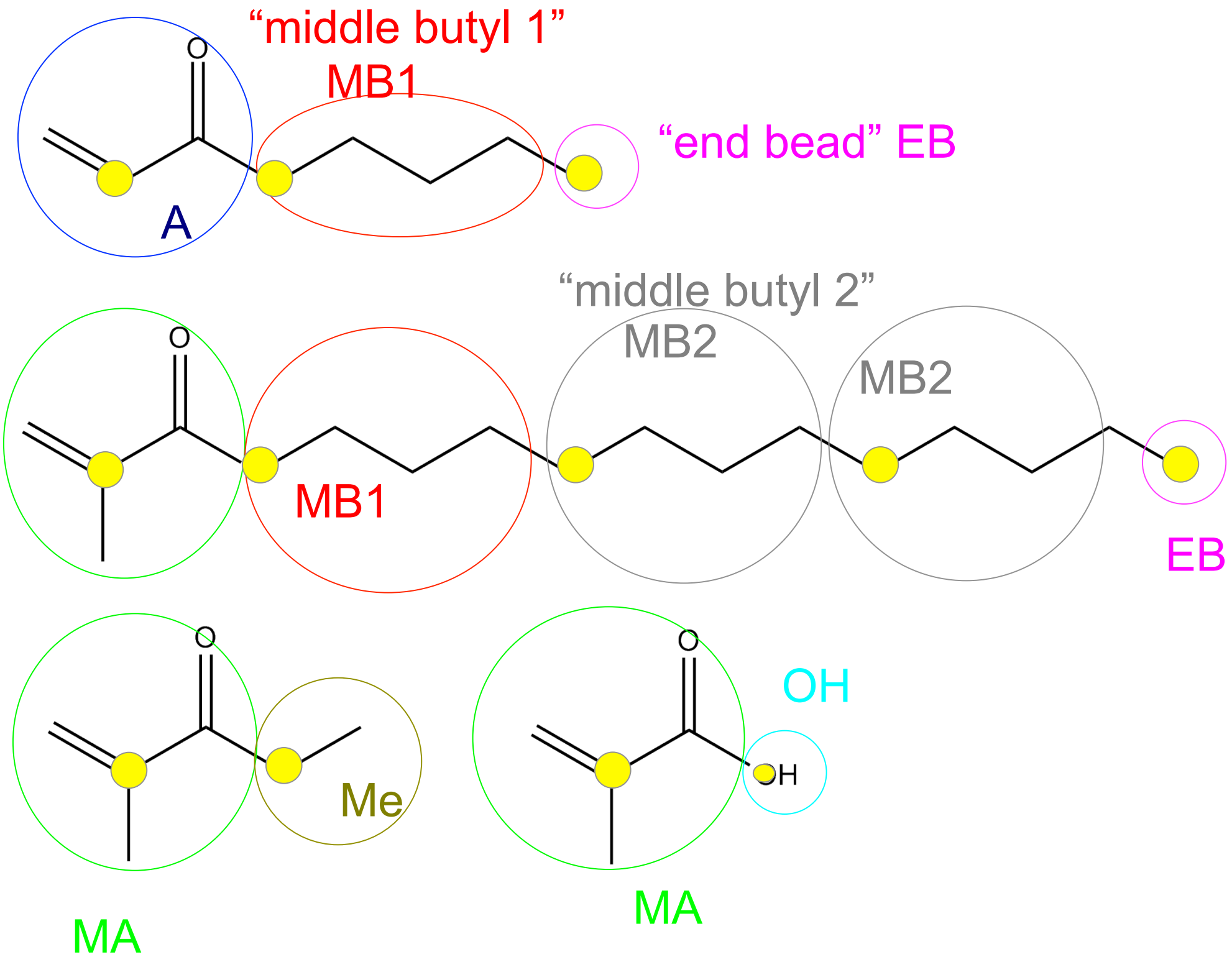
DOW-Caltech

12/6/2012


“middle butyl 1”
MB1
“end bead” EB
O
A
“middle butyl 2”
MB2
MB2
MB1
EB
O
Me
MA
O
OH
OH
MA

Summary of Modifications to CG FF

Remove Urey-Bradley term (simulations showed it had very little effect)

Refit nonbond parameters with shorter (10A) cutoffs

Fit separate polymer-polymer nonbond parameters for phobic, philic. Fit each case to its respective RDF (necessary to get correct density, structure) via genetic algorithm

Use water-polymer parameters straight from “spring” calculations (slide 4); no optimization

First Approximation to Nonbond Interactions

- Make atomistic models of each bead
  - 2 A beads shown left
- Consider them pairwise alone (in vacuum)
- Attach the centers of the beads by a spring (red arrow left) at a certain distance
- Do some dynamics (let beads move around). Calculate average net nonbond interaction between beads at the fixed spring distance
- Shorten spring, repeat ($0.75 < r < 30$ A)
- Fit a Morse function to E(r)
- Optimize parameters to give correct total and partial distribution functions (genetic algorithm)

Coarse-Grain Parameters: Bond (1-2)

Bond Type	K	r0
MA-Me	73.534	2.507
MA-MB1	61.947	2.492
MB1-MB2	2.047	4.713
EB-MB2	4.091	5.065
MB2-MB2	2.549	5.062
MA-MA	89.374	2.863
A-MA	76.578	2.772
MA-OH	109.422	2.519
A-MB1	55.244	2.472
A-A	83.514	2.706
MB1-EB	2.409	4.855

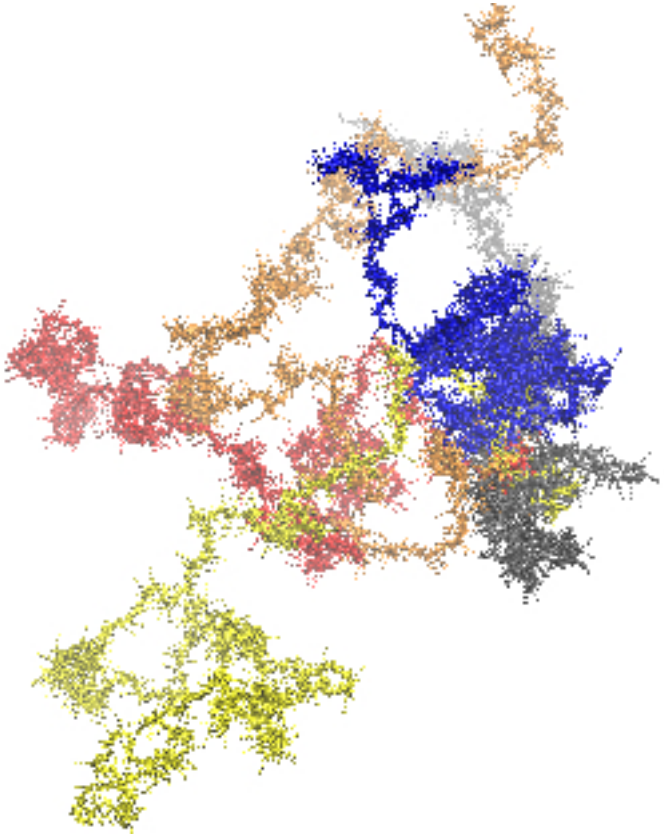
Coarse-Grain Parameters: Polymer-Polymer for Phobic (Morse Potential)

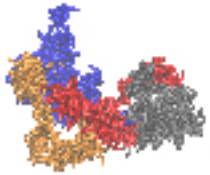
	A-A	A-MB1	A-EB	A-MA	A-Me	A-OH	A-MB2
D	0.71604	1.04719	1.08090	2.34742	0.88781	28.37712	1.45580
α	1.02535	1.86598	1.12633	2.26192	2.36577	0.40997	1.47176
r0	6.37085	5.30797	4.45610	4.50869	4.88589	2.56688	3.53001
	MB1-MB1	**MB1-EB**	**MB1-MA**	**MB1-Me**	**MB1-OH**	**MB1-MB2**	**EB-EB**
D	0.02668	0.000004	2.07183	0.00756	0.111771	0.00125	0.00004
α	1.02669	2.65552	1.19196	1.67879	2.40114	2.00946	3.26715
r0	3.93748	4.79364	3.94293	8.90981	4.76278	5.83608	5.93878
	EB-MA	**EB-Me**	**EB-OH**	**EB-MB2**	**MA-MA**	**MA-Me**	**MA-OH**
D	1.15628	0.00428	0.00076	0.00036	4.19944	1.43461	19.90436
α	1.14629	2.50045	2.43605	3.24620	0.53061	1.28800	0.42935
r0	5.27837	5.52156	6.36716	4.75927	3.64588	3.71336	3.33133
	MA-MB2	**Me-Me**	**Me-OH**	**Me-MB2**	**OH-OH**	**OH-MB2**	**MB2-MB2**
D	1.54776	3.93E-2	8.87E-1	6.07E-1	1.21E-2	4.13E-2	5.67E-1
α	1.17607	1.37015	2.89465	1.84133	2.28496	2.67778	1.26988
r0	7.09493	6.75477	4.40895	4.14551	4.13427	4.32086	6.56236

Water-Polymer Nonbond Parameters

	A-W	MB1-W	EB-W	MA-W	Me-W	OH-W	MB2-W
D	1.27E-006	3.27985	0.00018	9.42E-7	7.81E-9	6.31029	0.00001
α	3.03569	3.26571	3.19533	2.99605	3.56872	1.91161	3.19026
r0	5.13924	2.53969	4.19894	5.23491	5.23188	2.71191	4.74360

Coarse-grain versus Atomistic Modeling: Phobic system

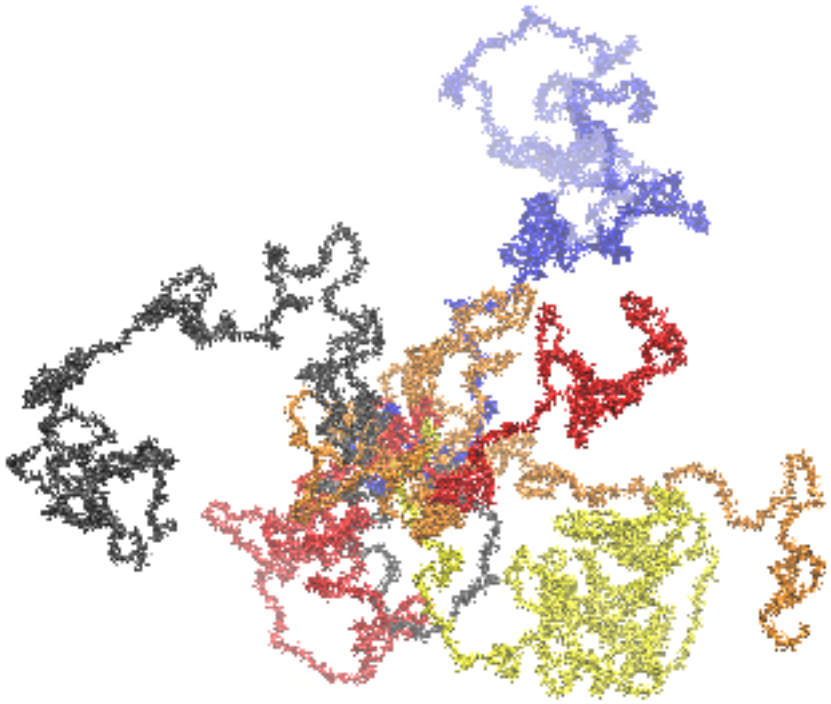


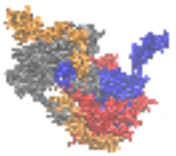


CG: 5 chains, DP = 3000
44,455 beads, 10fs timestep

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

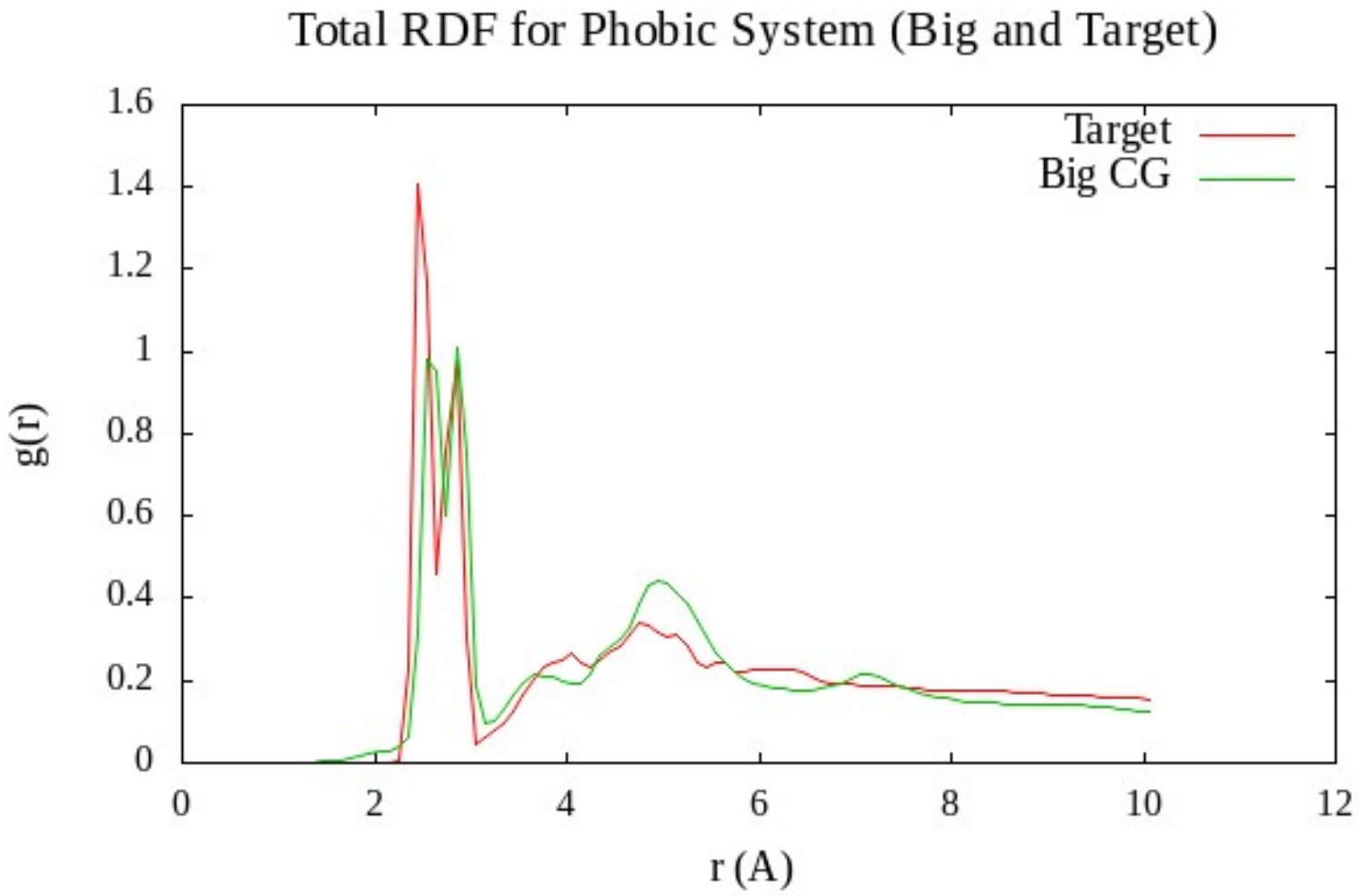
Atomistic: 4 chains, DP = 300
21,983 atoms, 1fs timestep

Tentative Preliminary Results

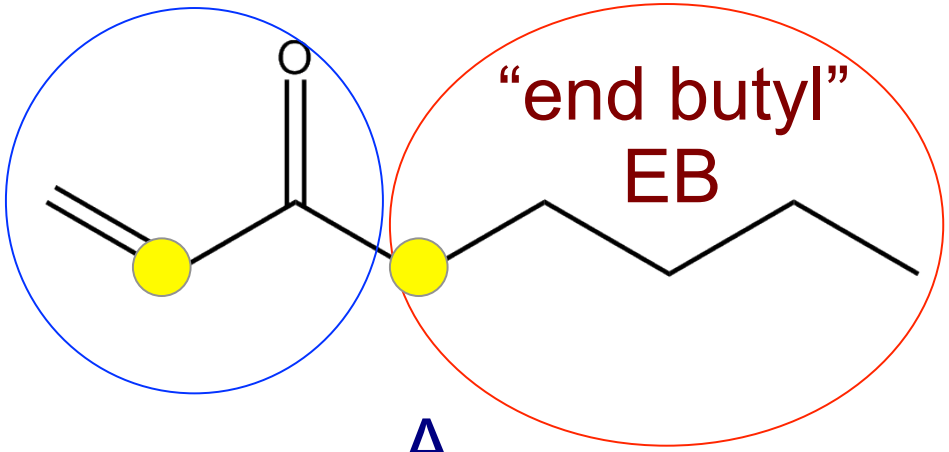
Large system for phobic: Density ~0.95

Large system for philic: Still equilibrating

Both systems are still running.



This result is still very preliminary, but so far it looks like our force field reproduces the target structure quite well in the large system

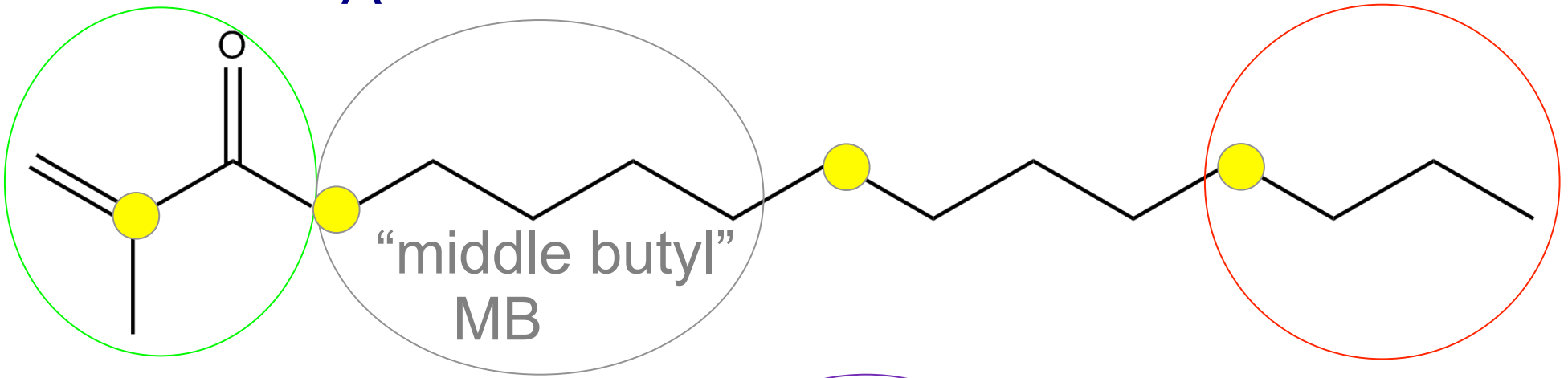


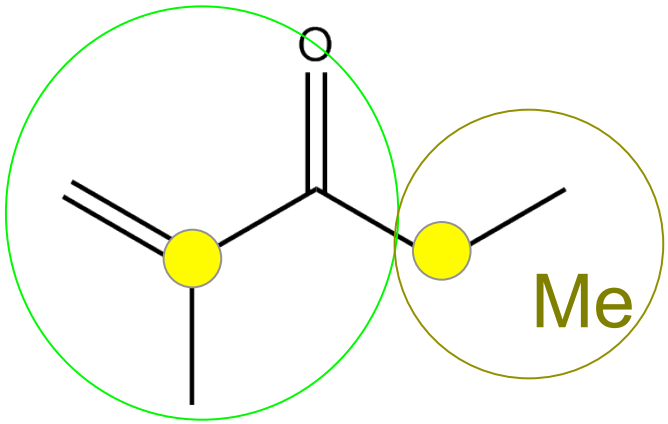
New bead placements

A

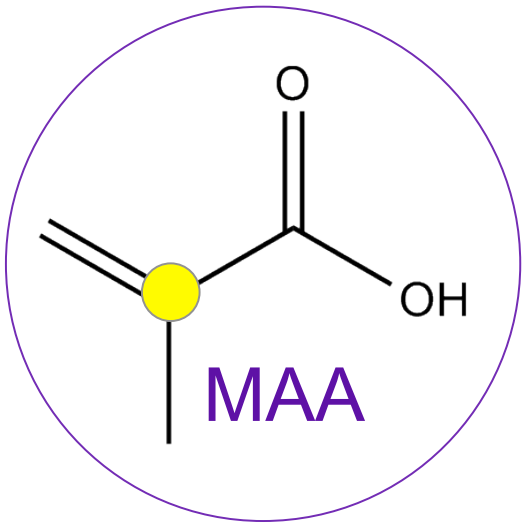
“middle butyl 2”
MB2

“end butyl 1”
EB1





MA



Introduce MB2 and EB1 to account for different masses (EB and MB now include an oxygen)

Bond coefficient (harmonic)

$$E_{bond} = K(r - r_0)^2$$

4	5	73.5344	2.50651
4	2	61.9467	2.49174
4	4	89.3737	2.86326
1	4	76.5779	2.77158
4	6	109.422	2.5192
1	2	55.2436	2.47211
1	1	83.5141	2.70619
2	3	2.4094	4.8548

Non-bond parameters (Morse)

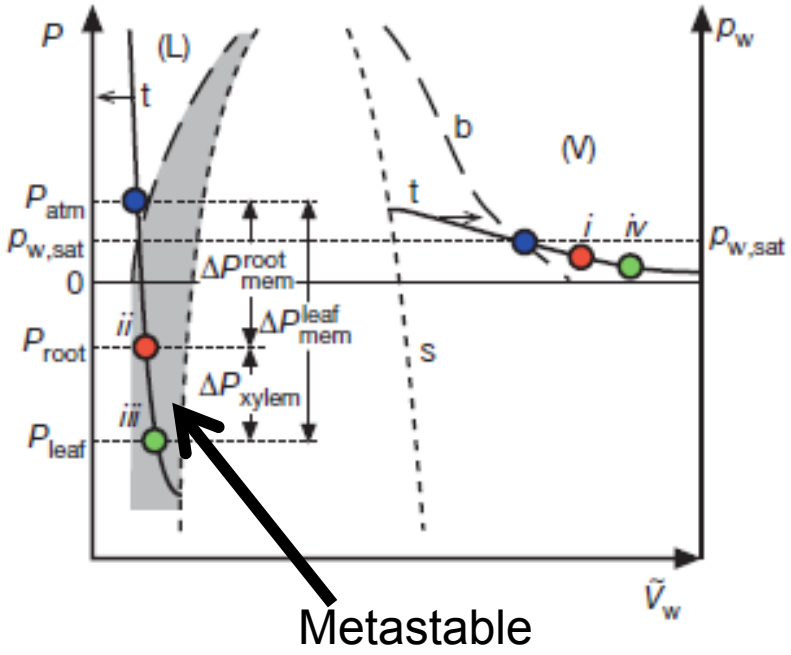
$$E_{nonbond} = D\left(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}\right)$$

Type 1	Type 2	D (kcal/ mol)	α (A^{-1})	r_0 (Angstrom)
1	1	0.271815	0.998861	4.111223
1	2	0.648291	0.546075	8.616739
1	3	0.711131	1.023365	5.411805
1	4	3.807914	1.598482	1.949401
1	5	0.847399	2.820771	5.011325
1	6	35.77229	0.699786	2.085994
1	7	2.677882	2.239555	3.630308
2	2	0.039274	1.609902	2.021534
2	3	0.000004	1.380162	3.806448
2	4	0.660678	1.588386	3.476449
2	5	0.007617	1.226333	5.534197

Non-bond parameters (Morse)

$$E_{nonbond} = D\left(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}\right)$$

Type 1	Type 2	D (kcal/ mol)	α (A^{-1})	r_0 (Angstrom)
2	6	0.163596	2.133694	2.981971
2	7	0.000757	1.80412	6.953686
3	3	0.000014	2.641531	6.290063
3	4	2.054321	0.574267	2.163598
3	5	0.004577	3.486313	4.69669
3	6	0.001231	1.985388	7.062118
3	7	0.000299	2.539202	7.217903
4	4	3.50484	0.396974	2.745834
4	5	1.867358	1.477765	2.369911
4	6	21.7325	0.487019	3.89987
4	7	1.208406	1.405692	6.003881

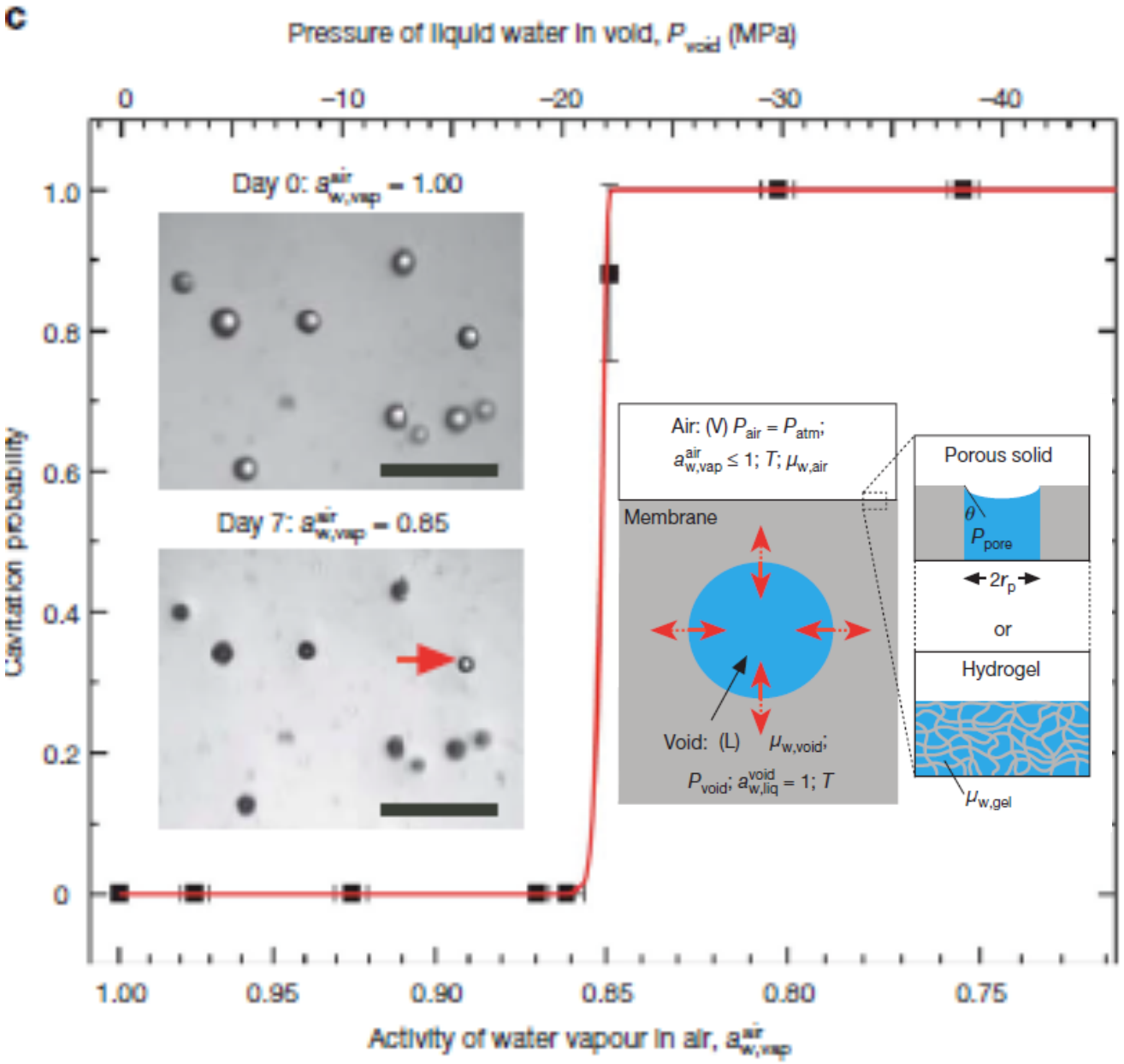


Could confinement of water in polymers lead to cavitation, hence degradation?

Transduction of subsaturation in the vapor phase of water into negative pressures in the liquid phase

Engineering demonstration

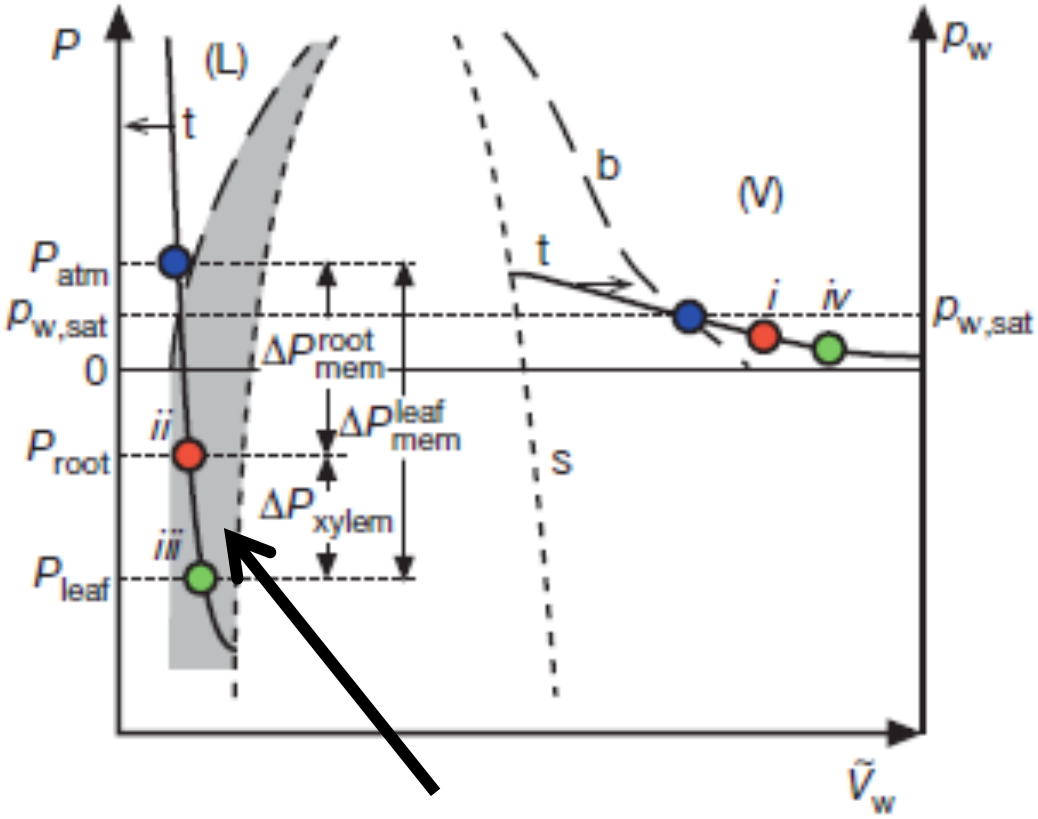
1. Made liquid-filled shells of poly(hydroxyethyl methacrylate)
2. Allowed the shells to equilibrate with water vapors
3. Observed that some shells collapsed
4. Suggests that equilibration led to lowering of pressuring within the confined liquid
5. Sharp transition at water vapor of activity 0.85



PV curve for water (IAPWS)

When P_{root}, P_{leaf} < $p_{w,sat}$ liquid water is mechanically stable and thermodynamically metastable with respect to the vapor state.

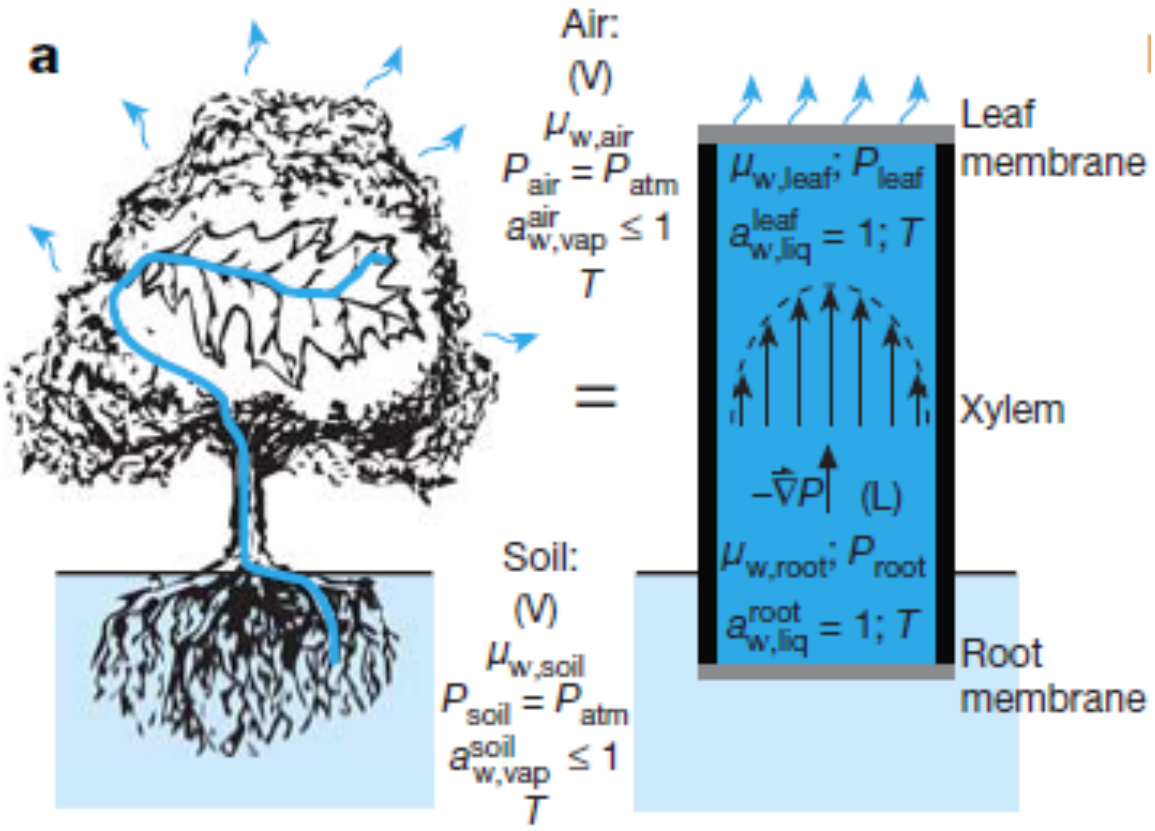
Entrapped liquid on equilibration with a substurated vapor might cavitate



Stroock & Co-workers, Nature (2008) Vol 455

Wagner & Prub, The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use, JCP (2002), Vol. 31, No. 2,

How does water climb up in a tree?



Stroock & Co-workers, Nature (2008) Vol 45

Xylem and leaves have water at negative pressure ~-10 MPa

$$\Delta P^{root}_{mem} = P_{soil} - P_{root} = -\frac{RT}{\tilde{V}_{w,liq}} \ln\left(a^{soil}_{w,vap}\right) \text{ and}$$

$$\Delta P^{leaf}_{mem} = P_{air} - P_{leaf} = -\frac{RT}{\tilde{V}_{w,liq}} \ln\left(a^{air}_{w,vap}\right)$$

$$P_{root} - P_{leaf} = \Delta P^{leaf}_{mem} - \Delta P^{root}_{mem} = \left(RT / \tilde{V}_{w,liq}\right) \ln\left(a^{soil}_{w,vap} / a^{air}_{w,vap}\right)$$

Directions

1. Plants can regenerate their tissues and polymers can not.

2. Cavitation could be responsible for degradation of polymer exposed to rain

3. Can we predict a PV curve for negative pressures?

4. Can we capture the process of cavitation as a function of sub-saturated vapor pressure?

5. Goddard-Molinero Water model vs New Molinero model

Ongoing Work

Finish big phobic, big philic, check results

Test water-polymer parameters, moving toward GCMC calculations for equilibrium water content and wetting/drying simulations