Systematic Coarse-Graining of DOW Latex Polymer Compositions

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Polymer Latex Systems

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

Coarsening Preferences

- Choose bead positions that lead to rigid bonds
- Single peaked versus double peaked distribution
- Gaussian with height/width=bond strength

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- Peak multiplicity leads to bond/angle potential interdependence
- Use spherical beads to avoid anisotropic potentials

Rationale

- The original bead placement resulted in multiple peaks and several bead bond distributions (see next slide)
- As discussed previously, unimodal distributions lend themselves more easily to coarse-graining therefore we optimized the bead placement with this in mind (as much as possible)
- We expect to retain reversibility







Red curve shows MA-Me bond distribution with methyl bead placed on the ester oxygen (red dot in inset).

Green curve shows MA-Me bond distribution with methyl bead placed on methyl carbon (green dot in inset)

With the methyl bead on the ester oxygen we get a unimodal distribution (as opposed to the bimodal distribution resulting from placing the bead on the methyl carbon).

Rotation around the bond between the carbonyl carbon and ester oxygen (red bead) leads to more than one possible MA-Me distance with the bead on the methyl carbon. This is not the case with the bead on the oxygen.



Coarse-Grain

Hydrophobic

4-CHAIN SYSTEM





Atoms: 28670 Bonds: 28666 Angles: 54924 Dihedrals: 77742



Beads: 3508 Bonds: 3504

New FF Parameters

- Abandon numerical potentials fitted from Inverted Boltzmann approach. They are less transferable once parameterized. Parameters may loose physical interpretation.
- Fit harmonic bond coefficients to bond distributions
- Get approximate nonbond (van der Waals) parameters by pairwise interactions between atomistic models of beads

Process

- 1. Bond coefficients obtained from harmonic fits into RDFs of beads after overlaying them on atomistic trajectory
- 2. Non-bond coefficients: (Pair coefficients)
 - i. bead-bead interactions as a function of distance,
 - ii. fitting Morse potential form into energydistance plots
- 3. Geometry optimization of CG model
- 4. Equilibration: NVT at 298 @1.5 ns

Nonbond Interactions (1st Approximation)

- Make atomistic models of each bead
 - 2 (Acrylate) beads shown left
- Consider them pairwise alone (in vacuum)
- Attach the bead centers by a spring at a certain distance
- Perform dynamics (let beads move around).
 Calculate average net nonbond interaction between beads at the fixed spring distance
- Shorten spring, repeat (3 < r < 30 A)
- Fit a Morse function to E(r)

AAAAA

9/10/2012

• Optimize parameters to give correct total and partial distribution functions (genetic algorithm)

60 BA/39 MMA/1 MAA//0.2 nDDM HYDROPHOBIC SYSTEM

AMA Nonbond Interaction



Example: Nonbond interaction between acrylate (A), methacrylate (MA) beads. Simulation data shown in red and fitted Morse function shown in green



MA-MA bonds, on the left, are considered to be single-peaked, and a force constant and equilibrium length are extracted by fitting to the dominant peak.

MB2-MB2 bonds, however, are bimodal (this is the result of the flexibility of atomistic torsions). We take the equilibrium length to be the weighted average of the r_0 's for the 2 individual peaks, then fit a force constant that is sufficiently soft to allow the coarse-grain model to easily access both states.

Final Bond Parameters

	$E_{bond} = K (r - r_0)^2$		
Bond Type	K (kcal/molA^2)	r0 (Angstrom)	
MA-Me	73.5344	2.50651	
MA-MB1	61.9467	2.49174	
MB1-MB2	2.04732	4.71252	
EB-MB2	4.09068	5.06526	
MB2-MB2	2.54868	5.06188	
MA-MA	89.3737	2.86326	
A-MA	76.5779	2.77158	
MA-OH	109.422	2.5192	
A-MB1	55.2436	2.47211	
A-A	83.5141	2.70619	
^{9/10/2012} MB1-EB	2.4094	4.8548	

Final Non-bond Parameters

$E_{nonbond} = D \left(e^{-2\alpha (r-r_0)} - 2 e^{-\alpha (r-r_0)} \right)$				
Type 1	Type 2	D (kcal/mol)	α (A^-1)	r0 (Angstrom)
Α	А	1.49115	0.206708	10.4389
A	MB1	4.12461	0.099224	13.4438
A	EB	0.597959	0.285537	10.1868
Α	MA	2.02994	0.185143	12.2426
Α	Me	2.99059	0.21937	9.15507
Α	OH	10.4385	0.222356	5.82179
Α	MB2	0.786927	0.210339	11.8778
MB1	MB1	1.50395	0.188889	11.7436
MB1	EB	0.333488	0.263122	11.8004
MB1	MA	3.47598	0.177119	10.7904
MB1	Me	1.25504	0.226193	10.7719
MB1	OH	2.23324	0.284068	7.46621
MB1	MB2	0.831736	0.18429	13.3028

EB	EB	0.891558	0.19747	12.8402
EB	MA	0.710576	0.263094	11.8382
EB	Me	0.478015	0.282301	11.0951
EB	OH	0.889122	0.369268	8.18064
EB	MB2	0.381042	0.268824	11.5301
MA	MA	1.82978	0.186752	12.6715
MA	Me	2.32492	0.222158	9.92364
MA	OH	10.5513	0.188079	6.66691
MA	MB2	0.945118	0.194971	12.8829
Me	Me	1.05174	0.264216	10.3829
Me	OH	0.889122	0.349268	8.18064
Me	MB2	0.586796	0.233504	11.8708
OH	OH	1.27828	0.3867	6.85388
OH	MB2	0.404699	0.204194	12.2823
MB2	MB2	0.757056	0.1835	13.6963

FF Validation

- Start with bead system corresponding to equilibrated atomistic structure.
- Minimize \rightarrow NVT \rightarrow NPT_V equilibration \rightarrow NVT_V for distributions
- Compare total and partial RDFs from coarsegrain FF to target (from 'piggy-backing' beads on atomistic trajectory
- Compare Rg's to atomistic
- Mechanical properties



Temperature vs Time

Coarse grain system stable and equilibrated at 298K



Total RDF in excellent agreement with atomistic target.

Density from CG model: 0.97 g/cc, compared to 0.83 from atomistic.

Radius of Gyration (Rg)

 Chain 1
 Chain 2
 Chain 3
 Chain 4

 Atomistic
 36.69167
 38.1882932
 26.5311218
 37.7594496

 CG
 37.2852298
 36.2846686
 26.6426326
 38.9552494

Radii of gyration from coarse-grained model agrees with those from atomistic model within 5%





Molinero-Goddard's coarsegrain water model

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

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).

bead type	R_0 (Å)	D_0 (kcal/mol) α	
_ <i>W</i>	3.77	1.15	5 8
water	ρ (g/cm ³)	E (kcal/mol)	$D (10^{-5} \text{ cm}^2/\text{s})$
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) **29**DATA Key Values for Thermodynamics; Cox, J. D., Wagman, D., Medeyev, V., Eds.; Hemisphere Publishing Corp.: NY, 1984.

Need Water-Polymer Non-Bond

- Start with our 1-bead water model (described by water-water Morse parameters)
- Derive water-polymer parameters by mixing rules

$$D_{ij} = \sqrt{D_i D_j}$$
$$R_{ij} = \sqrt{R_i R_j}$$
$$\alpha_{ij} = \frac{1}{2} (\alpha_i + \alpha_j)$$

 Optimize using genetic algorithm (fit polymer-water RDF to target from atomistic data)

20 BA/40 LMA/39 MMA/1 MAA//0.2 nDDM HYDROPHILIC CASE











r (Ang strom)



Other interactions are relatively minor

What's coming Thermodynamic properties

- 1. Validate polymer-water parameters
- Confirm mechanical properties for bulk MMA using coarse-grain model and predict properties of 3-systems
- 3. Confirm T-dependent properties over a range of 260-350K, and adjust model to T-dependence
- Compare thermodynamics (free-energy and entropy) through 40%wt water. Will use GCMC and Deposit with E and R insertion criterion

What's coming **Polymer-water surface interactions**

- 1. Build a system of larger coarse-grain entangled colloidal clusters in water
- 2. Evaporate water slowly applying isotropic compression
- 3. Study interparticle surface interactions as system is dehydrated (e.g. coallesence, structure changes, etc.)
- 4. Re-hydrate (fast) and repeat 2-5 (same evaporation)