Systematic Coarse-Graining and Concurrent Multiresolution Simulation of Molecular Liquids

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9 June 2005

IMA Workshop: “Effective Theories for Materials and Macromolecules”
Systematic molecular coarse-graining:
  Bulk bisphenol-A polycarbonate (BPA-PC)

Inhomogeneously resolved coarse-graining:
  BPA-PC at interfaces

*Concurrent multiresolution simulation of molecular liquids*
  Dual resolution NVT ensemble
The Tension Between Specificity and Generality in Polymer Molecular Simulation

**Bead-Spring Chains**: Bonded and nonbonded degrees of freedom: GENERIC; RELATIVELY EASY TO EQUILIBRATE

**Bisphenol-A Polycarbonate** (BPA-PC): An atomically resolved system (~50K atoms); SPECIFIC; DIFFICULT TO EQUILIBRATE

\[
U_{bs}(\mathbf{R}) = \sum_{i}^{NM} U_{bs}^{b}(X_i) + U_{bs}^{nb}(\mathbf{R})
\]
The Compromise: Systematic Molecular Coarse-Graining

Bisphenol-A Polycarbonate

Important considerations
- mapping points
- potentials
Generalized Coarse-Graining: “Mapping”

$r^N$ Fine-scale degrees of freedom

$R^M$ Coarse-grained (“CG,” “collective”) degrees of freedom: “Mapping Points”

$M$ mapping matrix

\[
\begin{pmatrix}
R_1 \\
R_2 \\
R_3 \\
\vdots \\
R_M
\end{pmatrix}_{M \times 1} =
\begin{pmatrix}
M_{1,1} & M_{1,2} & M_{1,3} & \cdots & \cdots & \cdots & M_{1,N} \\
M_{2,1} & M_{2,2} & M_{2,3} & \cdots & \cdots & \cdots & M_{2,N} \\
M_{3,1} & M_{3,2} & M_{3,3} & \cdots & \cdots & \cdots & M_{3,N} \\
\vdots & \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\
M_{M,1} & M_{M,2} & M_{M,3} & \cdots & \cdots & \cdots & M_{M,N}
\end{pmatrix}_{M \times N} \times
\begin{pmatrix}
\mathbf{r}_1 \\
\mathbf{r}_2 \\
\mathbf{r}_3 \\
\vdots \\
\mathbf{r}_N
\end{pmatrix}_{N \times 1}
\]

Configuration $\mathbf{r}$ “satisfies a mapping $R$” if $R - Mr = 0$
Linking the Statistics at Different Scales: Boltzmann Inversion

Probability of observing CG configuration $\mathbf{R}^M$ is an ensemble average:

$$P(\mathbf{R}^M) = \frac{1}{Z} \int d\mathbf{r}^N \exp \left[-\beta U(\mathbf{r}^N)\right] \prod_{i=1}^{M} \delta \left( \sum_{j=1}^{N} M_{ij} r_j - R_i \right)$$

$$= \frac{1}{"Z_{CG"}} \exp \left[-\beta U_{CG}(\mathbf{R}^M)\right]$$

Defines CG “potential” $U_{CG}$ (actually a restricted free energy)

$$\beta U_{CG}(\mathbf{R}^M) = -\ln \left[P(\mathbf{R}^M)\right] + \beta U_{\text{ref}}$$

$U_{CG}(\mathbf{R}^M)$ can be generated by Monte Carlo simulation on an ensemble spanned by fine-scale configurations $\mathbf{r}^N$ [an evaluation of $P(\mathbf{R}^M)$]
Determining $U_{CG}$: Reasonable Assumption #1

Bonded and nonbonded variables are uncorrelated $\Rightarrow$ Probability distribution factorizes

$$P(R^M) = \left[ \prod_{i=1}^{N_m} P_i^c (X_i) \right] P^p \left( R_{cm}^{N_m}, \Omega_i^{N_m} \right)$$

- Probability of observing molecule $i$ in conformation $X_i$
- Probability of observing molecule configuration of center-of-mass positions & molecular orientations
Determining $U_{CG}$: Reasonable Assumption #2

Intramolecular bonded CG degrees of freedom $X$ are not (strongly) correlated

→ Intramolecular bonded coarse-grained probability distributions factorize

$$\beta U_{CG}^b(X) = -\ln \left[ P^b(X) \right]$$

$$P^b(X) \equiv P_1(X_1)P_2(X_2)P_3(X_3)\ldots$$

→ Intramolecular CG potential has a useful additive form:

$$U_{CG}^b(X) = \sum_i U_i^b(X_i)$$
Determining $U_{CG}$: Reasonable Assumption #3

Nonbonded correlations are constructed primarily of independent pairwise contributions

Nonbonded potential energy is pairwise additive

$U_{CG}^{nb}(R^M) = \sum_{i}^{M} \sum_{j \neq i}^{M} U_{ij}^{nb}(R_{ij})$

An example: The Weeks-Chandler-Andersen Potential

$U^{wca}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} + \frac{1}{4} \right] ; r < 2^{1/6}\sigma$
Practical Matters: Systematic Molecular Coarse Graining of Bisphenol-A Polycarbonate (BPA-PC)

Atomically resolved intramolecular bonded degrees of freedom are backbone torsions, $\phi_i$.

Total potential:

$$U_{CG}(\mathbf{R}^M) = U_{CG}^b(\mathbf{X}) + U_{CG}^{nb}(\mathbf{R}^N)$$

Tasks:
1. Generate atomically resolved potential $U(\phi)$: \textit{ab initio} calculations
2. Construct a mapping scheme
3. Generate intramolecular coarse-grained potential $U(\mathbf{X})$ at $T = 570$ K using MC sampling and Boltzmann inversion
4. Nonbonded: Determine bead diameters (e.g., second virial coeff.)
Bisphenol-A Polycarbonate: Torsional Potentials

HF/6-31G* SPE calculations

Bisphenol-A Polycarbonate: 4:1 Boltzmann Inversion of Carbonate Angle Potential
MD of Coarse-Grained Bisphenol-A Polycarbonate: Prediction of atomically resolved structure factor

A topological representation of a bulk sample of BPA-PC; the “primitive path” method predicts $N_e \sim 5$ repeat units.

Leon, Delle Site & Kremer (in prep)
Generality vs. Specificity: Modeling Polymer/Metal Interfaces

Chain-like molecules:
conformational freedom influenced by the surface

Specific molecule-surface interactions: local interface structure and properties

Atomic-scale interactions:
small-scale conformations
Ab initio Car-Parrinello MD Investigations of Comonomer Analogs on Nickel (with L. Delle Site)

... but phenol interaction orientational...

carbonate & isopropylidene do not stick to nickel...

...not accessible in our coarse-grained representation!
Solution: Dual-Resolution CG BPA-PC

- Terminal CG carbonate → atomically resolved carbonate
- C atom “carries” total carbonate excluded volume
- (Bridging O)→(CG phenoxy end) bond vector → C1-C4
- Interaction of terminal phenoxy with Ni site is orientation dependent
Dual-Res MD of a Confined BPA-PC Melt
N = 10 repeat units; Nm = 240 chains

Center of mass density profiles

Three regimes:
\( z < R_g \):
both ends ads.
\( R_g < z < 2R_g \):
single-end ads.
\( z > 2R_g \):
no ends ads.
Dual-Res MD of a Confined BPA-PC Melt: “Stratified” Chain Structure

Gyration tensor zz-component vs COM distance from wall

Three regimes:

\( z < R_g \):
- chains flattened
- \( R_{g,zz} < R_{g,xx,yy} \)
- both ends ads.

\( R_g < z < 2R_g \):
- chains extended
- \( R_{g,zz} < R_{g,xx,yy} \)
- single-end ads.

\( z > 2R_g \):
- bulk structure
Conclusions: The Liquid Polycarbonate/Nickel Interface

*Ab initio* (CPMD) calculations: A mechanism of PC/Ni adhesion:
- Phenoxy chain ends adsorb on nickel
- Internal chain segments do not stick

Dual-resolution simulations: Specificity gives a new picture of interface structure
- Chain sequence apparent from liquid structure
- Adsorbing ends influence liquid structure out to $2R_g$
- Two-layer (compressed-stretched) structure in chain anisotropy

Publications:
Concurrent multiresolution simulation of molecular liquids

Why?
Conduct full-blown atomistic MD with realistic boundary conditions

Enforce collective behavior to test hypotheses

AKA: “Concurrent Coupling of Length Scales”
What is “concurrent multiresolution simulation”?

MAAD Silicon

Broughton et al.
What is “concurrent multiresolution simulation”?

Continuum-particle hybrid coupling for liquids

R. Delgado-Buscalioni and P. V. Coveney
Concurrent multiresolution simulation of molecular liquids

Why is it difficult?

- Mass can cross resolution boundaries.
- No fixed reference (e.g., crystal lattice)
- Interaction potentials must be compatible across scales AND resolution interface.
  - System equation of state must (ideally) be independent of particle resolution
  - Interface can dominate
Monte Carlo Simulations of Liquid Methane in the “Dual-Resolution NVT” ensemble

\( N \) total molecules, cubic periodic box, two domains \( V_1 + V_2 = V \)

\( n_1 \) explicit CH\(_4\) molecules in \( V_1 \)

resolution boundary

\( N-n_1 \) superatom CH\(_4\) in \( V_2 \)

**Goal:** \( \langle n_1 \rangle = \frac{V_1}{V} N \)
The “dual-resolution NVT” ensemble

Partition function

\[ Q = \sum_{n_1=0}^{N} \frac{q_{t,1}^{n_1} q_{t,2}^{N-n_1}}{n_1! (N-n_1)!} \int ds_1^{n_1} \int d\Omega_1^{n_1} \int ds_2^{N-n_1} e^{-U\left(s_1^{n_1}, \Omega_1^{n_1}, s_2^{N-n_1}\right)/k_BT} \]

- \( q_t \): single-molecule translational pattern function (all molecules)
- \( q_r \): single-molecule rotational pattern function (explicit only)
- \( s_1 \): scaled coordinates of explicit molecules \( \equiv (V_1)^{1/3} R_1 \)
- \( \Omega_1 \): Euler orientations of explicit molecules
- \( s_2 \): scaled coordinates of superatoms \( \equiv (V - V_1)^{1/3} R_2 \)

Potential:

\[ U\left(s_1^{n_1}, \Omega_1^{n_1}, s_2^{N-n_2}\right) = U_{11} \left(s_1^{n_1}, \Omega_1^{n_1}\right) + U_{22} \left(s_2^{N-n_1}\right) + U_{12} \left(s_1^{n_1}, \Omega_1^{n_1}, s_2^{N-n_1}\right) \]

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<th>bulk explicit</th>
<th>bulk superatom</th>
<th>resolution interface</th>
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<td>( s_2^{N-n_1} )</td>
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The "dual-resolution NVT" basic idea

**Bulk explicit**

\[ U_{11} = \sum_{i=1}^{n_1-1} \sum_{j=i+1}^{n_1} u_{11}(R_{ij}, \Omega_i, \Omega_j) \]

given this…

**Bulk superatom**

\[ U_{22} = \sum_{i=n_1+1}^{N-1} \sum_{j=i+1}^{N} u_{22}(R_{ij}) \]

find these…

**Dual-res. interface**

\[ U_{12} = \sum_{i=1}^{n} \sum_{j=n_1+1}^{N} u_{12}(R_{ij}, \Omega_i) \]

…such that

\[ \langle n_1 \rangle = \frac{V_1}{V} N \]
$u_{11}$: 5-Center Lennard-Jones Pseudo-Methane

$$u_{11} (\mathbf{R}_{ij}, \Omega_i, \Omega_j) = \sum_{\alpha \in i} \sum_{\beta \in j} u_{\alpha \beta} (r_{\alpha \beta})$$

$$u_{\alpha \beta} (r_{\alpha \beta}) = 4\epsilon_{\alpha \beta} \left[ \left( \frac{\sigma_{\alpha \beta}}{r_{\alpha \beta}} \right)^{12} - \left( \frac{\sigma_{\alpha \beta}}{r_{\alpha \beta}} \right)^6 \right]$$

length: $\sigma = 3.733$ Å;
energy: $\epsilon = 1.496$ kJ/mol (179.9 K)
$u_{22}$ Option 1: Zero-Density Reversible Work (ZDWR)  

$$u_{22}(r) = -k_B T \ln \left< e^{-\beta u_{11}(R_{ij})} \right>_{\Omega_i, \Omega_j}$$

Averaged over angular orientations of 2 molecules $i$ and $j$ at fixed $r$.
$\rightarrow$ Density-independent
Option 2: Reverse Monte Carlo (RMC)

- Iteratively refine $u_{22}$ beginning with a reasonable guess
- Corrections to mimic correlations in bulk atomic fluid

\[ u_{22}(R) \leftarrow u_{22}(R) + k_B T \ln \left[ \frac{g_{22}(R)}{g_{11}^{(0)}(R)} \right] \]
Bulk phase chemical potentials: How good is $u_{22}$ for a single-resolution description?

- chemical potential: $\mu \equiv \frac{dF}{dn} = \mu^{id} + \mu^{ex}$

- Interface complicates things: in its absence,

$$\langle n_1 \rangle = \frac{V_1}{V} N \rightarrow \mu_{11} = \mu_{22}$$

- change in free energy upon insertion of explicit into bulk explicit phase SAME as insertion of superatom into bulk superatom phase

$\rightarrow u_{22}$ should satisfy $\mu_{11}^{ex} - k_B T \ln q_r - \mu_{22}^{ex} = 0$

for $V_1 = V/2$

- For CH$_4$ at 179K, (spherical rotor) $k_B T \ln q_r = 2.55 k_B T$
Bulk phase chemical potentials: How good is $u_{22}$ for a single-resolution description?

ZDRW looks great; both are pretty good.
What about mixed-resolution interactions, $u_{12}$? Assume explicit-superatom interaction identical to a superatom-superatom interaction:

$$u_{12} \left( R_{ij}, \Omega_i \right) = u_{22} \left( R_{ij} \right)$$

Conduct standard NVT Monte Carlo, except trial displacements include resolution changes if a boundary is crossed.

$$N = 1000, \quad \rho = 0.879 \ \sigma^{-3}$$

$$V_1 = V/2, \quad T = 1$$
Dual resolution NVT MC: ZDRW vs RMC for $u_{22}$ & $u_{12}$

Can we tweak the RMC $u_{22}$?
Tweaking $u_{22}$ from RMC: Ad hoc hardening

Idea: Make repulsive branch of $u_{22}$ more repulsive. Should increase $\mu_{22}$ and drive superatoms into the explicit subdomain.

\[ u'_{22} (R) \leftarrow u_{22} (R) f (R) \]

where $f(R_0) = 1$ and $\left. \frac{df}{dR} \right|_{R_0} = 0$.

\[ f (R) = \begin{cases} A (R_0 - R)^n + 1 & \text{if } R < R_0, \\ 0 & \text{otherwise.} \end{cases} \]

where $u_{22} (R_0) = u_{22} (R_{min}) + 1$, and $R_0 < R_{min}$, and $\left. \frac{du_{22}}{dR} \right|_{R_{min}} = 0$. 
Tweaking $u_{22}$ from RMC: Hardening, $n = 2$

$A = 300, n = 2$
Conclusions and outlook

Successful demonstration of a “systematic” way to generate $u_{22}$ for dual-resolution liquid simulation.

Particular to small molecules?

Useful in non-equilibrium setting?

Real surfaces?

Polymers?
Acknowledgments

- Luigi Delle Site, Kurt Kremer (MPIP)
- BMBF (German Ministry of Education and Research)
- US Office of Naval Research (award No. N00014-03-1-0655)