Systematic Coarse-Graining and Concurrent Multiresolution Simulation of Molecular Liquids

Cameron F. Abrams

Drexel University
Department of Chemical and Biological Engineering
Philadelphia, PA USA

28-30 August 2006

ORNL/CNRS NanoFocUL

Drexel
UNIVERSITY

Ph.D. Students in the Abrams Group

Ehsan Jabbarzadeh
Angiogenesis in Tissue Engineered Bone (NSF)

Yelena Sliozberg
Inhomogeneous Simulation of Protein Assemblies (NSF)

David Richardson (CompSci)
Simulation Studies of Polymer Nanocomposites (ONR)

Harish Vashisth
Multiscale Simulation of Protein Diffusion in Hydrogels (NSF)

Dan Rundle
Simulation Studies of Thermoset Polymers (Army)

Outline

Systematic molecular coarse-graining:
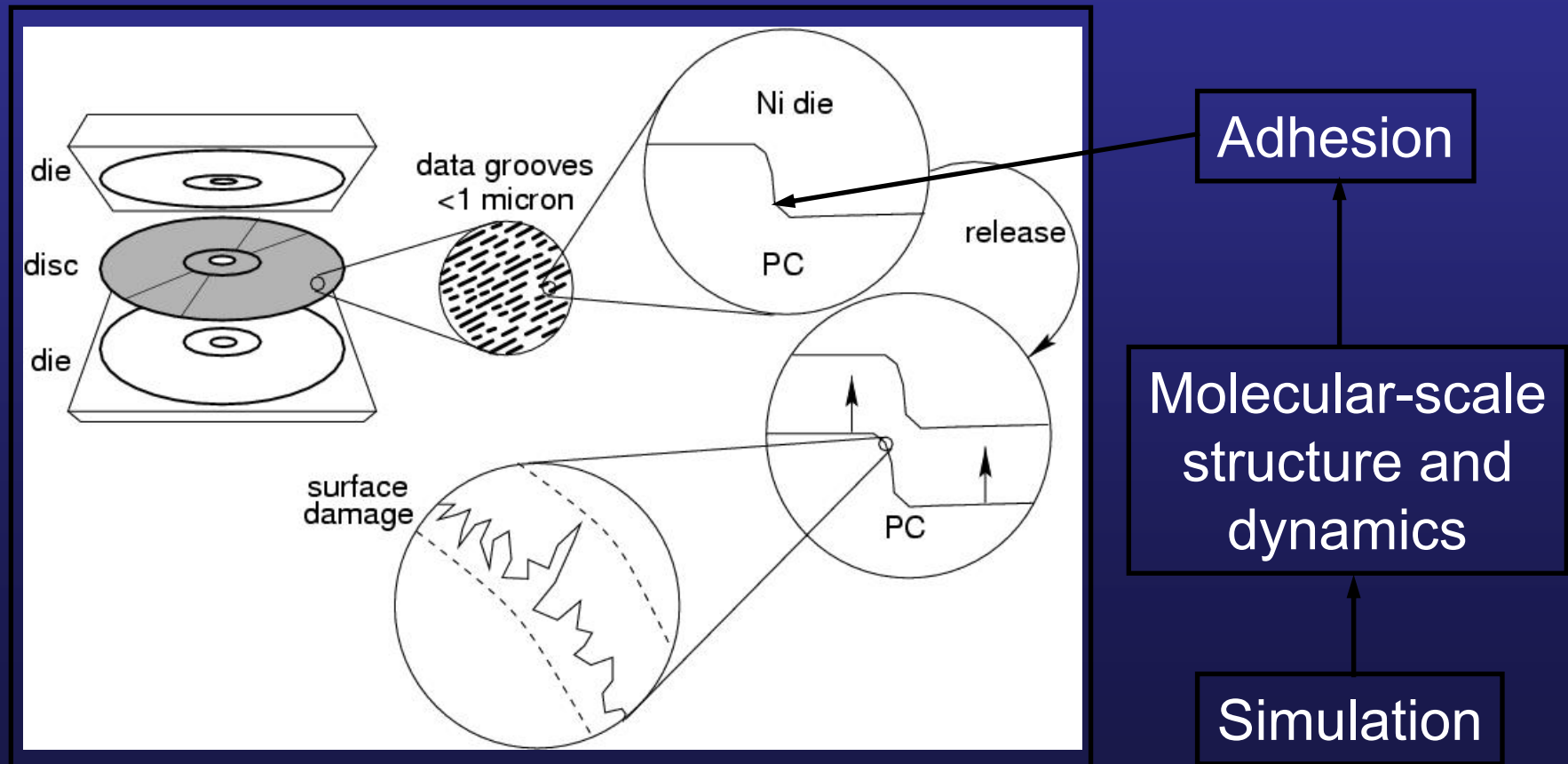Bulk bisphenol-A polycarbonate (BPA-PC)

Inhomogeneously resolved coarse-graining:
BPA-PC at interfaces

Concurrent multiresolution simulation of molecular liquids
Dual resolution NVT ensemble Monte Carlo

Motivation: Structure/Property Relationships at the Polycarbonate/Nickel Interface

Surface damage in molding of *optical data storage* media

The basic problem…

$$G_{\mathrm{obs}} = \sum_{\nu} \left[\frac{1}{\mathcal{N}} \left(\begin{array}{c} \text{number of times state } \nu \text{ is} \\ \text{observed in } \mathcal{N} \text{ observations} \end{array} \right) \right] G_{\nu}$$

$$\underbrace{\phantom{\frac{1}{\mathcal{N}}}}_{*}$$

$$\text{Finite } \mathcal{N} : \ [* \to P_{\nu}] \iff [\mathcal{N} \text{ observations } uncorrelated]$$

Simple fluids/small molecules:
Many small displacements → OK.

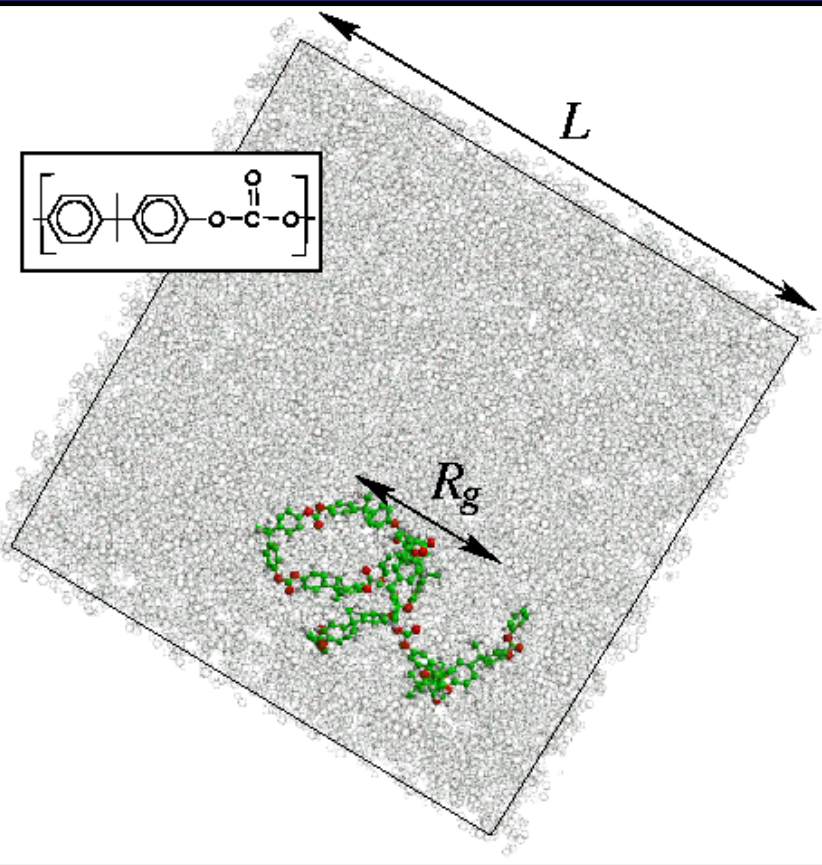$$\max(\tau_{\mathrm{relax}}) \gtrsim \tau_0$$

Polymeric fluids/large molecules:
Many small displacements →
  Large collective displacements.
Expensive!

$$\max(\tau_{\mathrm{relax}}) \gg \tau_0$$

The Tension Between Specificity and Generality in Polymer Molecular Simulation
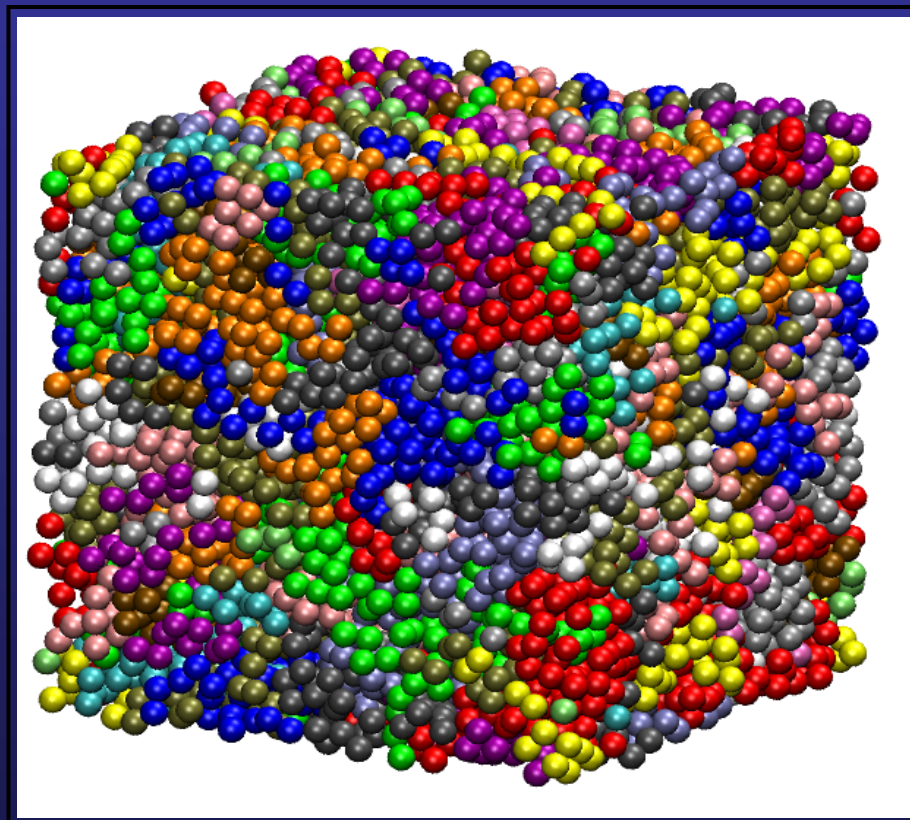
e.g., Bisphenol-A Polycarbonate (BPA-PC):

Kremer-Grest bead-spring chains

An atomically resolved system is
- **SPECIFIC, but**
- **HARDER TO EQUILIBRATE/SAMPLE**

A bead-spring system is
- **EASIER TO EQUILIBRATE/SAMPLE,**
- **GENERIC**

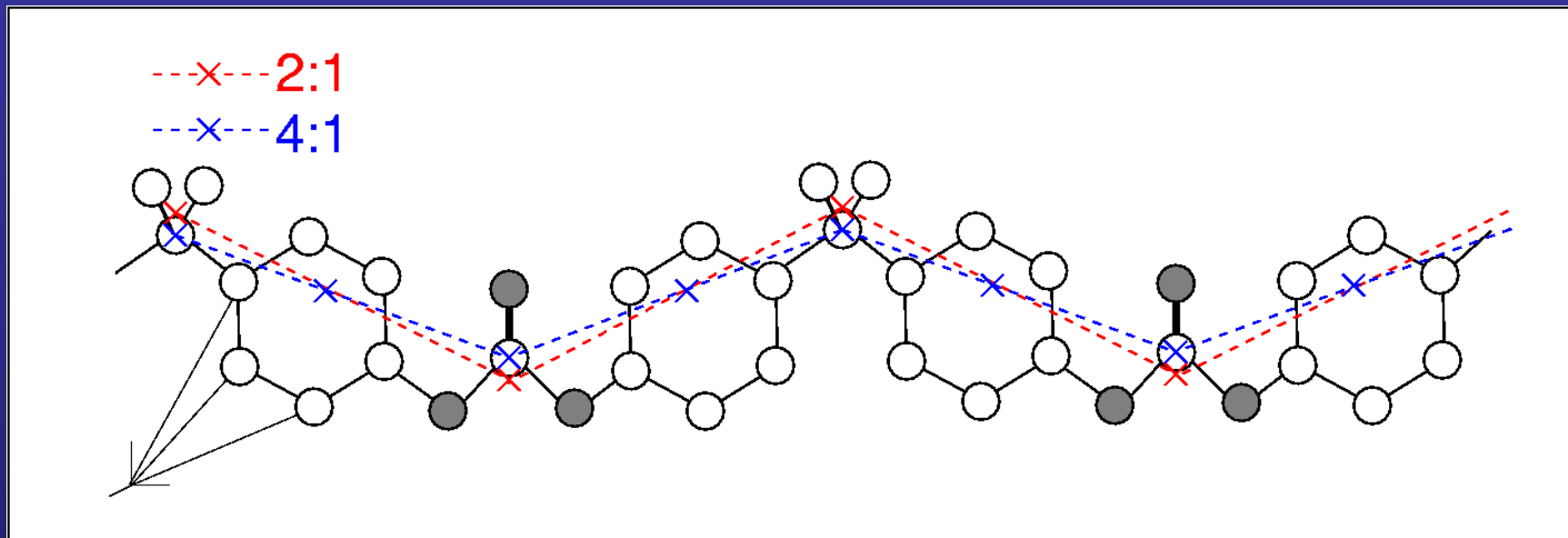# A Compromise: Systematic Molecular Coarse-Graining
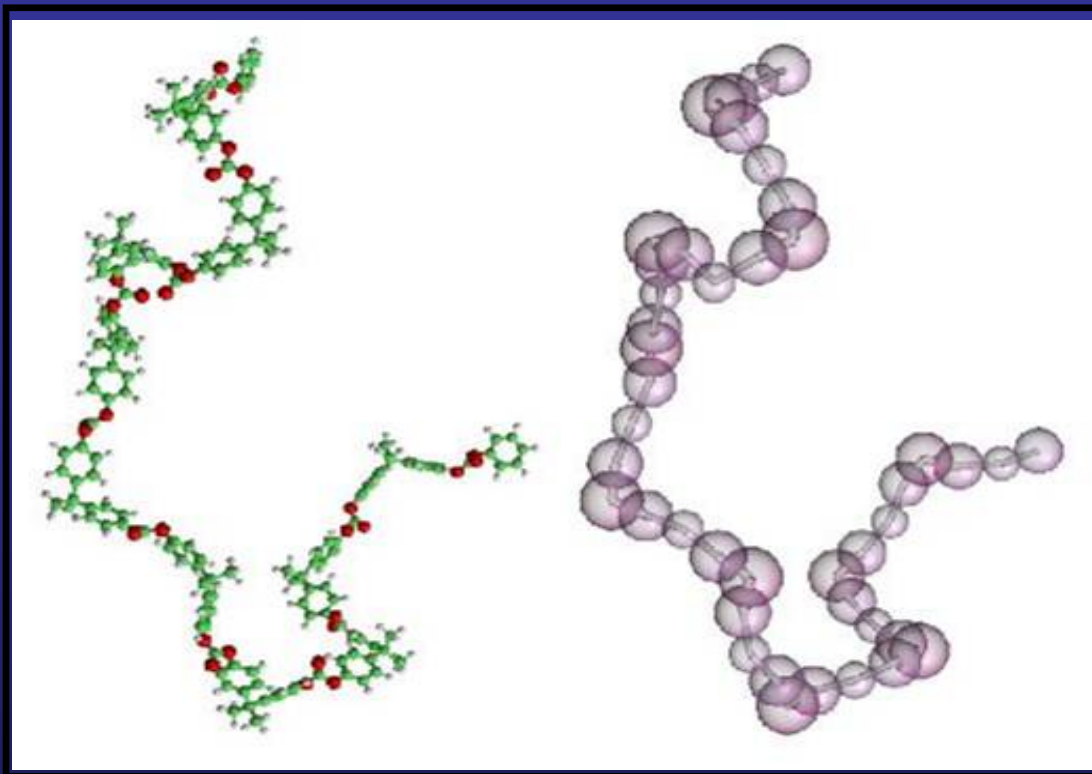
"mapping"

General procedure:

1. Build CG model

2. Generate CG system

3. Equilibrate/Propagate

4. Reintroduce details

5. Sample

6. Repeat 3 to 5
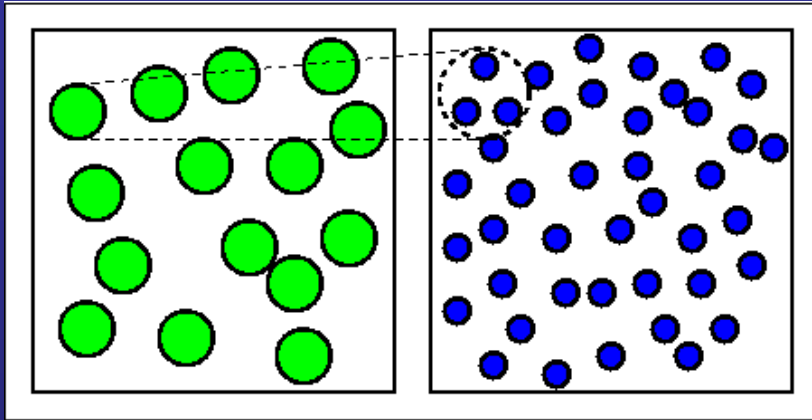
Bisphenol-A Polycarbonate: Mapping Schemes

2:1 – repeat unit replaced with 2 mapping points:
>   1. centroid of –$C(CH_2)$–
>   2. centroid –O–(C=O)–O–

4:1 – repeat unit replaced with 4 mapping points:
>   1. backbone C of –$C(CH_2)$–
>   2. C of –O–(C=O)–O–
>   3&4. "Floating" centers of phenylenes

Generalized Coarse-Graining: "Mapping"

$\mathbf{r}^N$ Fine-scale degrees of freedom

$\mathbf{R}^M$ Coarse-grained ("CG," "collective") degrees of freedom: "<u>Mapping Points</u>"

$\underline{\mathbf{M}}$ mapping matrix

$$\begin{pmatrix} \mathbf{R}_1 \\ \mathbf{R}_2 \\ \mathbf{R}_3 \\ \vdots \\ \mathbf{R}_M \end{pmatrix}_{M \times 1} = \begin{pmatrix} \mathbf{M}_{1,1} & \mathbf{M}_{1,2} & \mathbf{M}_{1,3} & \cdots & \cdots & \cdots & \mathbf{M}_{1,N} \\ \mathbf{M}_{2,1} & \mathbf{M}_{2,2} & \mathbf{M}_{2,3} & \cdots & \cdots & \cdots & \mathbf{M}_{2,N} \\ \mathbf{M}_{3,1} & \mathbf{M}_{3,2} & \mathbf{M}_{3,3} & \cdots & \cdots & \cdots & \mathbf{M}_{3,N} \\ \vdots & \vdots & \vdots & & \ddots & & \vdots \\ \mathbf{M}_{M,1} & \mathbf{M}_{M,2} & \mathbf{M}_{M,3} & \cdots & \cdots & \cdots & \mathbf{M}_{M,N} \end{pmatrix}_{M \times N} \times \begin{pmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \mathbf{r}_3 \\ \vdots \\ \vdots \\ \vdots \\ \mathbf{r}_N \end{pmatrix}_{N \times 1}$$

Configuration $\mathbf{r}$ "satisfies a mapping $\mathbf{R}$" if $\quad \mathbf{R} - \mathbf{Mr} = 0$

Linking the Statistics at Different Scales: Boltzmann Inversion in NVT Ensembles

Probability distribution of collective configurations, $\mathbf{R}^M$

$$P(\mathbf{R}^M) = \frac{1}{Z} \int d\mathbf{r}^N e^{-U(\mathbf{r}^N)/kT} \prod_{i=1}^{M} \delta \left(\sum_{j=1}^{N} \mathbf{M}_{ij}\mathbf{r}_j - \mathbf{R}_i \right) = \frac{1}{Z} e^{-F(\mathbf{R}^M)/kT}$$

$$F(\mathbf{R}^M) = -kT \ln \left[P(\mathbf{R}^M) \right] + A \quad \text{...a restricted free energy}$$

$$U_{\mathrm{CG}}(\mathbf{R}^M) \equiv -kT \ln \left[P(\mathbf{R}^M) \right] = F - A \quad \text{...a "Boltzmann-inverted potential"}$$

$U_{\mathrm{CG}}(\mathbf{R}^M)$ can be generated by sampling an ensemble spanned by fine-scale configurations $\mathbf{r}^N$: *We still have a sampling problem!*

Strategy: Use reasonable assumptions (for polymers) to decompose $P(\mathbf{R}^M)$ into bits that can be attacked individually*…*

Building U_{CG}: Reasonable Assumption #1

Bonded and nonbonded
variables are uncorrelated
(i.e., they have widely disparate energy
scales at temperatures of interest)
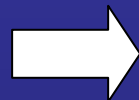
➡️ Probability distribution
factorizes

$$P(\mathbf{R}^M) = \left[\prod_{i=1}^{N_m} P_i^c(\mathbf{X}_i) \right] P^p\left(\mathbf{R}_{cm}^{N_m}, \mathbf{\Omega}_i^{N_m}\right)$$

Probability of observing
molecule i in
conformation $\mathbf{X}_i$

Probability of observing
molecule configuration
of center-of-mass
positions & molecular
orientations

Building U_{CG}: Reasonable Assumption #2

Intramolecular bonded
CG degrees of freedom
$\mathbf{X}$ are not (strongly)
correlated
(i.e., molecular orbitals are well-localized on length-scales of collective variables)
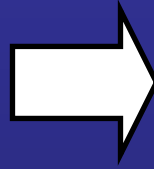
Intramolecular bonded
coarse-grained probability
distributions factorize

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

$$P^b(\mathbf{X}) \equiv P_1(X_1) P_2(X_2) P_3(X_3)...$$

$\rightarrow$ Intramolecular CG potential has a useful additive form:

$$U_{CG}^b(\mathbf{X}) = \sum_i U_i^b(X_i)$$

Building U_{CG}: Reasonable Assumption #3

Nonbonded correlations are constructed primarily of *independent pairwise contributions*

⬇

Nonbonded potential energy is *pairwise additive*

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

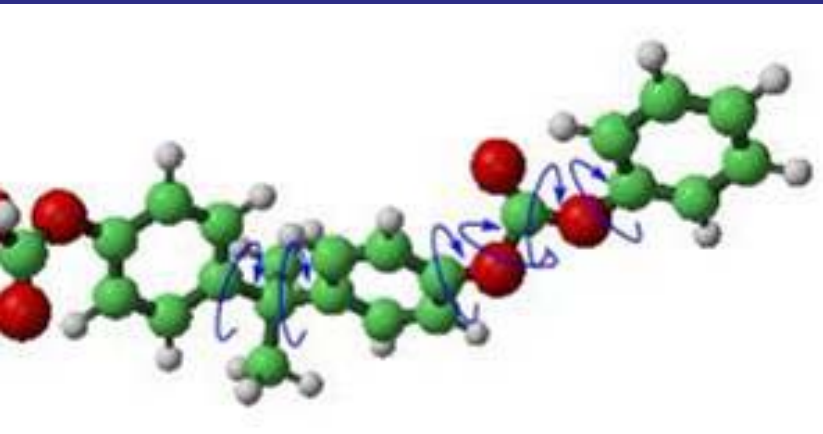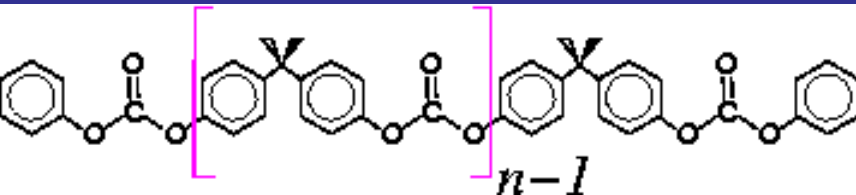BPA-PC: The repulsive Weeks-Chandler-Andersen (WCA) Potential

$$U_{ij}^{wca}(r) = 4\epsilon \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^{6} + \frac{1}{4} \right] \quad ; \quad r < 2^{1/6}\sigma_{ij}$$
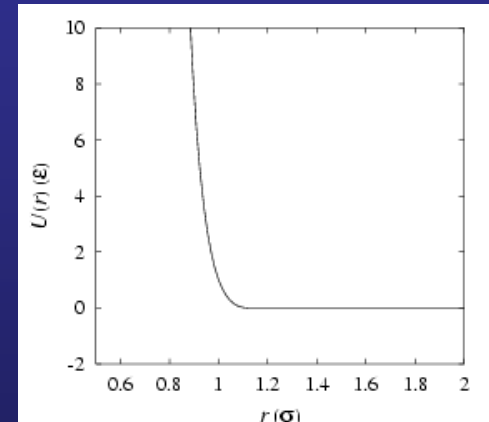
Key: Basis for choice of σ_{ij} is *geometrical:* satisfy ϕ at given ρ in the melt state.

No cohesive energy; no EOS! (ok for understanding equilibrium liquid structure)

Practical Matters: Systematic Molecular Coarse Graining of Bisphenol-A Polycarbonate (BPA-PC)

Atomically resolved intramolecular bonded degrees of freedom are *backbone torsions*, φ_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 $U(\varphi)$: *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

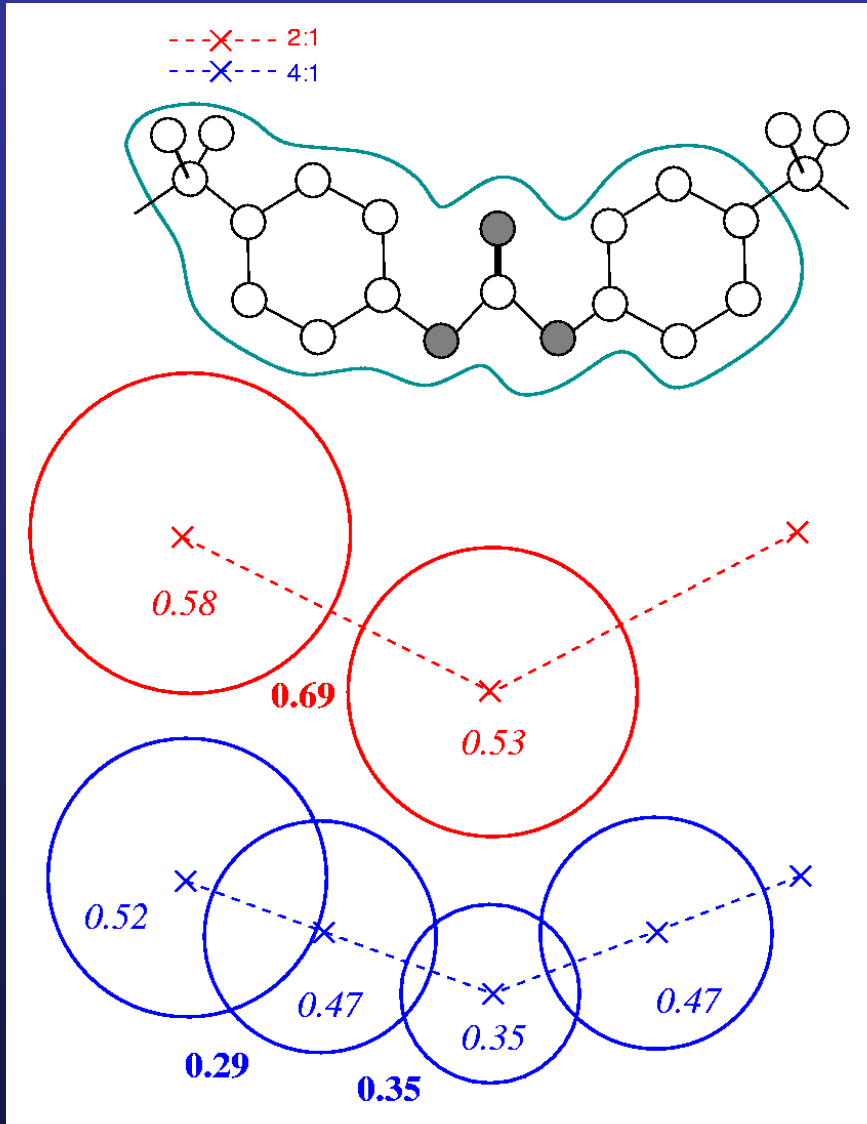# Bisphenol-A Polycarbonate: Torsional Potentials

HF/6-31G* SPE calculations

ph-c

ph-o

c-o

+nb
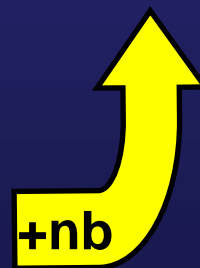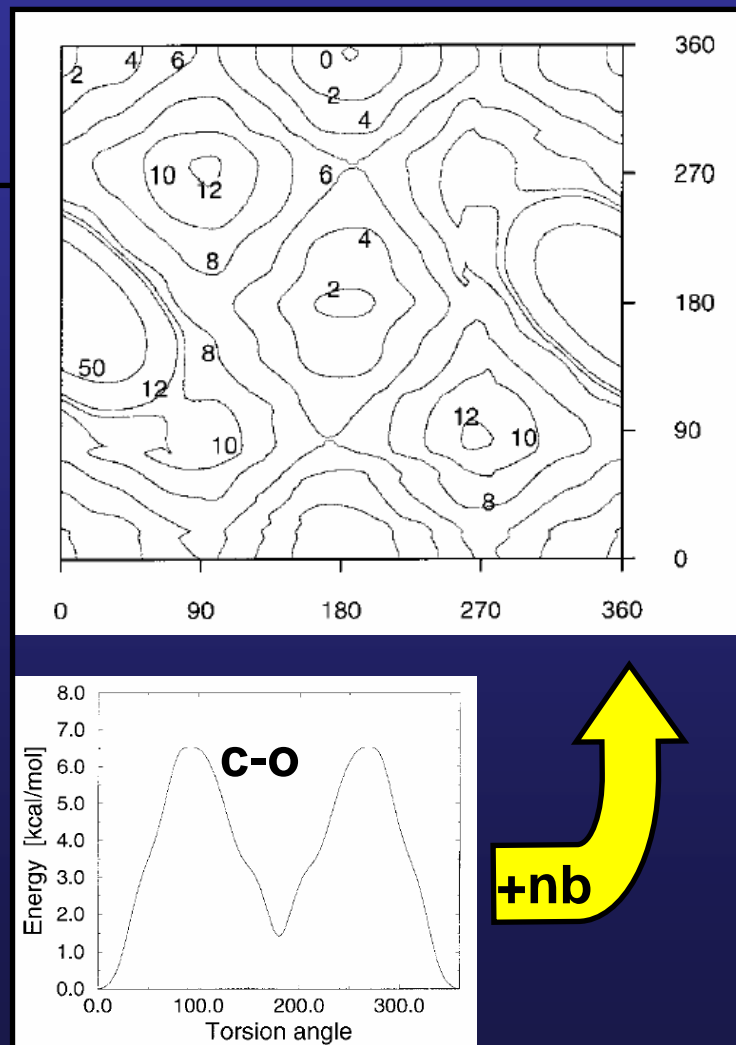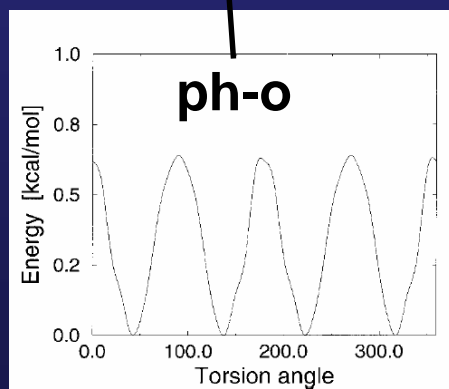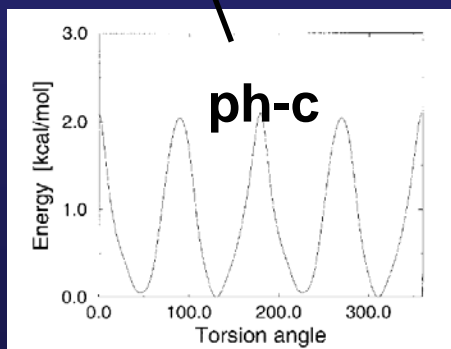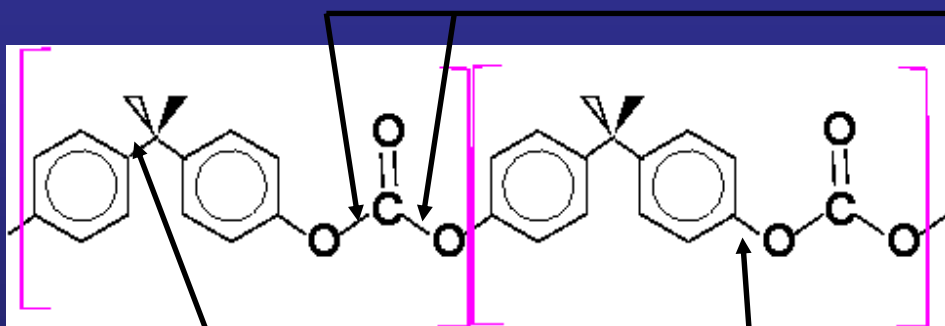
# Bisphenol-A Polycarbonate: 4:1 Boltzmann Inversion of Carbonate Angle Potential
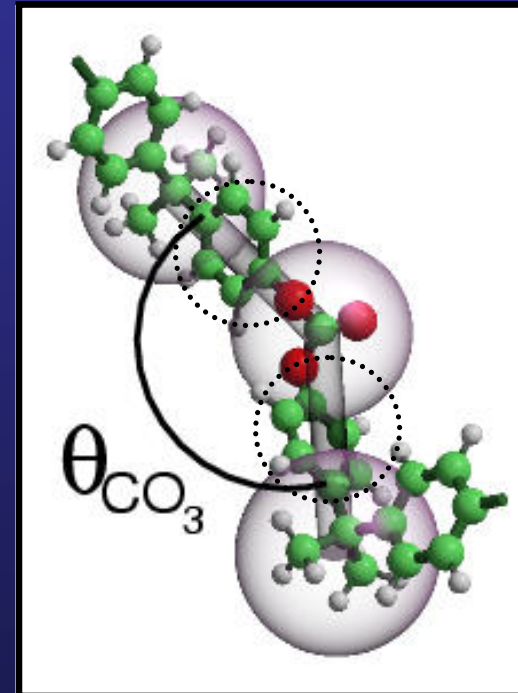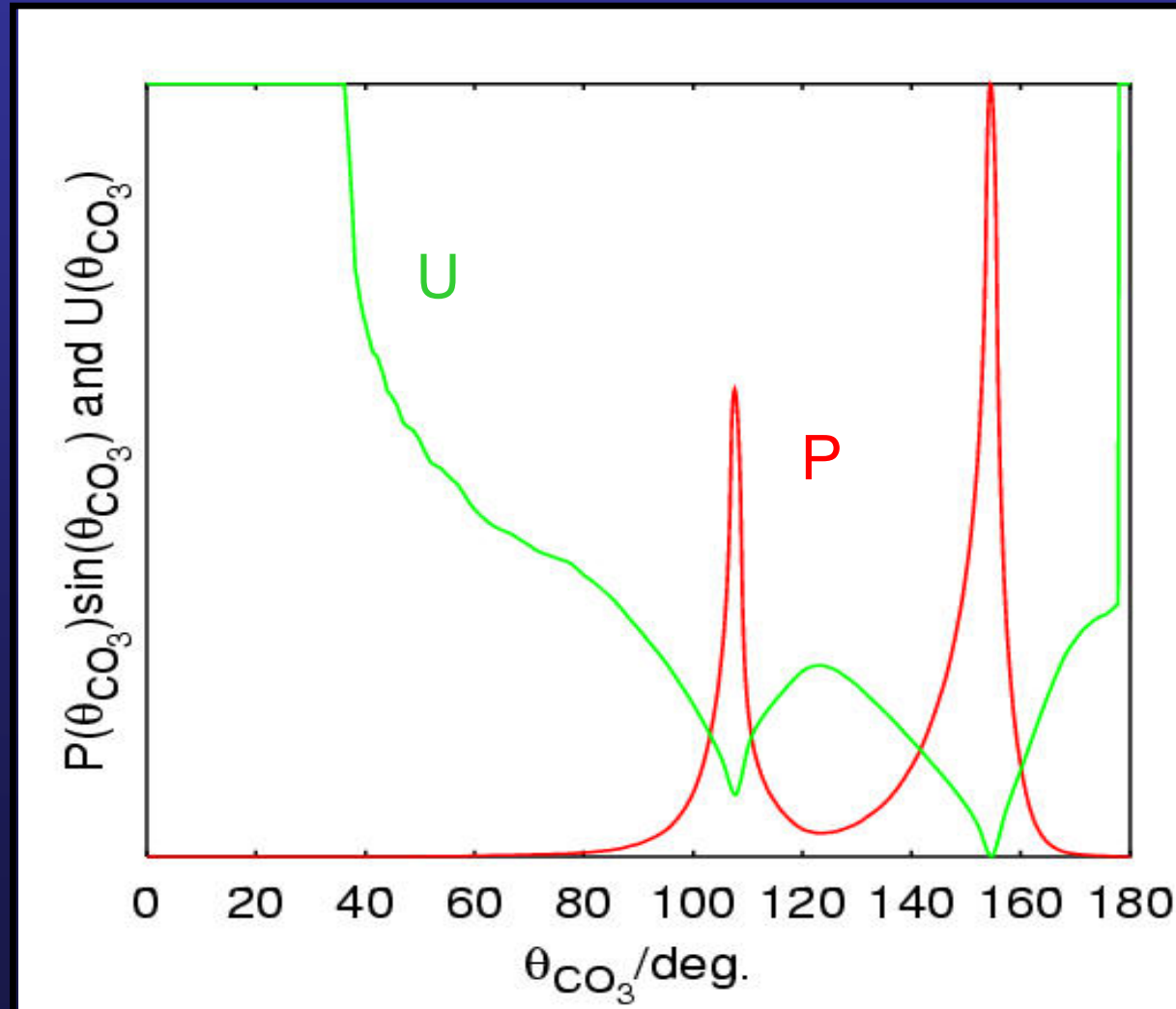
Determining Sizes of CG Beads

Repeat unit vdW volume is ~0.2 nm^3 [Sanchez and Cho, *Polymer* **36**:2929 (1995)]

1. Estimate v_2 for set of atoms belonging to each bead
   → **bare diameters**

2. Scale each bare diameter such that total volume is 0.2 nm^3
   → **effective diameters**

# Dynamic comparison of mapping schemes in the melt
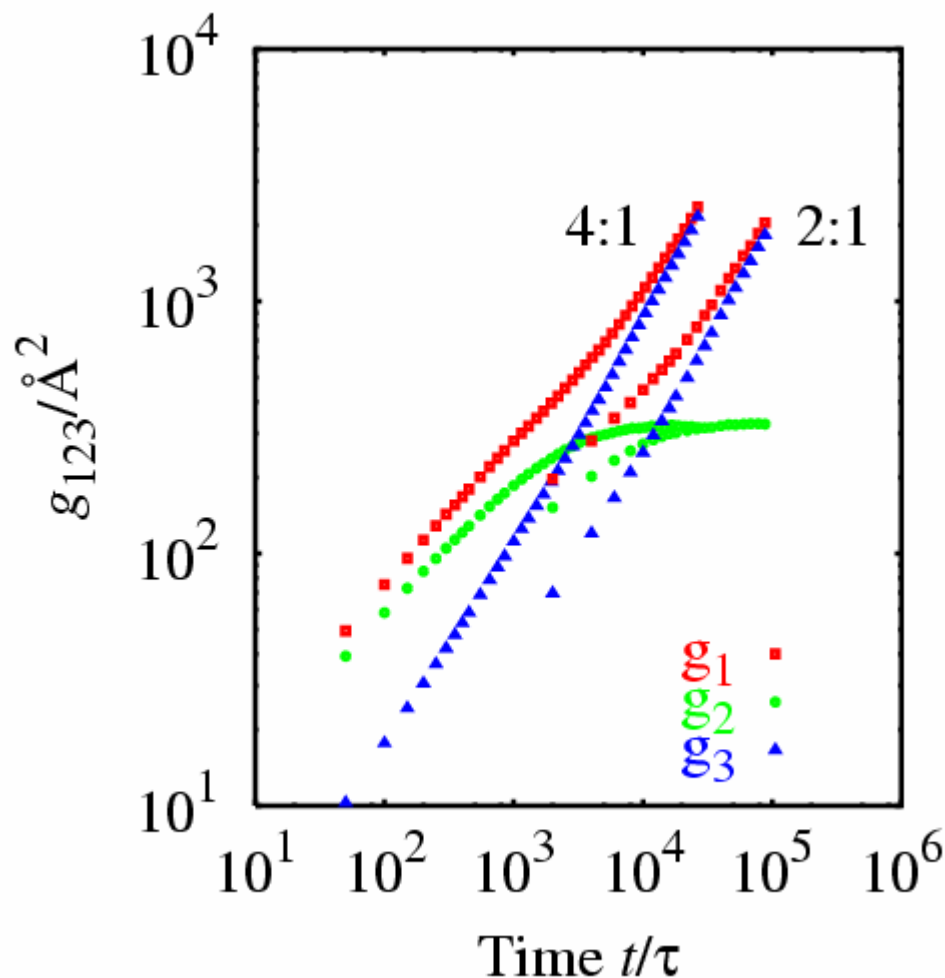
g_1 : msd of all beads

g_2 : msd of beads relative to mol. center

g_3 : msd of mol. centers

4:1 melts equilibrate faster

4:1 model is computationally more efficient

*CFA & K. Kremer, Macromolecules **36**:260 (2003)*

4:1 is Faster: An Explanation Based on Sphere-Packing Artifacts

Radial distribution function shows signature of dense sphere packing in 2:1 melts
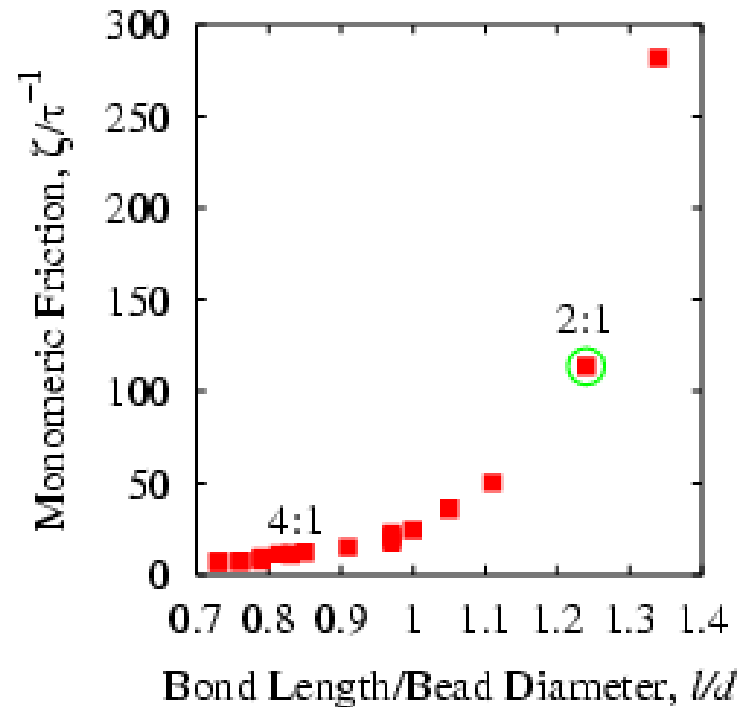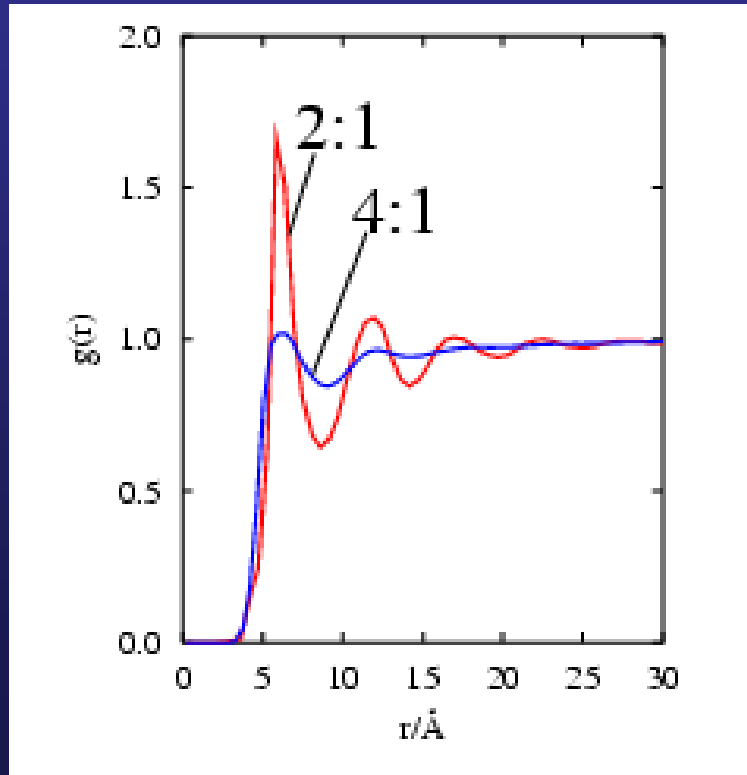

Dense packing increases friction, and is sensitive to ratio of bead diameter to bond length

CFA & K. Kremer, Macromolecules **36**:260 (2003)

CFA & K. Kremer, J. Chem. Phys. **115**(6):2776 (2001)

MD of Coarse-Grained Bisphenol-A Polycarbonate: Prediction of atomically resolved structure factor
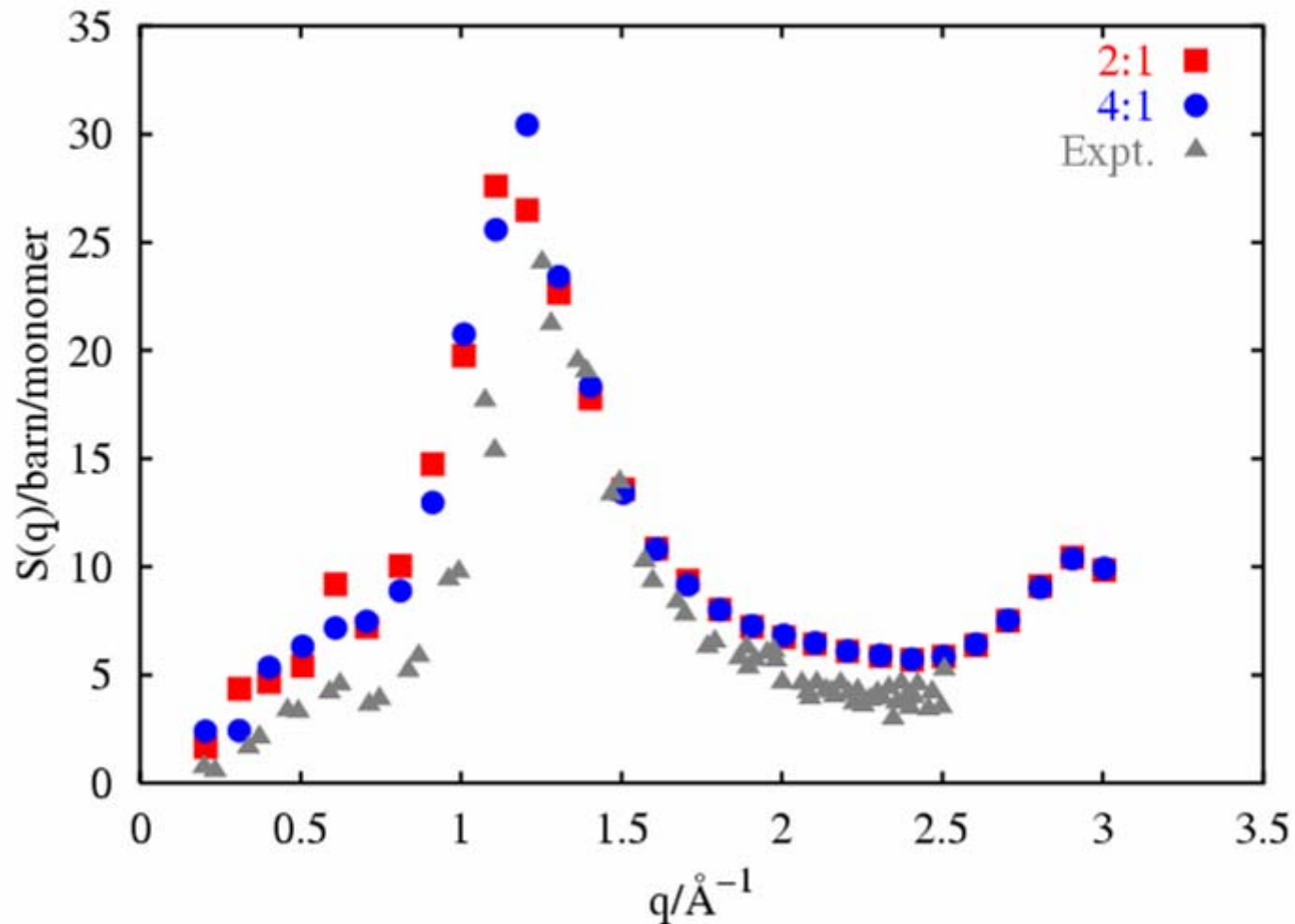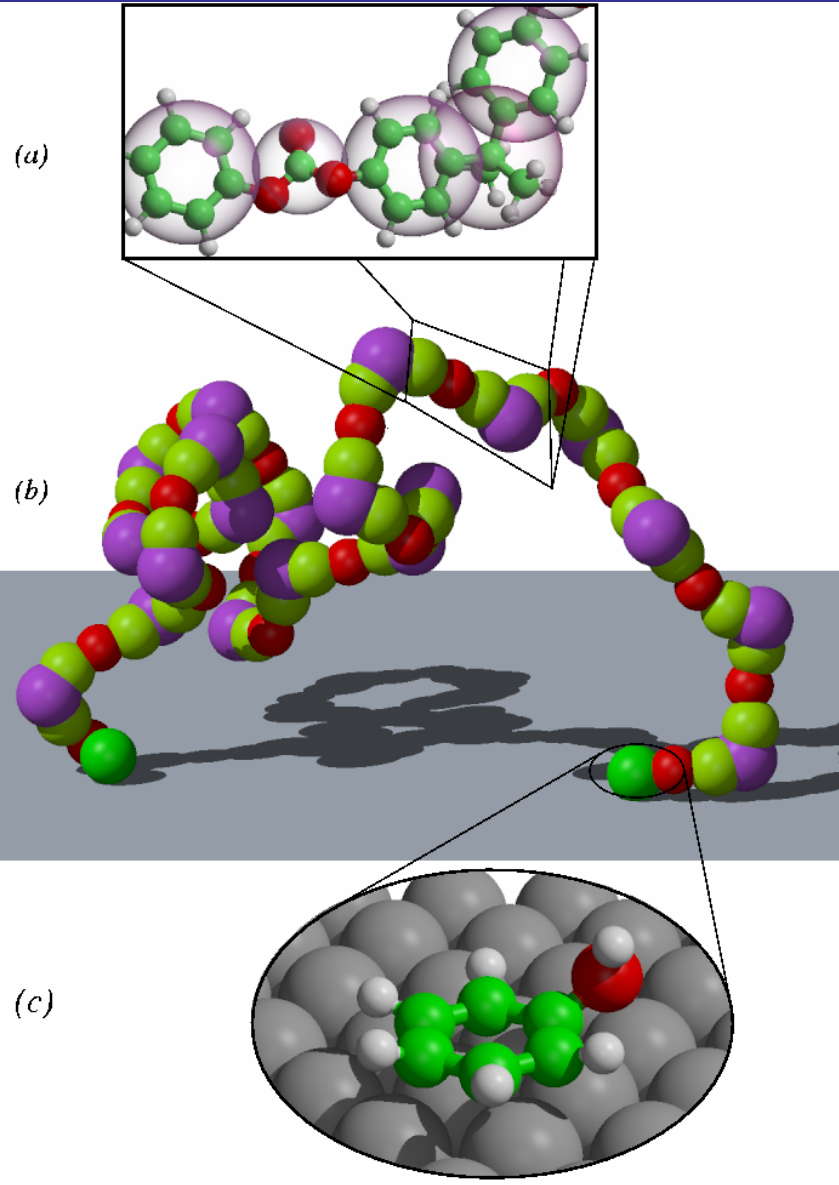
MD of Coarse-Grained Bisphenol-A Polycarbonate: Prediction of Entanglement Molecular Weight
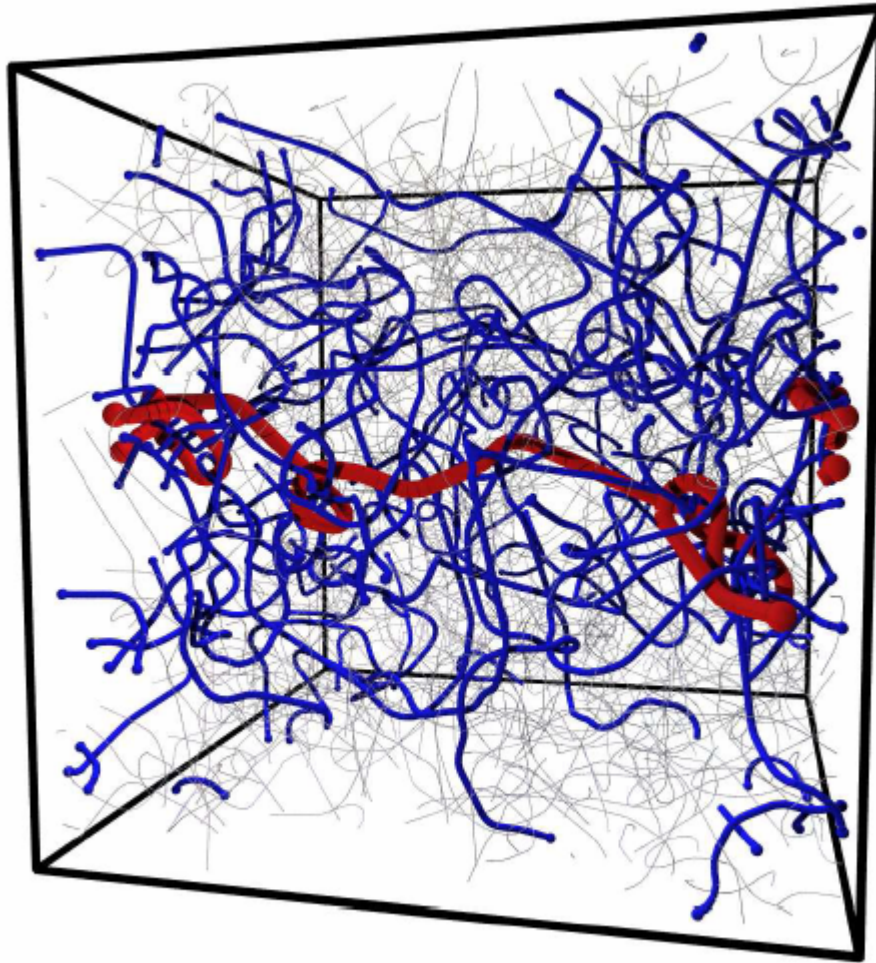
A topological representation of a bulk sample of BPA-PC;

the "primitive path" method predicts $N_e \sim 5$ repeat units

Generality *vs.* Specificity: Modeling Polymer/Metal Interfaces

(a)

(b)

(c)

Atomic-scale interactions: small-scale conformations

Chain-like molecules: conformational freedom influenced by the surface

Specific molecule-surface interactions: local interface structure and properties

Ab initio Car-Parrinello MD Investigations of Comonomer Analogs on Nickel *(with L. Delle Site)*

… but phenol interaction orientational…

BPA-PC repeat unit

carbonic acid
benzene
propane
phenol
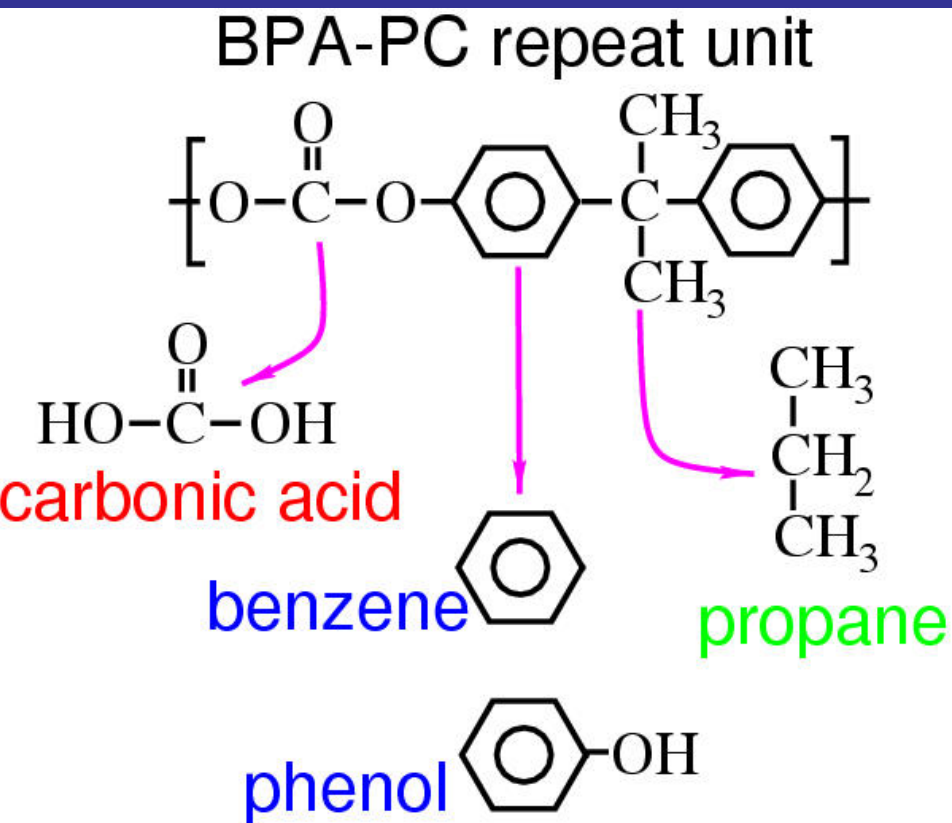
carbonate & isopropylidene do not stick to nickel…
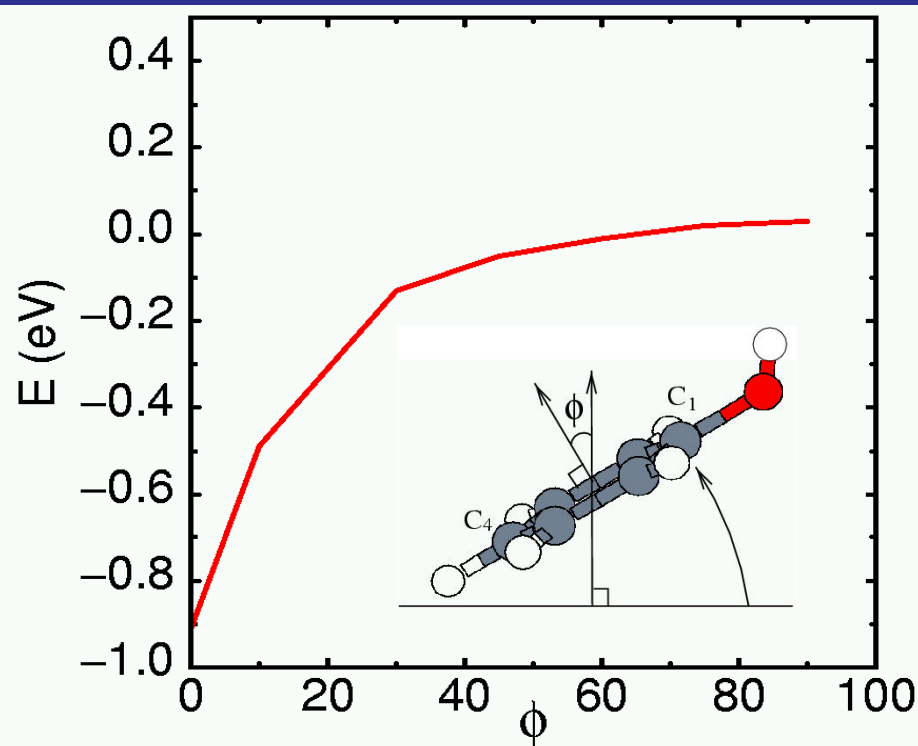
…not accessible in our CG representation!

L. Delle Site, A. Alavi, and CFA, *Phys. Rev. B* **67** (19):193406 (2003).
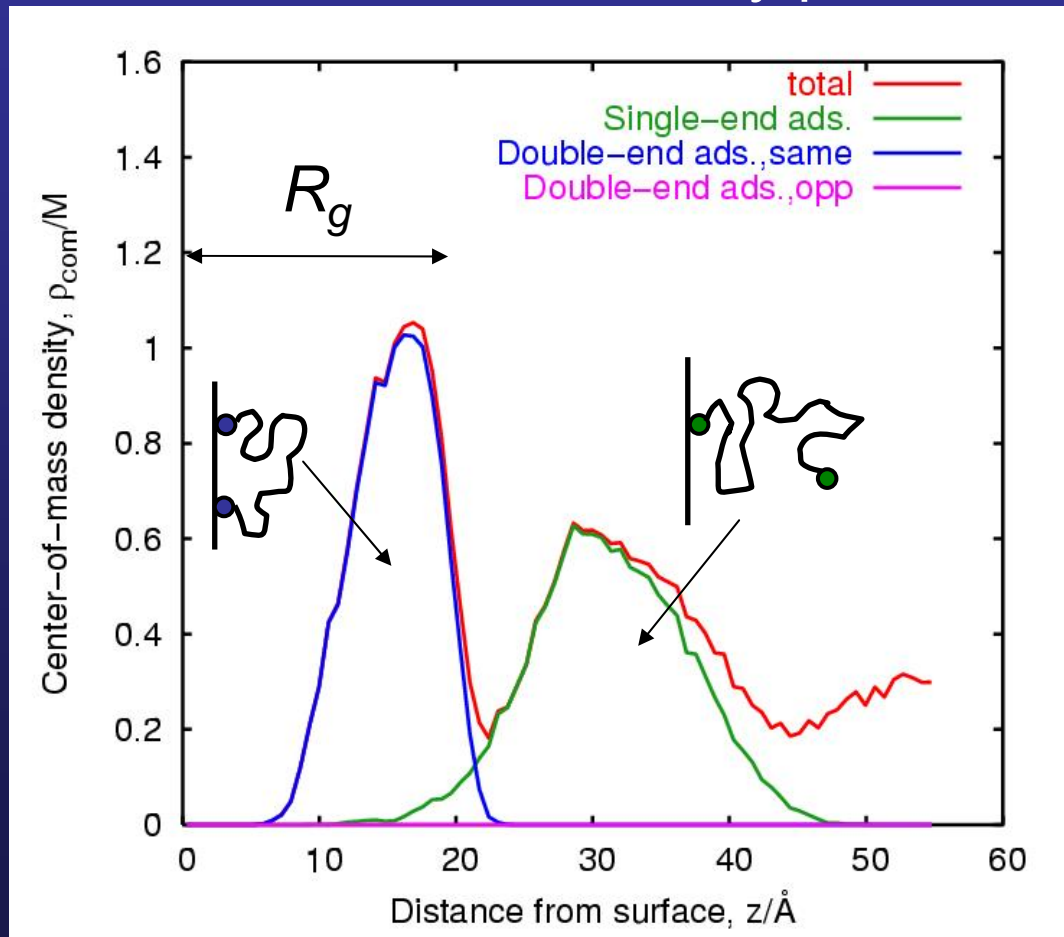
Solution: Dual-Resolution CG BPA-PC
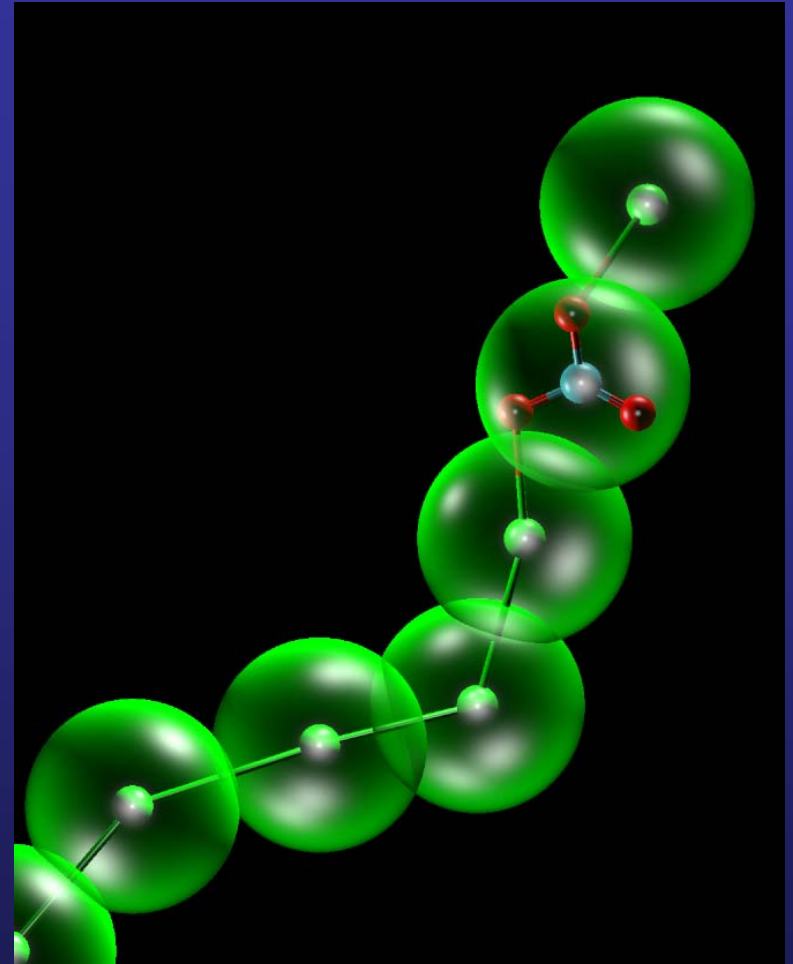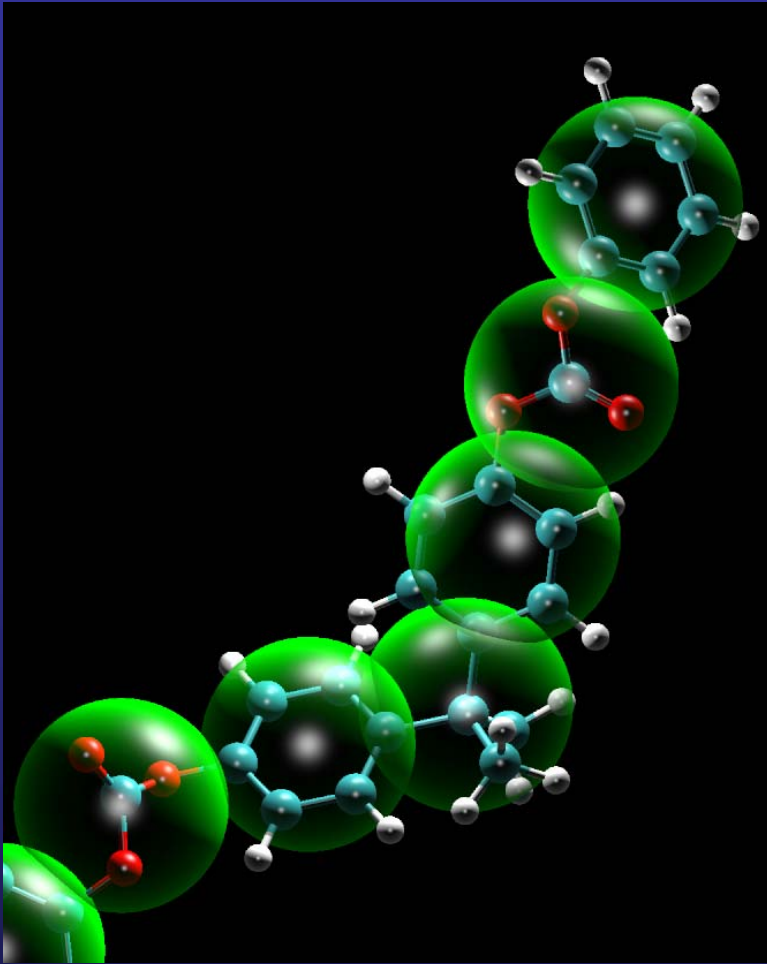
- Terminal CG carbonate → atomically resolved carbonate
- C atom "carries" total carbonate excluded volume
- (Bridging O)—(CG phenoxy end) bond vector → C1-C4
- Interaction of terminal phenoxy with Ni site is orientation dependent

Dual-Res MD of a Confined BPA-PC Melt

N = 10 repeat units; N_m = 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.

CFA, L. Delle Site, and K. Kremer, *Phys. Rev. E* **67**:021807 (2003).

Ongoing BPA-PC Coarse-Graining…

1. Ultra-long atomistic trajectories
   Hess et al, *Soft Matter* **5**:409 (2006)

2. Blend adhesion on Nickel
   Andrienko et al, *Macromolecules* **38**:5810 (2005)

3. Effects of surface defects on melt adhesion
   Delle Site et al, *J. Phys. Cond. Mat.* **17**:L53 (2005)

4. Effects of various chain ends
   Delle Site et al, *JACS* **126**:2944 (2004)

Concurrent multiresolution simulation of molecular liquids
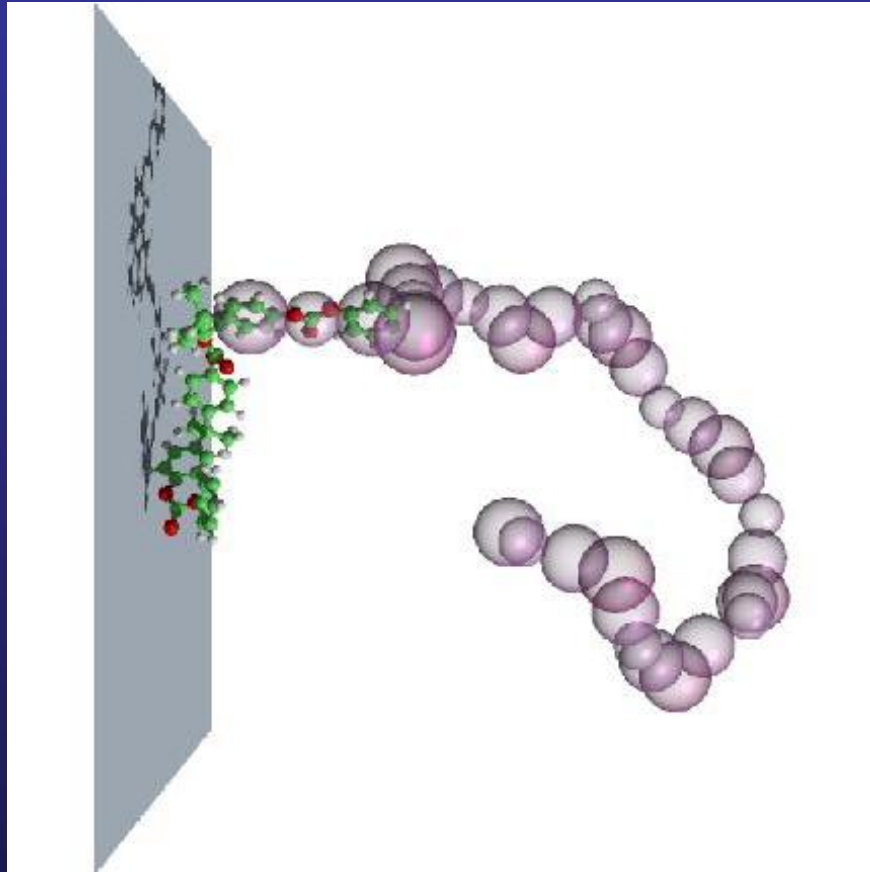
Why?

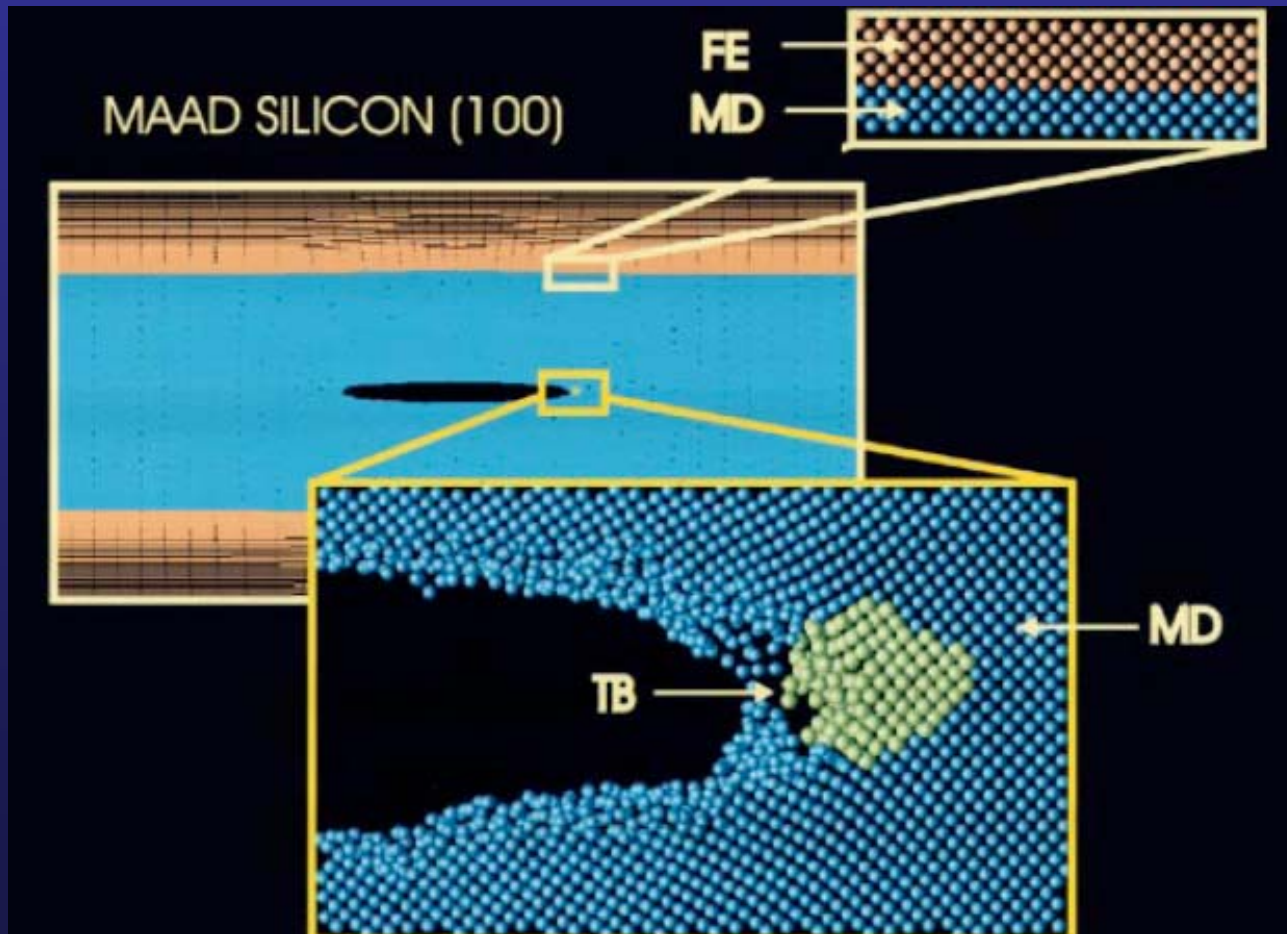Conduct full-blown atomistic MD with realistic boundary conditions

Enforce collective behavior to test hypotheses

AKA: "Concurrent Coupling of Length Scales"

What is "concurrent multiresolution simulation"?

MAAD Silicon

Broughton et al.
*Phys. Rev. B. **60**:2391 (1999)

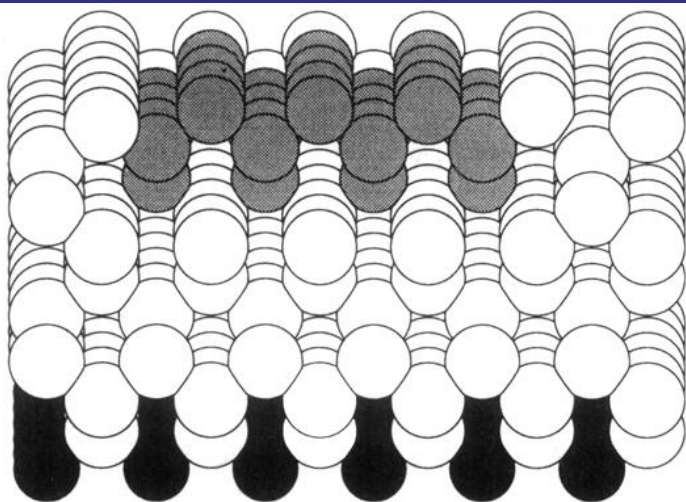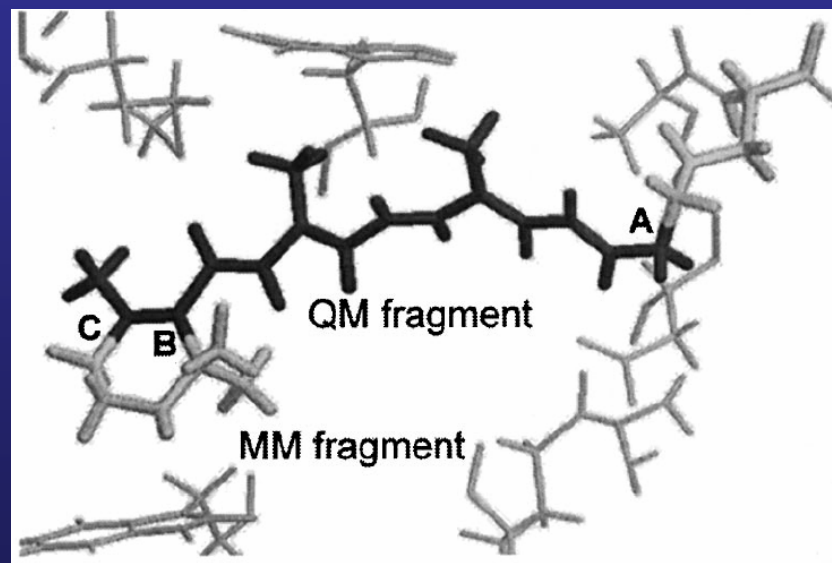# What is "concurrent multiresolution simulation"?

QM/MM

FIG. 1. Model of the 360-atom diamond (100) surface used in the MD simulations of a dimer row surface. Shaded circles represent quantum mechanically described atoms, white circles—empirical atoms, and black circles—empirical atoms held in fixed positions throughout the simulations.

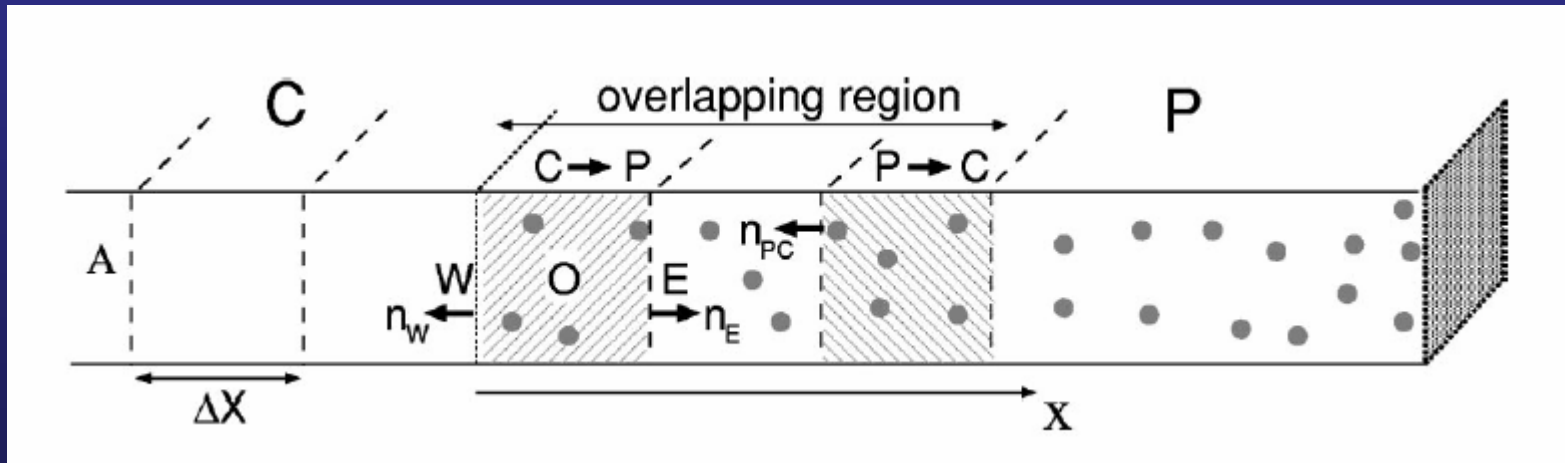Skoko, Carmer, Weiner, **Frenklach**
PRB 49 (8): 5662 (1994)

Eichinger et al. *J. Chem. Phys.*
110:10452 (1999)

What is "concurrent multiresolution simulation"?

Continuum-particle hybrid coupling for liquids

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 $V_1 + V_2 = V$
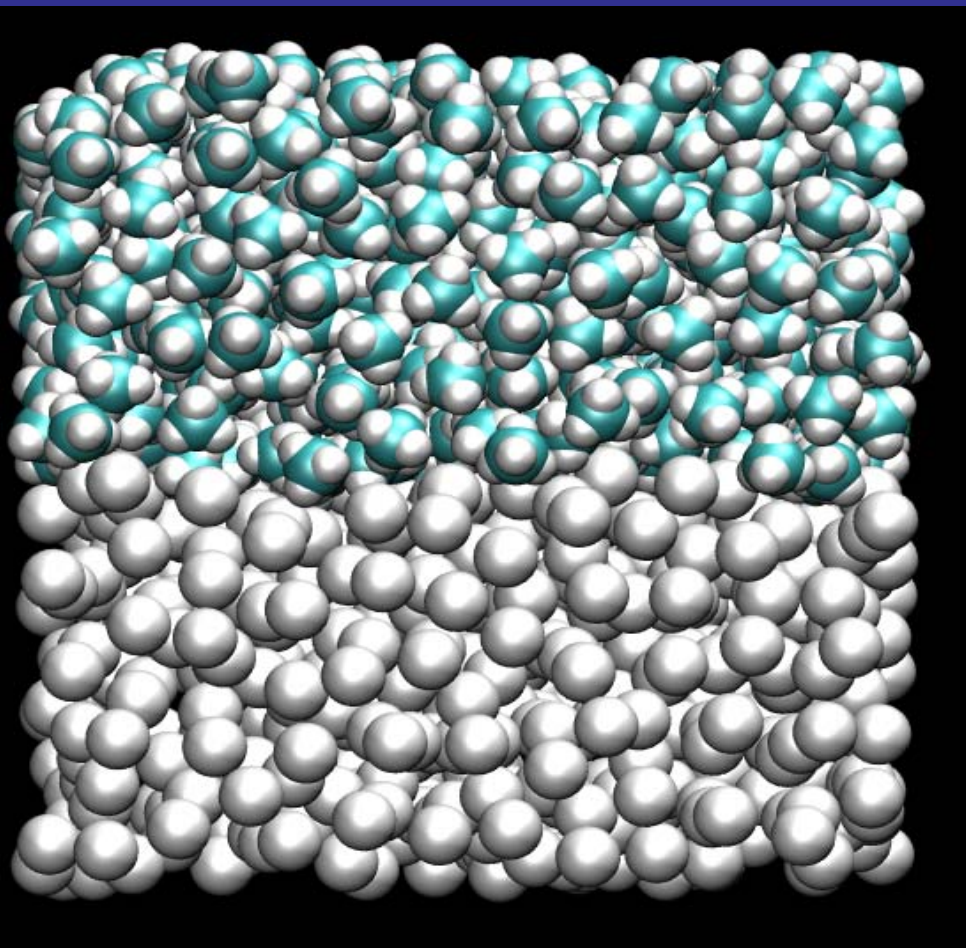
n_1 explicit CH_4 molecules in V_1

resolution boundary

N-n_1 united-atom CH_4 in V_2

$$Goal: \langle n_1 \rangle = \frac{V_1}{V} N$$

The dual-resolution NVT ensemble

- N interacting particles in box of volume V at temperature T
- n_1 explicits and N-n_1 united-atoms (explicits with "averaged over" orientations)
- Explicits are rigid rotors (no vibrational or internal energy) w/ orientations $\mathbf{\Omega}_1$
- Resolution can spontaneously fluctuate between explicit and united-atom
- Resolution boundary defined by field U_{res} that selects resolution based on position

Ideal/rotational

Configurational

$$Q = \frac{1}{\Lambda^{3N}} \sum_{n_1=0}^{N} \frac{q_r^{n_1}}{n_1! \, (N-n_1)!} \int_V d\mathbf{r}_1^{n_1} \int d\mathbf{\Omega}_1^{n_1} \int_V d\mathbf{r}_2^{N-n_1} \exp\left[-\beta U'\left(\mathbf{r}_1^{n_1}, \mathbf{\Omega}_1^{n_1}, \mathbf{r}_2^{N-n_1}\right) - \beta U_{\text{res}}\left(\mathbf{r}_1^{n_1}, \mathbf{r}_2^{N-n_1}\right)\right]$$

$$\equiv -\beta U$$

Ideal/translational

indistinguishability

Monte Carlo must randomly vary
i.   Explicit positions & orientations;
ii. united-atom positions; and
iii. molecule resolution.

Dual-resolution NVT Monte Carlo

Acceptance criterion, united-atom → explicit resolution switch trial move:

$$\text{acc}\left[o(n_1) \rightarrow p(n_1 + 1)\right] = \min\left[1, \left(\frac{N - n_1}{n_1 + 1}\right)\exp\left(-\beta\Delta U - \beta\mu_r^{\text{id}}\right)\right]$$

Acceptance criterion, explicit → united-atom resolution switch:

$$\text{acc}\left[o(n_1) \rightarrow p(n_1 - 1)\right] = \min\left[1, \left(\frac{n_1}{N - n_1 + 1}\right)\exp\left(-\beta\Delta U + \beta\mu_r^{\text{id}}\right)\right]$$

Ideal-gas free energy (chemical potential) of an explicit:

$$\mu_r^{\text{id}} \equiv -\frac{1}{\beta}\ln q_r \approx -2.55 \quad @ \; 180\text{K}$$

Problem: ideal gas prefers explicits!

Solution(?): set $\mu_r^{\text{id}} = 0$; equivalent to giving united-atoms rotational free energy!

Dual-resolution NVT Monte Carlo: Potentials

Orientational averaging of interactions:

$$U'\left(\mathbf{r}_1^{n_1}, \mathbf{\Omega}_1^{n_1}, \mathbf{r}_2^{N-n_1}\right) = -\frac{1}{\beta} \ln \int d\mathbf{\Omega}_2^{N-n_1} \exp\left[-\beta U\left(\mathbf{r}_1^{n_1}, \mathbf{\Omega}_1^{n_1}, \mathbf{r}_2^{N-n_1}, \mathbf{\Omega}_2^{N-n_1}\right)\right]$$

Convenient, approximate decomposition into molecular pairwise interactions:

$$U'\left(\mathbf{r}_1^{n_1}, \mathbf{\Omega}_1^{n_1}, \mathbf{r}_2^{N-n_1}\right) \approx \frac{1}{2}\sum_{i}^{\mathrm{ex}}\sum_{j}^{\mathrm{ex}} u'_{11}(r_{ij}, \mathbf{\Omega}_i, \mathbf{\Omega}_j) + \frac{1}{2}\sum_{i}^{\mathrm{ua}}\sum_{j}^{\mathrm{ua}} u'_{22}(r_{ij}) + \sum_{i}^{\mathrm{ex}}\sum_{j}^{\mathrm{ua}} u'_{12}(r_{ij}, \mathbf{\Omega}_j)$$

explicit/explicit   united-atom/united-atom   explicit/united-atom

Given u_{11}, assume $u_{12} = u_{22}$, and find optimal u_{22}.

Resolution field, $U_{\rm res}$

$$U_{\rm res} = \sum_i u_{\rm res}\left(\mathbf{r}_i\right)$$

$$u_{\rm res}\left(\mathbf{r}_i\right) = \begin{cases} -\frac{1}{\beta}\ln p_{\rm exp}\left(\mathbf{r}_i\right) & \text{if } i \text{ is explicit, and} \\ -\frac{1}{\beta}\ln\left[1 - p_{\rm exp}\left(\mathbf{r}_i\right)\right] & \text{if } i \text{ is united-atom} \end{cases}$$
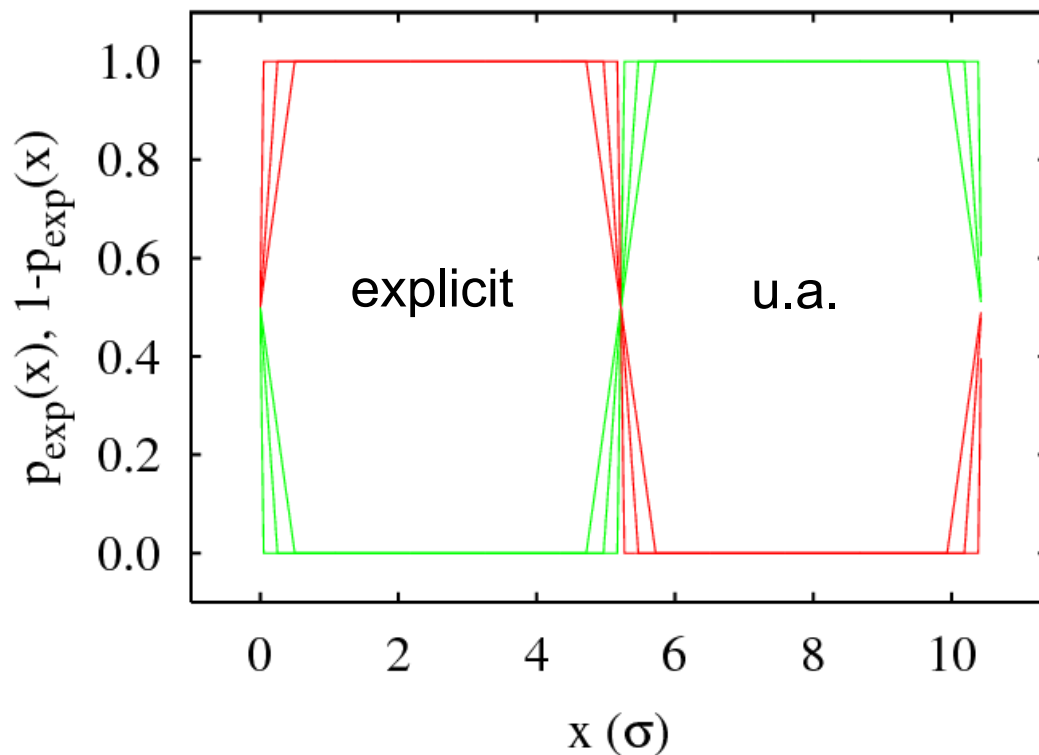
Interface width controlled by construction of $p_{\rm exp}$

u_{11}: 5-Center Lennard-Jones Pseudo-Methane
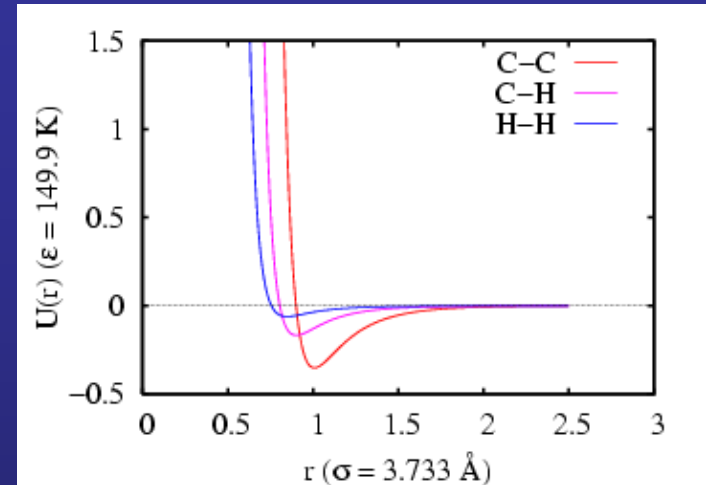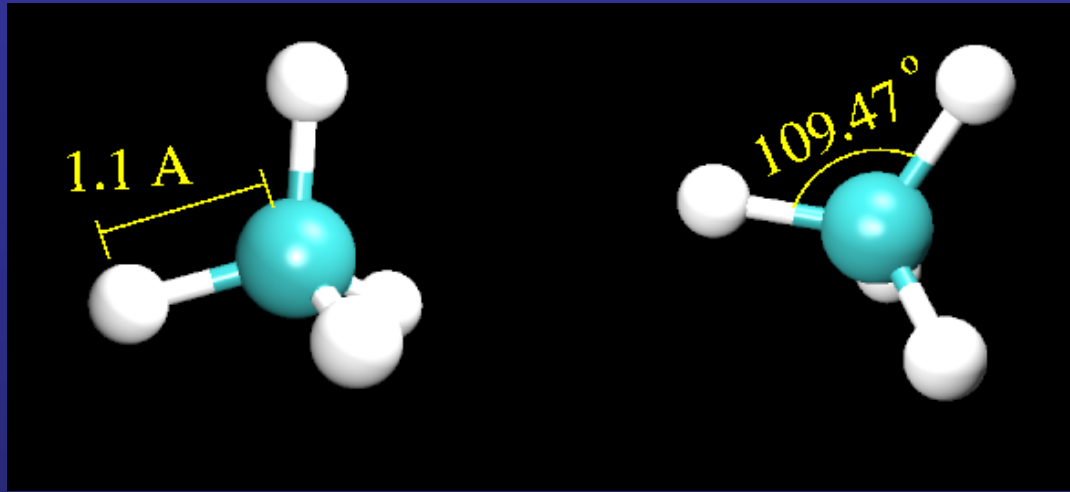
$$u_{11}\left(\mathbf{r}_{ij}, \boldsymbol{\Omega}_i, \boldsymbol{\Omega}_j\right) = \sum_{\alpha \in i} \sum_{\beta \in j} u_{\alpha\beta}\left(r_{\alpha\beta}\right)$$
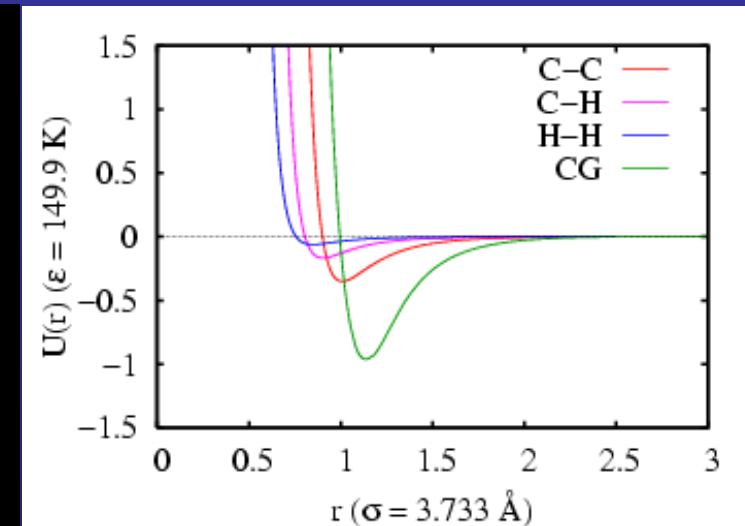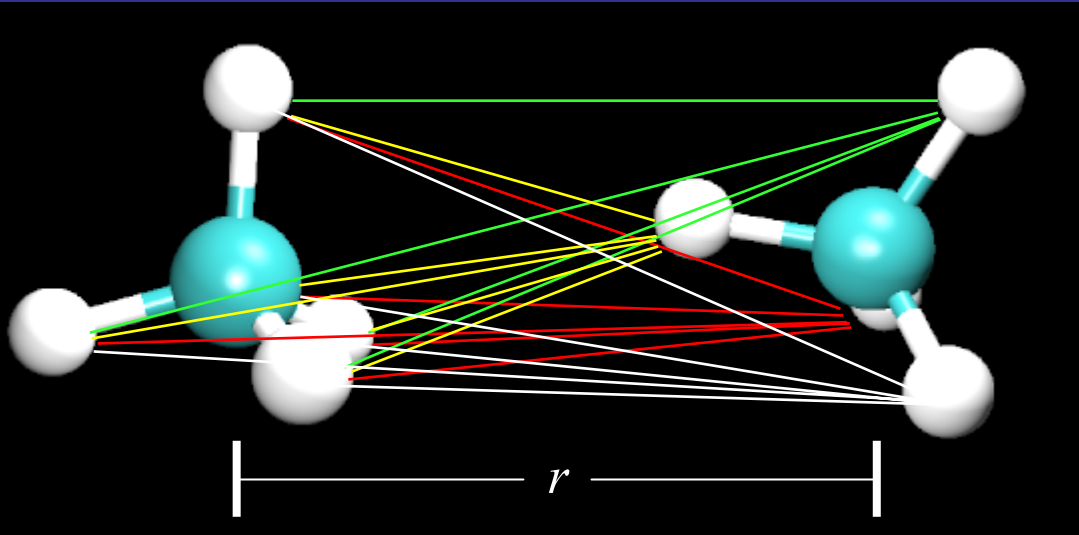
$$u_{\alpha\beta}\left(r_{\alpha\beta}\right) = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{6}\right]\underbrace{\exp\left(\frac{\gamma}{r_{\alpha\beta} - r_c}\right)}_{\text{smooth cutoff}}$$

length: $\sigma = 3.733$ Å

energy: $\epsilon = 1.496$ kJ/mol (179.9 K)

$$u_{22}(r) = -kT \ln \left\langle e^{-u_{11}(r_{12}, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2)/kT} \right\rangle_{\boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2}$$
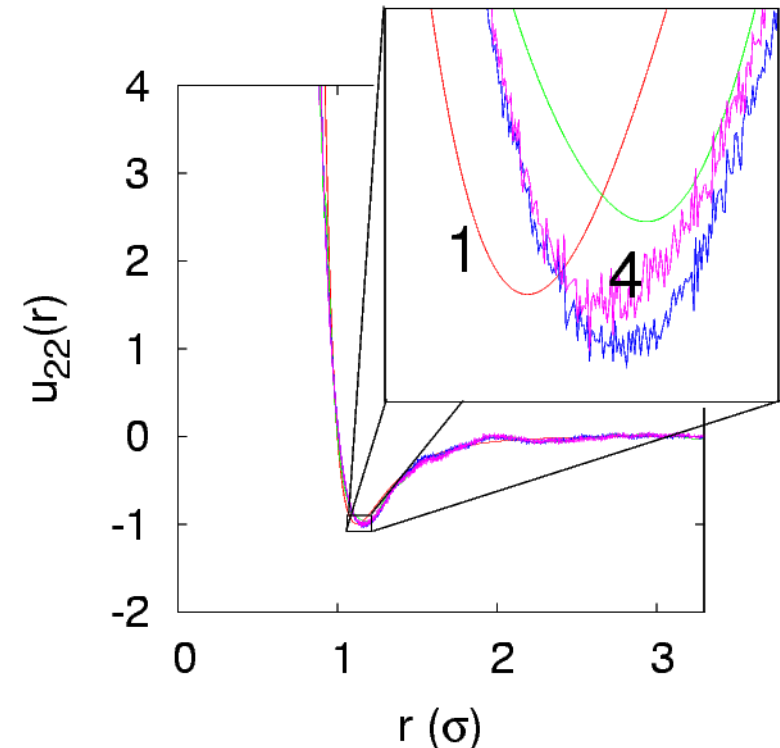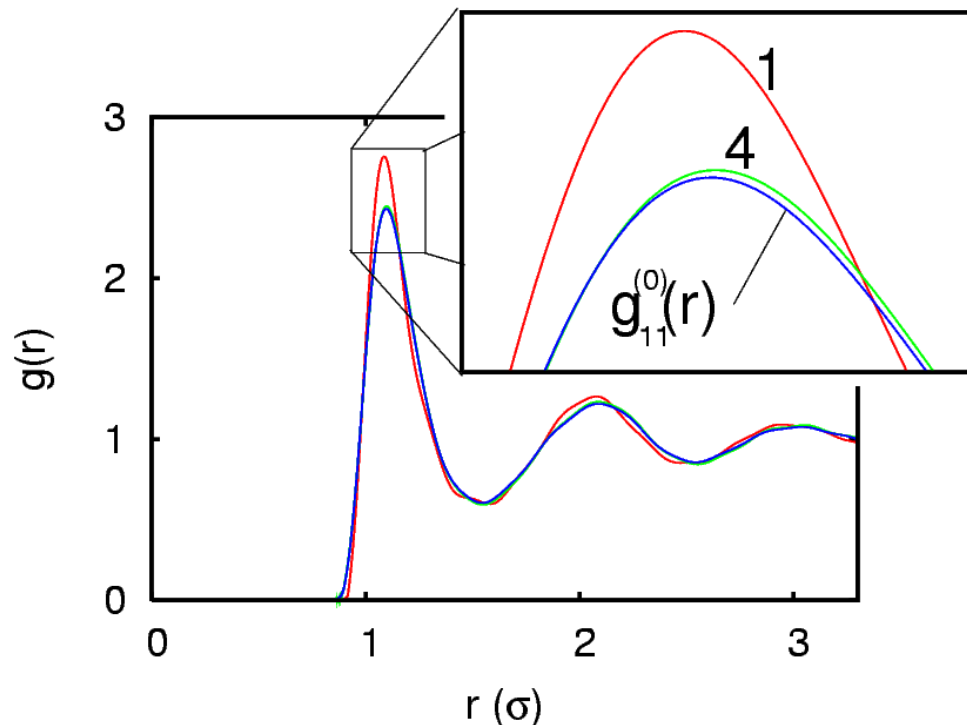
Average over ~10^5 angular orientations of
2 molecules per value of r.
$\rightarrow$ Density-independent

u_{22} Option 2: Reverse Monte Carlo (RMC)

Soper, *Chem. Phys.* **202**:295 (1996); Reith and Pütz, *J. Comput. Chem.,* **24**:1624 (2003).

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

$$u_{22}\left(r\right) \leftarrow u_{22}\left(r\right) + kT \ln \left[\frac{g_{22}(r)}{g_{11}^{(0)}(r)}\right]$$
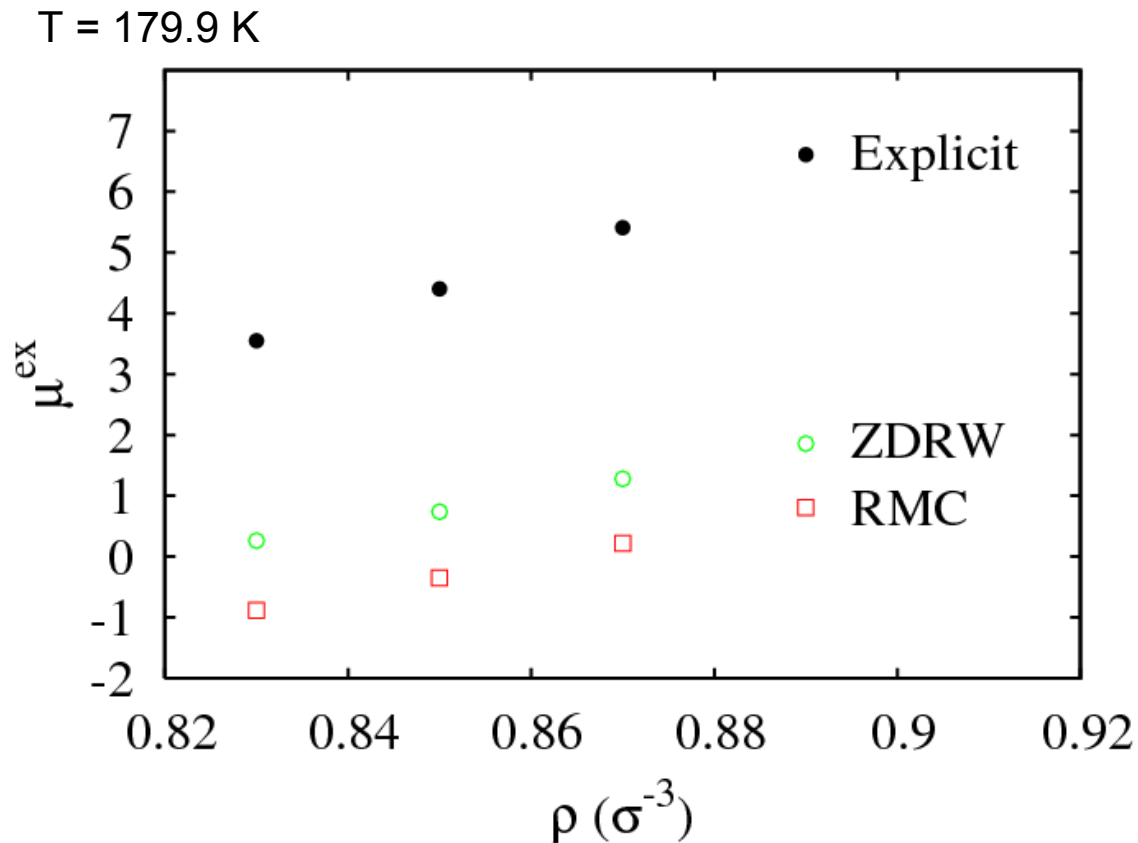
Evaluating u_{22} options in bulk simulations

μ_{ex}^{ee} Excess chemical potential, explicit-in-explicit
Measured using thermodynamic integration

μ_{ex}^{uu} Excess chemical potential, u.a.-in-u.a.
Measured using Widom's method

$$\mu_r^{\text{id}} = 0 \Rightarrow \mu_{\text{ex}}^{ee} = \mu_{\text{ex}}^{uu}$$

T = 179.9 K

Problem: configuration prefers united-atoms!
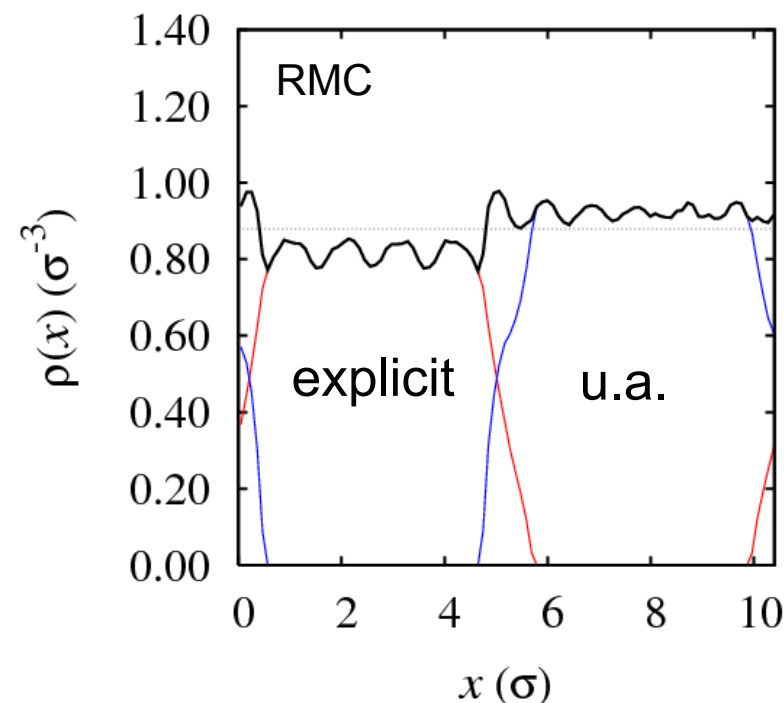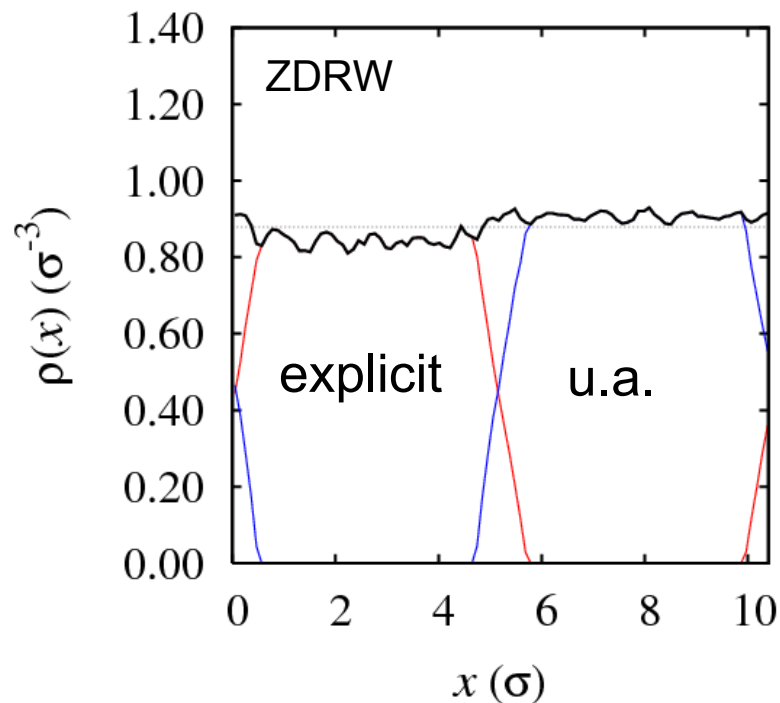
Maybe we need to keep
$$\mu_r^{\text{id}} \neq 0$$

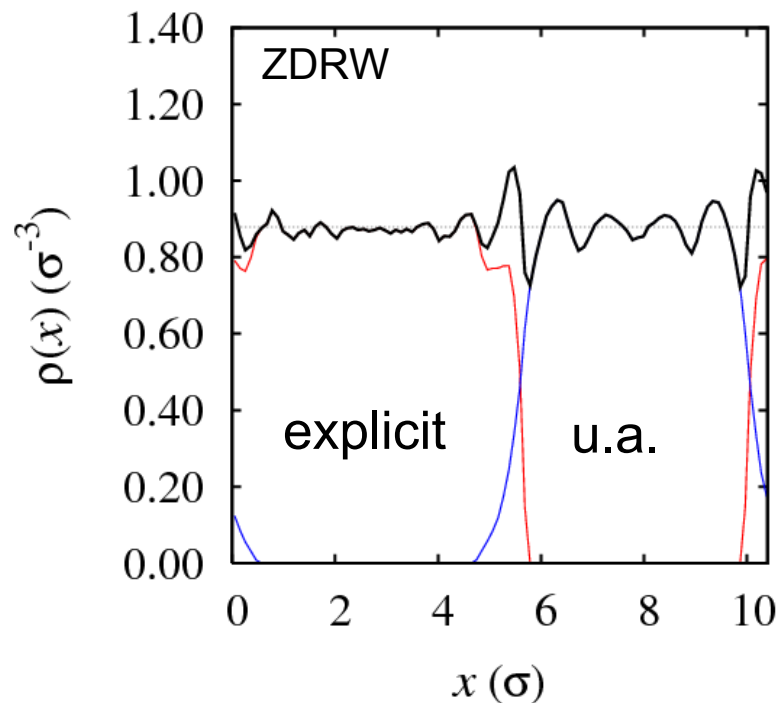But the interface will complicate matters…

- N = 1000
- ρ = 0.879
- T = 179.9 K
- V_1 = V/2
- 10^5 cycles (10^3 displacements/cycle)
- 25% of moves are resolution switch attempts

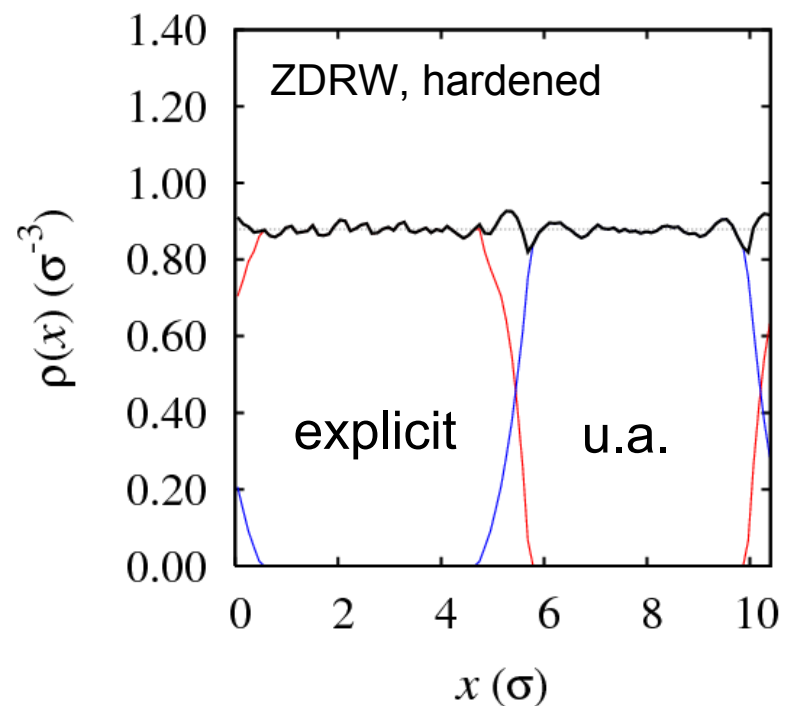# Dual resolution NVT MC: Raw U.A. Potentials

Density inhomogeneities reflect incompatibility of potentials

Dual resolution NVT MC: Variations

$$\mu_r^{\mathrm{id}} = -2.55$$

Densities equal, but
large u.a. fluctations

$$u^{\mathrm{H}}(r) = \begin{cases} Au(r) - (A-1)u(2) & \text{if } u < 2 \\ u(r) & \text{if } u > 2 \end{cases}$$

$$A = 1.027.$$

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)
- German Federal Ministry of Education and Research
- US Office of Naval Research award No. N00014-03-1-0655