Systematic Coarse-Graining of Polymers

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Atomistic to Coarse-grain forward/reverse mapping



Justification

- Bonds and angles have characteristic time scales τ~10⁻¹³s and torsion τ~10⁻¹¹s
- 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 $n_p \ge n_e$ (reptation model)
- PE has $n_e \sim 100$, therefore relaxation time for a chain with $10^2 \le n_p \le 10^2$ is $\tau \sim 10^7 10^4$ s
- For low temperatures (near T_g) relaxation time may be much larger (macroscopic)
- DOW polymers considerably more complicated than PE

Motivation

- Reduce the number of degrees of freedom
- Reduce the number of iterations
- Reduce the total cost per iteration (potential)
- Increase the time scale of simulations
- Smoother potential energy surface (artifact)

Exact coarse-graining

• Given a potential V at a state point NpT $\rho(R) = \exp\left(-\frac{V(R)}{LR}\right)$

$$= \exp\left(-\frac{k_B T}{k_B T}\right)_{NpT}$$

• Split system in "wanted" R_w and "unwanted" R_u coordinates

$$\rho_{w}(R_{w}) = \int_{R_{u},(NpT)} \rho(R) = \int_{R_{u},(NpT)} \exp\left(-\frac{V(R)}{k_{B}T}\right)$$

• where R_w can be any set of coordinates: specific atoms, centers of mass or geometric center of atomic groups, distances between atoms, etc.

Exact coarsening

• Convert ρ_w to a free energy F_w

$$F_{w,NpT}(R_w) = -k_B T \log \rho_w(R_w)$$

= $-k_B T \log \int_{R_u,(NpT)} \exp\left(-\frac{V(R)}{k_B T}\right)$
= $V_w(R_w) - k_B T \log \int_{R_u,(NpT)} \exp\left(-\frac{V(R) - V_w(R_w)}{k_B T}\right)$

- Strictly speaking, $F_{w,NpT}$ only valid at $N_0p_0T_0$, e.g. $N_0 = \{N_w = 100, N_u = 1000\}$. $F_{w,NpT} \Rightarrow N_w/N_u = 1/10$
- $F_{w,NpT}$ is NOT a potential so virial "pressure" \neq thermodynamic pressure, and we simulate at $\langle V \rangle_{NpT}$

n-body expansion

 Expand F_w in n-body terms for all w particles, w/ out loss of generality

 $F_{w,NpT}(R_w) = \sum_{i < j} F_2(r_{ij}) + \sum_{i < j < k} F_3(r_{ij}, r_{ik}, r_{jk}) + \sum_{i < j < k < l} F_4(r_{ij}, r_{ik}, r_{jk}, r_{jk}, r_{jl}, r_{jl}, r_{kl}) + \dots$

• Summing over all particles, and using the infinite dilution approximation (**p**otential of **m**ean **f**orce)

$$F_{w,NpT}(R_w) \approx \sum_{i < j} F_2(r_{ij}) + \sum_{i < j < k} F_3(r_{ij}, r_{ik}, r_{jk}) + \sum_{i < j < k < j} F_4(r_{ij}, r_{ik}, r_{jk}, r_{jk}, r_{jl}, r_{jl}) + \dots$$

• Leads to an effective PMF: $F_{w,NpT}(R_w) \approx \sum_{i=1}^{N} F_p(r_{ij})$



$$PMF(r) = \int_{\infty}^{r} \langle F_{Constraint} \rangle_{S} \, dS$$

PMF determined from constrained inter-bead distance and monitoring the constraint force during MD

Effective pair potential: iterative Boltzmann inversion

- Simulate the (finer-grain) atomistic system
- Find RDF $(g_{ref}(r))$ between coarse-grain centers
- Use F_w as first guess potential: $F_0(r) = -k_B T \log(g_{ref}(r))$
- Determine RDF: g₀(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 $g_{ref}(r)$

Graphic summary of iterative Boltzmann method



Coarsening polymers

- Exact coarsening
- Non-bonded: use iterative Boltzmann inversion
- Bonded: use direct Boltzmann inversion
- May be complicated by multicomponent and solvent interactions, i.e. multiple target RDFs

Lyubartsev and Laaksonen, Phys. Rev. E 52, 3730 (1995)

• Alternative: use inverse Monte Carlo method

Linking atomistic and coarsegrain models: 3 choices

I. We want to reproduce: Structural Props

- Distribution of geometries
 - Distances, angles, dihedrals, principal R_g, center of mass between chains, etc.
- Penalty function for automatic fits, e.g. inverted Boltzmann, RDFs

$$f(p) = \int_{0}^{cutoff} w(r) \left[RDF(r,p) - RDF_{target}(r) \right]^{2} dr$$

• where p is the parameter vector

Linking atomistic and coarsegrain models: 3 choices

II. Degree of coarsening

- How many atoms collected into one super-atom
 - Incorrect number may lead to artifacts (e.g. melts near an interface)



Linking atomistic and coarsegrain models: 3 choices

III. Mapping of super-atoms

- Coincident with real atoms or others, e.g. center of mass or geometrical center of grouped atoms
- Choice leads to different coarse-grain potentials
- Still, can be parameterized to reproduce structure



Diphenyl carbonate Coarse-grain CM RDFs: 3-site, 2-site and 1-site models



Preferences

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



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

Polyetheylene coarse-grain model example

Terminal (T=CH₂-CH₂-CH₂) and middle (M=CH₂-CH₂-CH₂-CH₂) beads



Interaction	Form	Parameters	
Bond	$E = \frac{1}{2}k_{\rm b}(r_{\rm b} - r_0)^2$	$k_{\rm b} = 6.96 ({\rm TT}), k_{\rm b} = 6.16$	
		(1 ^M , MM) kcal/mol A ² $r_0 = 3.65$ (TM), $r_0=3.64$ (MM) Å	
Angle	$E = \frac{1}{2}k_{\theta}(\theta - \theta_0)^2$	$k_{\theta} = 1.09 \text{ (TMT)}, k_{\theta} = 1.19$	
		(1 MM, MMM) kcal/mol $\theta_0 = 175.5 (TMT), \theta_0 = 175$	
		$(TMM), \theta_0 = 173 (TMM) \text{ degree}$	
Nonbonded	$E = \left(\frac{27\varepsilon}{4}\right) \left \left(\frac{\sigma}{r}\right)^9 - \left(\frac{\sigma}{r}\right)^6 \right $	ε = 0.469 (TT), $ε = 0.444$ (TM),	
		$\varepsilon = 0.42$ (MM) kcal/mol	
		$\sigma = 4.585 (TT), \sigma = 4.5455 (TM),$	
		σ = 4.506 (MM) Å	
		$r_{\rm c} = 15$ Å (truncation radius)	

Polyetheylene coarse-grain model example

Total energy (Dreiding)

 $U_{Total} = \sum_{i} \left[U_{bond}^{CG}(r_i, T) + U_{angle}^{CG}(\theta_i, T) + U_{torsions}^{CG}(\varphi_i, T) \right] + \sum_{i < j} U_{nb}^{CG}(r_{ij}, T)$ $U_x^{CG}(x, T) = -K_B T \ln P_x^{CG}(x, T) \text{ where } x = bond, angle, torsion$

Non-bonds have higher entropic contributions at >T

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 I atm.
 Diffusion coefficient also considered (because of water transport in polymer film).

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 exptl	0.97(2) 0.996 ^a	-10.2(1) -10.517^{a}	1.7 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., Medeyev, V., Eds.; Hemisphere Publishing Corp.: NY, 1984.

Coarse-Graining Polyethylene



Ex: A small segment of a polyethylene chain Atomistic model contains all carbons and hydrogens (gray and white). Coarse grain model contains only beads (green)

- Suppose each bead contains 2 carbon atoms
- Rather than modeling 2 carbons and 4 (or 5) hydrogens, consider one particle with mass 28 (or 29)
- Place bead at center of mass of group of atoms it represents

Coarse-Graining Polyethylene



Ex: A small segment of a polyethylene chain Atomistic model contains all carbons and hydrogens (gray and white). Coarse grain model contains only beads (green)

- Suppose each bead contains 3 carbon atoms
- Rather than modeling 3 carbons and 6 (or 7) hydrogens, consider one particle with mass 42 (or 43)
- Place bead at center of mass of group of atoms it represents

Representing Atomistic Dynamics With Coarse-Grained Particles

- Atomistic simulations of polyethylene for 1 or 3 chains of 300-mers (with or without water)
- Use standard CED polymer equilibration method (heat while expanding, contract while cooling, relax volume)
- Further NVT dynamics on equilibrated structure
- From this trajectory, calculate bead positions at each frame (every 500ps) (movie)
- Fit bonds, angles, dihedrals, nonbond interactions to atomistic energy expression via distributions (described on following slides)

Fitting Coarse-Grained Parameters

- Note: The distributions showed no sensitivity to the number of chains or the presence or absence of water; thus, only one set of distributions is shown in the following slides.
- We see multiple peaks in the distributions because the distance, angle, and dihedral between beads can vary with the conformation of the underlying atomistic structure











Non-bond Interactions (2 C Per Bead)

- Get van der Waals interaction of beads from that between atomistic models of two beads
 - e.g.: Consider the net pairwise interaction between two ethane molecules (representing beads of 2 carbons each)
 Attach centers of mass of the two
- Attach centers of mass of the two molecules by a spring, do dynamics to let the molecules adjust to each other.
- Slowly decrease distance between beads
- Fit a Morse function to E(r)





Fitting to one Morse function gives us a potential that is too repulsive at small r and at 10 < r < 6 Angstrom. It is also too attractive (by ~1 kcal/mol) for r > 10 Angstrom



Fitting 2 Morse functions, one in the repulsive region (say r < 6, green plot) and one for the attractive region (say 6 < r < 20, blue plot) gives a much better overall fit. Of course, we must enforce continuity of the potential.

Non-bond Interactions (2C Per Bead)

- Get van der Waals interaction of beads from that between bead, water
 - e.g.: Consider the net pairwise interaction between an ethane molecule and a water
- Attach centers of mass of the two molecules by a spring, do dynamics to let the molecules adjust to each other.
- Slowly decrease distance between beads
- Fit a Morse function to E(r)





Same problem with a single Morse function for the water-bead nonbond interactions



And again fitting to 2 Morse functions gives a much better fit

Coarse-Graining DOW Latex

- Choose bead assignment (see next slide)
 - 6 bead types: Acrylate, Methacrylate, "End butyl",
 "Middle butyl", methyl, methacrylic acid
- Map coarse-grained model onto atomistic trajectory (NVT for equilibrated system)
- Extract distribution of bead bonds, angles, dihedrals



Atomistic

Coarse-Grain

Hydrophobic system





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



Beads: 2916 Bonds: 2912 Angles: 4615 Dihedrals: 5600



We may ultimately use the RDF to validate or fit our coarse-grain model.

g(r)

As expected, fine detail (r < 2 Angstroms) is lost going from atomistic \rightarrow coarse grain



Bond Distributions

- Make histograms of bond lengths for each bond type (shown in red on following slides)
- Want a smooth potential, so use boxcar averaging (green)
 - "Rough" potential \rightarrow large derivatives \rightarrow large forces \rightarrow unstable dynamics









Raw distribution

Smooth distribution



Angles

- 46 angle types
 - For practical purposes when writing the code, ABC angles are treated distinctly from CBA angles
- The following slides show a few representative cases
- The important thing to note here is that these do not look like the distributions arising from a harmonic angle potential
- Use Boltzmann inversion here as well









Dihedrals

- 140 angle types
- The following slides show a few representative cases
- The important thing to note here is that these do not look like the distributions arising from a standard dihedral potential
- Use Boltzmann inversion here as well
- Note that almost all possible values of the dihedrals are sampled.



Smooth distribution



Non-bond Interactions

- Get van der Waals interaction of beads from that between atomistic models of two beads
- Attach atoms representing bead location by a spring, do dynamics to let the molecules adjust to each other.
- Slowly decrease distance between beads
- Fit a Morse function to E(r)

MA-MA Nonbond Interactions



MA-MA Nonbond Interactions



Ongoing Work

- All bond, angle, dihedral potentials prepared
- All nonbond coefficients (piecewise, 2 Morse functions) fit
- Currently testing force field (compare density, rg, rdf to atomistic)