.4	228	1.008
SPCE	(215)	0.74	1.007	0.950	0.999	10.76	**2.4**	61.3	241	1.012
TIP3P	(146)	0.30	1.017	0.947	0.986	10.17	5.3	49.5	182	1.038
TIP4P	232	1.05	1.002	0.940	1.001	10.65	3.9	54.7	253	1.008
TIP5P	(274)	1.75	0.987	0.982	0.999	10.46	2.6	52.3	**285**	0.989

Melting temperatures of hexagonal ice, densities of liquid, and crystal phase at coexistence and enthalpy of melting are from [1]. Parentheses enclosing a *T*m signal that the stable crystal is ice II, not hexagonal ice, for these models [2]. Diffusion coefficients *D* and density at 298 K are from [3] and [4]. Liquid-vacuum surface tensions are from [5]. TMD and its corresponding liquid density Fliquid,MAX are from ref [6]. Bold numbers signal the closest agreement with the experiment

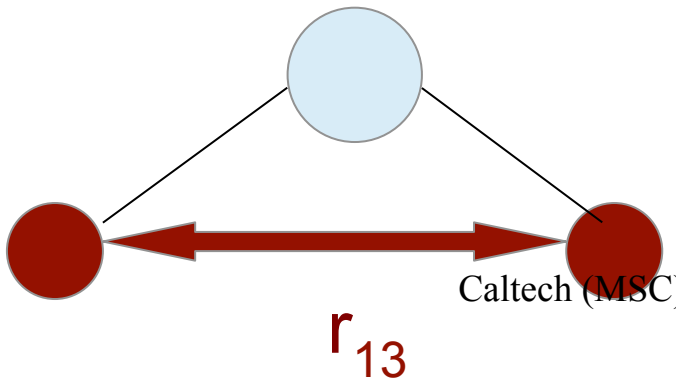
1. Vega, C.; Sanz, E.; Abascal, J. L. F. *J. Chem. Phys.* **2005**, *122*, 114507.
2. Vega, C.; Abascal, J. L. F.; Sanz, E.; MacDowell, L. G.; McBride, C. *J. Phys.: Condens. Matter* **2005**, *17*, S3283.
3. Wu, Y. J.; Tepper, H. L.; Voth, G. A. *J. Chem. Phys.* **2006**, *124*, 024503.
4. Abascal, J. L. F.; Vega, C. *J. Chem. Phys.* **2005**, *123*, 234505.
5. Chen, F.; Smith, P. E. *J. Chem. Phys.* **2007**, *126*, 221101.
6. Vega, C.; Abascal, J. L. F. *J. Chem. Phys.* **2005**, *123*, 144504.

CG FF Modification: Urey-Bradley Term

- Add repulsive 1-3 interactions to the force field by a harmonic Urey-Bradley term

$$E_{UB}(r_{13}) = K_{UB}(r_{13} - r_{UB})^2$$

where r_{13} is the distance between 1-3 pairs, K_{UB} is a force constant and r_{UB} is the equilibrium 1-3 distance. Use same fit procedure as for bonds



SUMMARY OF CG FORCE FIELD PARAMETERS FOR DOW LATEX

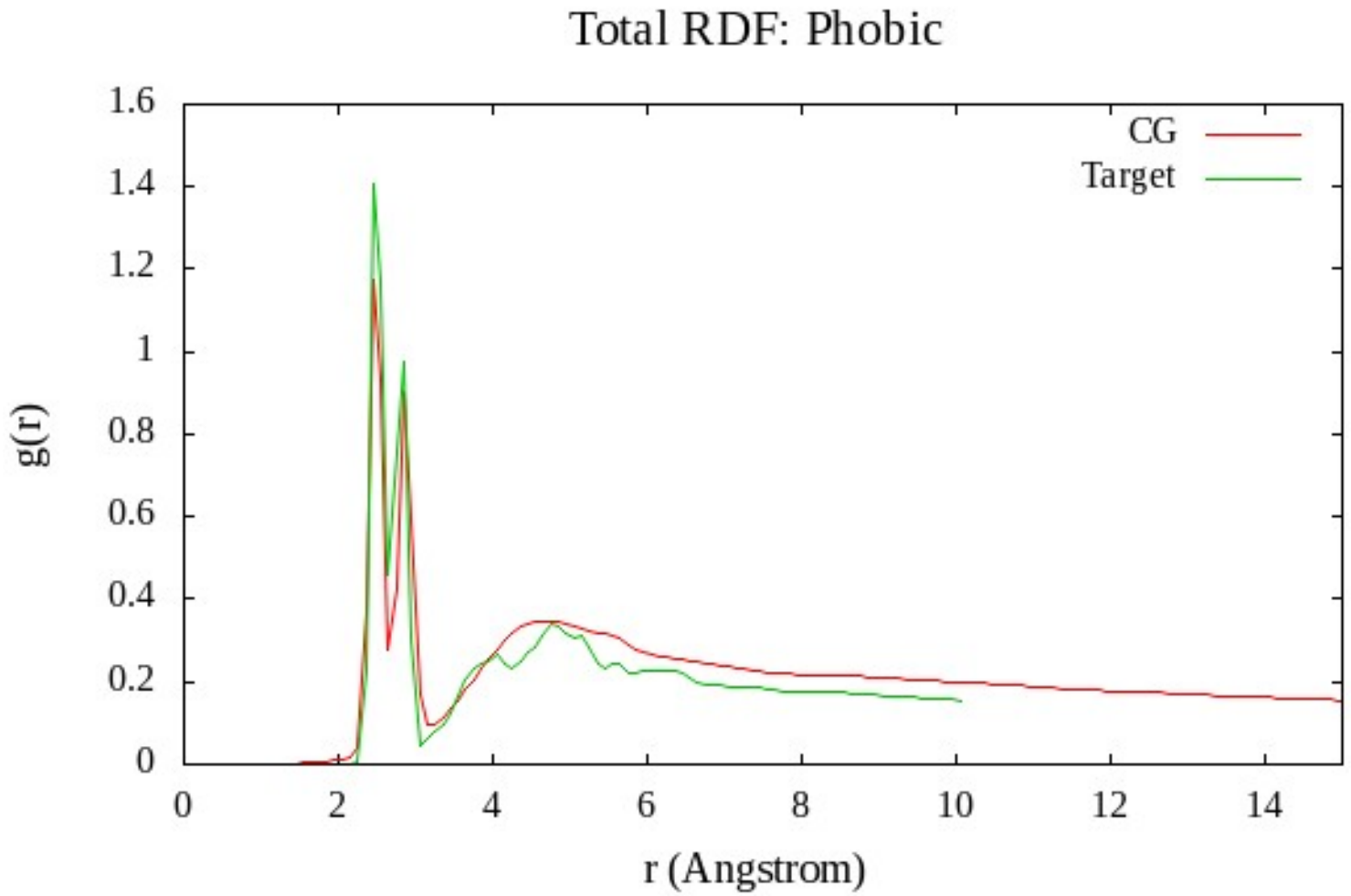
Coarse-Grain Parameters: Bond (1-2) and Urey-Bradley (1-3)

Bond Type	K	r0	UB Type	K_UB	r_UB
MA-Me	73.534	2.507	**A-A**	1.557	4.840
MA-MB1	61.947	2.492	**A-MA**	3.926	4.922
MB1-MB2	2.047	4.713	**A-EB**	4.962	7.048
EB-MB2	4.091	5.065	**A-MB1**	1.054	4.391
MB2-MB2	2.549	5.062	**A-Me**	6.154	3.633
MA-MA	89.374	2.863	**A-OH**	1.068	4.553
A-MA	76.578	2.772	**MA-MA**	4.329	5.050
MA-OH	109.422	2.519	**MA-MB2**	0.357	10.710
A-MB1	55.244	2.472	**MA-MB1**	1.938	4.289
A-A	83.514	2.706	**MA-Me**	1.765	4.097
MB1-EB	2.409	4.855	**MA-OH**	5.173	3.559
			EB-MB2	0.207	8.649
			MB1-MB2	0.339	8.870

Coarse-Grain Parameters: Polymer-Polymer and Polymer-Water Nonbond Interactions (Morse Potential)

	A-A	A-MB1	A-EB	A-MA	A-Me	A-OH	A-MB2
D	1.579	3.892	0.598	2.710	2.991	10.512	0.787
α	0.375	0.325	0.286	0.400	0.219	0.324	0.210
r0	10.771	10.718	10.187	11.224	9.155	6.710	11.878
	MB1-MB1	**MB1-EB**	**MB1-MA**	**MB1-Me**	**MB1-OH**	**MB1-MB2**	**EB-EB**
D	1.504	0.333	3.476	1.255	2.233	0.832	0.892
α	0.189	0.263	0.177	0.226	0.284	0.184	0.197
r0	11.744	11.800	10.790	10.772	7.466	13.303	12.840
	EB-MA	**EB-Me**	**EB-OH**	**EB-MB2**	**MA-MA**	**MA-Me**	**MA-OH**
D	0.711	0.478	0.889	0.381	1.830	2.325	10.551
α	0.263	0.282	0.369	0.269	0.187	0.222	0.188
r0	11.838	11.095	8.181	11.530	12.672	9.924	6.667
	MA-MB2	**Me-Me**	**Me-OH**	**Me-MB2**	**OH-OH**	**OH-MB2**	**MB2-MB2**
D	0.945	1.052	0.889	0.587	1.278	0.405	0.757
α	0.195	0.264	0.349	0.234	0.387	0.204	0.184
r0	12.883	10.383	8.181	11.871	6.854	12.282	13.696
	A-W	**MB1-W**	**EB-W**	**MA-W**	**Me-W**	**OH-W**	**MB2-W**
D	1.842	4.894	0.110	2.408	3.173	2.970	0.447
α	0.430	0.580	0.580	0.480	0.630	0.580	0.580
r0	7.816	9.046	9.891	8.910	6.856	5.919	7.630

CG MODEL VALIDATIONS AGAINST ATOMISTIC



Density for CG 2.2% lower than density for atomistic (0.81 for CG versus 0.82 for atomistic)

Phobic (dry) Rg

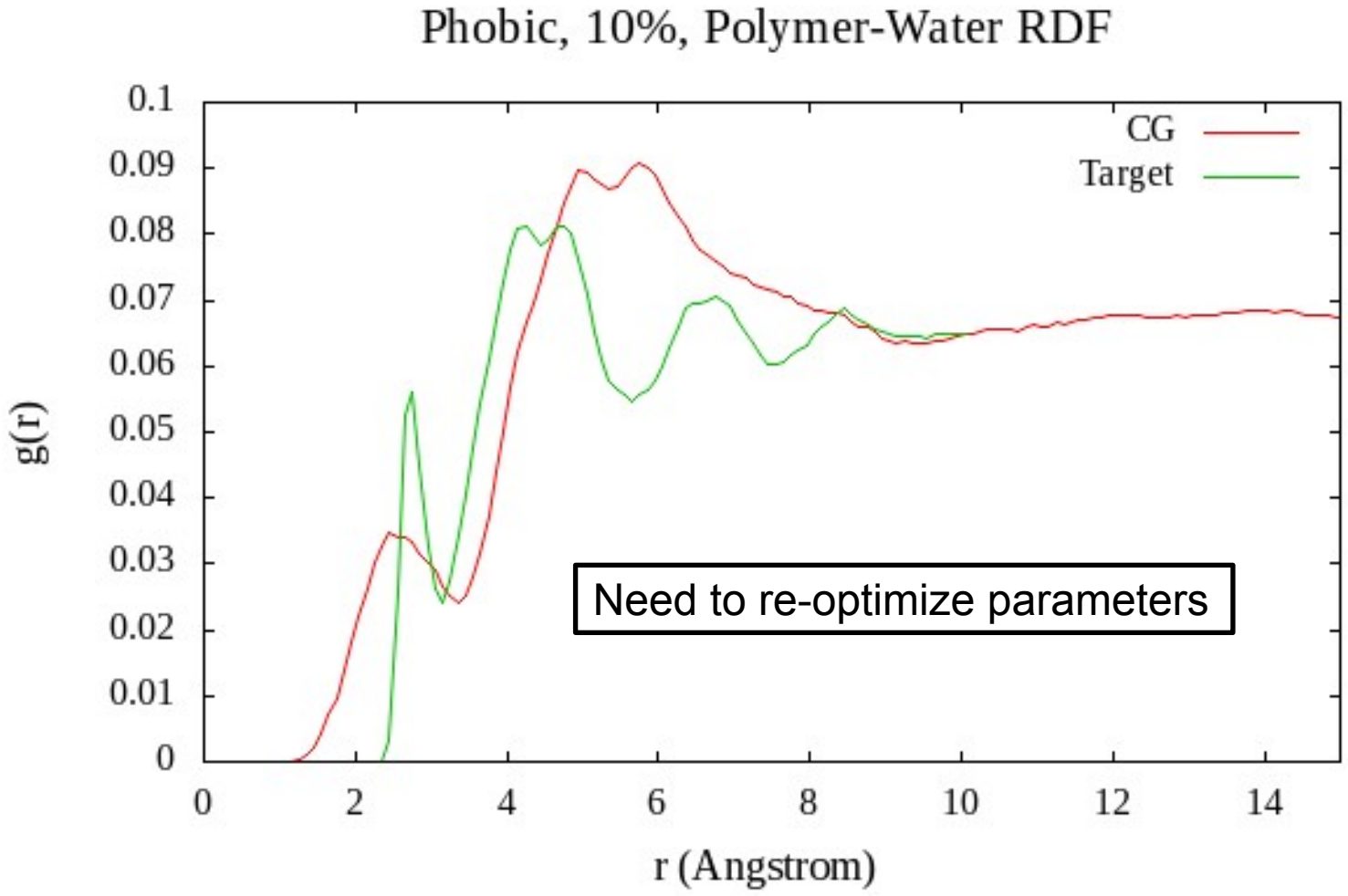
	Chain 1	Chain 2	Chain 3	Chain 4
CG	37.65	39.23	27.47	39.62
Atomistic	36.69	38.19	26.53	37.76

Phobic (10%) Rg

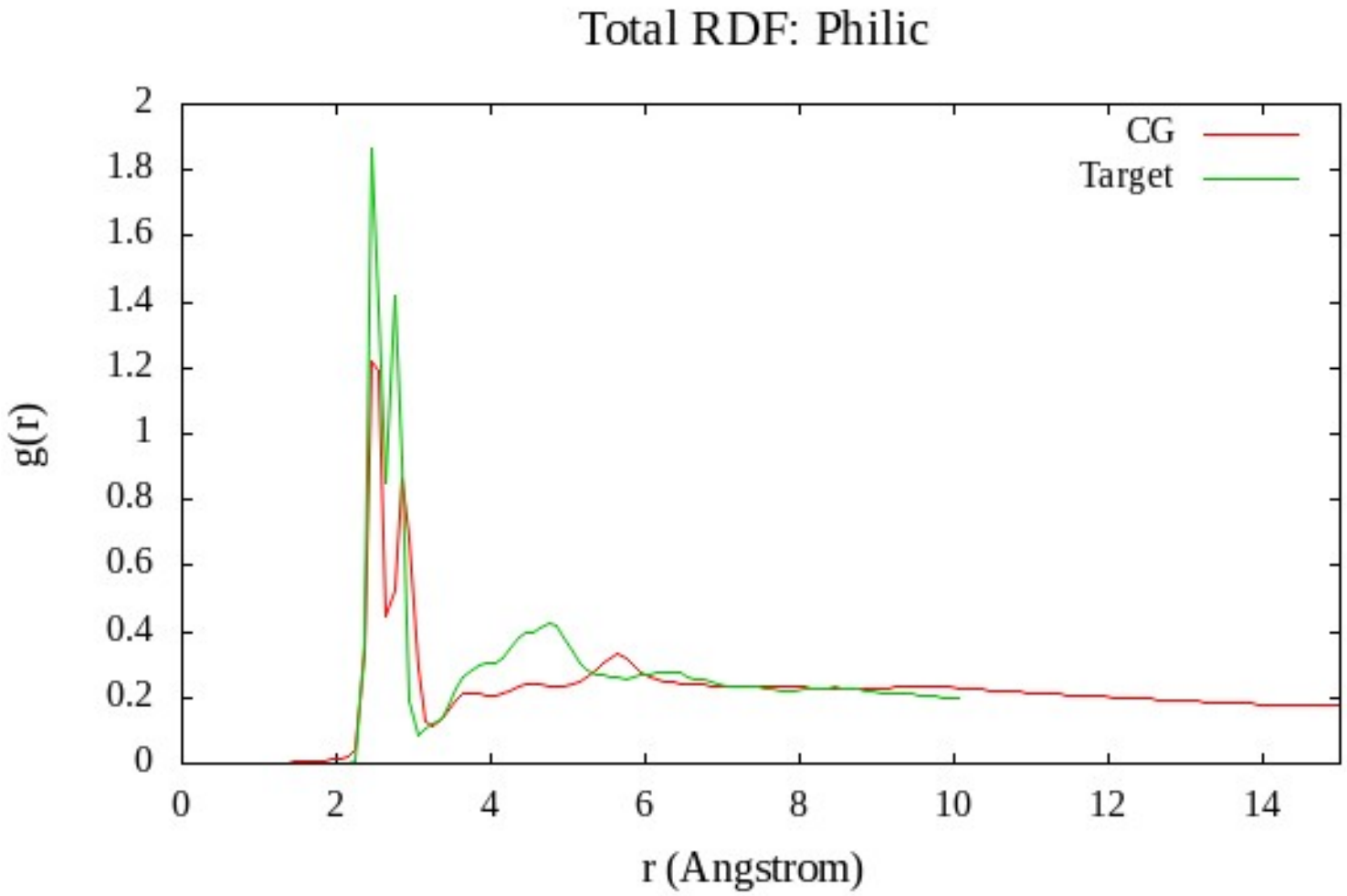
	Chain 1	Chain 2	Chain 3	Chain 4
CG	37.86	40.44	28.70	39.52
Atomistic	36.98	38.46	26.69	37.90

Philic (dry) Rg

	Chain 1	Chain 2	Chain 3	Chain 4
CG	31.36	31.68	27.56	43.34
Atomistic	29.38	29.69	27.54	41.84

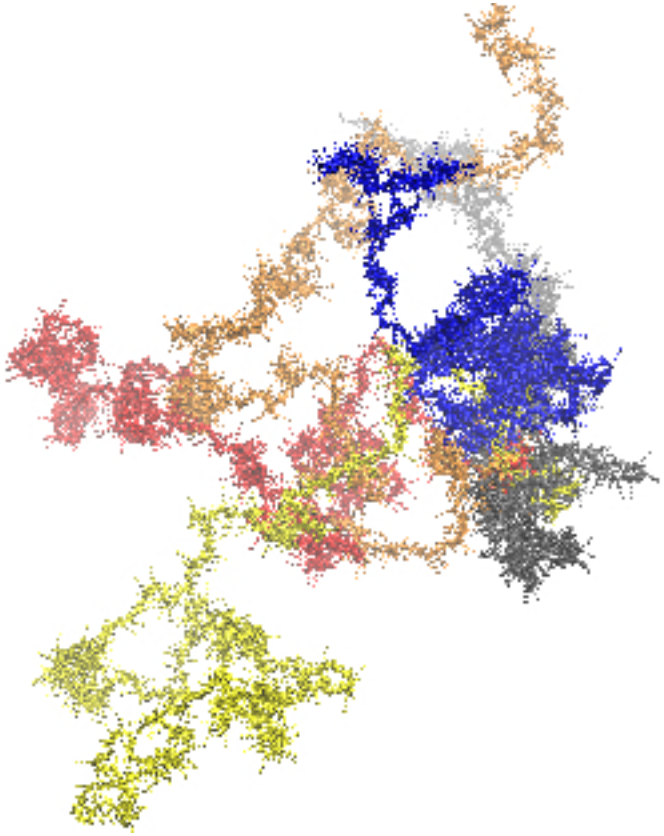


Density 1.6% lower than atomistic (swelling ratio consistent)

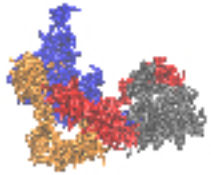


Density for CG 0.4% higher than atomistic

Coarse-grain versus Atomistic Modeling: Phobic system



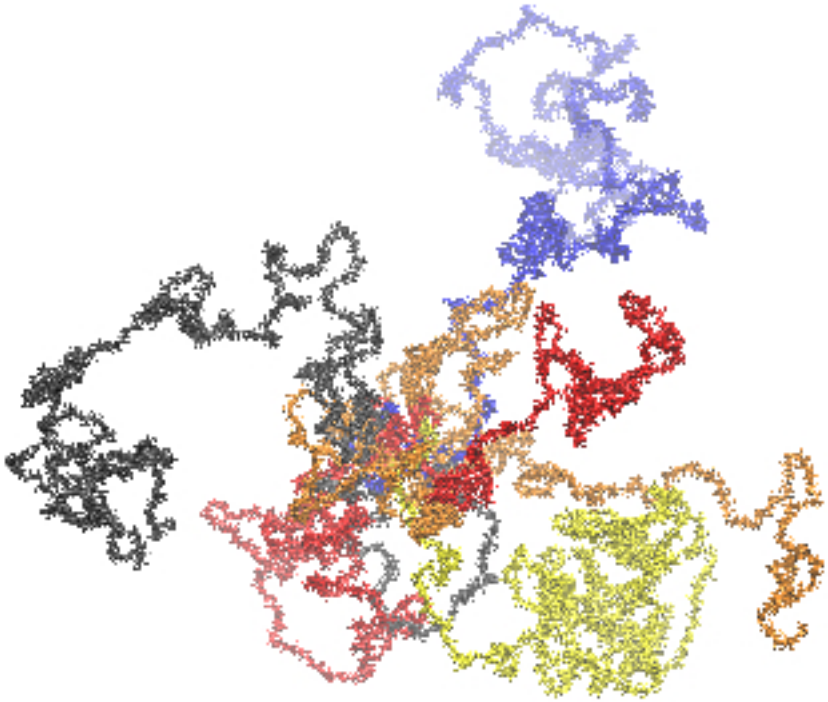
We can now do much larger systems over longer runs

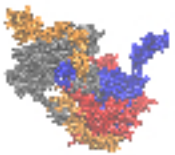


CG: 5 chains, DP = 3000
44,455 beads, 10fs timestep

Atomistic: 4 chains, DP = 300
28670 atoms, 1fs timestep

Coarse-grain versus Atomistic Modeling: Philic system





CG: 5 chains, DP = 3000
38,082 beads, 10fs timestep

Atomistic: 4 chains, DP = 300
21,983 atoms, 1fs timestep

Next …

- Use large-scale models for all cases to study the effect of water solvation cycles (i.e. evaporation+absorption) on structural transformations
- Use GCMC on CG models to detect changes in equilibrium water content after cycling (long CG-MD)
- Analyze intermediate structures
- Potential challenges: long equilibration/relaxation times (options: Accelerated CG-MD)