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# **REPORT: DOW 6-27-2012**

## From last time (6-29-2012)



MSC-DOW 2

# Note on PE 1C Per Bead Bond Distance

The distance in question here is the bead-bead distance, that is, the distance between the centers of mass of successive CH2 units. While it should be very close to the C-C distance, it is not the case that it must be the same. Using an H-C-H angle of 109 degrees and a C-H bond distance of 1.09 Angstrom (the Dreiding parameters), one can easily show that the center of mass is displaced by a distance of 0.087 Angstroms from the carbon atom. If the displacements of the centers of mass of 2 successive units are both in the bead-bead bond direction, we would get a bead-bead distance of 1.54 + 2\*0.087 ~1.7 Angstroms. In general, this will not be the case directions, so we should find a bead-bead distance of slightly less than 1.7, which is exactly what we see (~1.67).



# Atomistic to Coarse-grain forward/reverse mapping



# Effective pair potential: iterative Boltzmann inversion

Simulate the (finer-grain) atomistic system

Find RDF (*g*<sub>ref</sub>(*r*)) between coarse-grain centers

Use  $F_w$  as first guess potential:  $F_0(r) = -k_B T \log(g_{ref}(r))$ Determine RDF:  $g_0(r)$ 

Iterate:  $F_i(r) = F_{i-1}(r) + k_B T \log\left(\frac{g_{i-1}(r)}{g_{ref}(r)}\right)$ Determine RDF:  $g_i(r)$ 

Converged when  $g_i(r)$  is close to  $g_{ref}(r)$ 

Question: Is it possible to fit a simple analytical function, like Morse or Harmonic potential, to map the complex interactions of coarse-grained beads @Dow polymers?

Answer: No, the interactions are too complex to be captured by simple potentials. Even though piece-wise fitting could address this problem, but it might be computationally expensive. Piece-wise fitting may capture the complex interactions of beads in Dow polymers, but different derivatives across interfaces would drive the computational cost up, defeating the premise of coarse-graining.

Thus, an alternative method involving a 'Boltzman inversion' method has been applied.

# Methodology: Iterative Boltzmann Inversion

- Make initial guess for potential by inverting radial distribution function g (from atomistic data)
- Use this potential to run dynamics, calculate a new RDF
- Calculate a corrected potential based on the difference between this new RDF and the target.
- Iteratively repeat this process until some convergence criteria are met
- Typically this is done on the total RDF (any atom in the center and any atom as the neighbor)

# Methodology: Iterative Boltzmann Inversion

- Our approach: use this method for every pairwise
  interaction
- So, consider the A-EB RDF, A-MA, etc.
- This approach allows us computational simplicity (only one set of forces/energies) while maintaining the underlying chemistry (bond/angle distributions)
- First task: validate this approach with a small "toy" system, then move on to the full latex systems

#### Inter-Bead RDF and Boltzmann Inversion Distributions



- An array of distances, Free Energies, and Forces for every possible inter-bead interaction can serve as a Coarse-Grain "force-field."

- Used this approach for the small test model.

#### Atomistic

Coarse-Grain



Blue: Ima White: ba Red: maa Yellow: mma



Yellow: EB Red: MB Blue: A Tan: EB Cyan: MA Large Cyan: MAA White; Me

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#### Atomistic

#### **Coarse-Grain**



- Comparison of Atomistic and Coarse-Grain RDFs between all atoms/beads in the respective model.

- The fine detail ( r < 2 Angstroms ) is not seen in the Coarse-Grain model  $^{18}$ 







































































# Force-Field Validation

- Use distributions from previous slides as pairwise potentials
- Run dynamics (NPT at 298K)
- 5 fs timestep (compared to 1fs for atomistic calculations)
- 1 iteration of iterative Boltzmann inversion
- Calculate RDF's and compare to target (next slides)



A-MAA RDF

A-MB RDF









#### Total RDF



Excellent agreement of total RDF and almost all pairwise RDFs





We use energy versus time as a test of the stability of our force field. While there are some large fluctuations, overall the stability looks reasonable

# Comparing to atomistic trajectory



# Putting Away the Toys...

- Next steps: Apply this methodology to real systems
- Again, validate for one case (phobic)

☑ This allows us to work out the bugs in our method with one case (saving a lot of wasted cpu hours)

Solution State State

 The following slides show the target RDFs for each pairwise interactions









