Dynamically-consistent coarse-grained models

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Spring school MULTISCALE SIMULATION OF SOFT MATTER, Shiraz, Iran, April 9-12, 2018

Outline

Monday, April 9
• Recap of free energy calculation methods
• Conditional Reversible Work (CRW) coarse graining

Tuesday, April 10
• Applications to soft matter problems
• Dynamically-consistent coarse-grained models

Dynamics of coarse-grained models

Coarse graining the potential energy surface

- Energy barriers are smaller
- Faster barrier crossing
- Accelerated dynamics
- Fast equilibration (static properties)

But:
- Does coarse-graining change dynamic pathways?
- Does coarse-graining change relative barrier heights?
- Is CG dynamics realistic?
**Simple model**

- One-dimensional barrier crossing

![Diagram of barrier crossing](image)

- Boosted time step / total boosted time

\[
\Delta t_b^* = \Delta t^* \exp \left( \frac{\Delta V_b(x(t))}{k_B T} \right)
\]

- Average boost factor

\[
\alpha(T) = \frac{1}{n} \sum \exp \left( \frac{\Delta V_b(x(t))}{k_B T} \right)
\]

**A posteriori time mapping**

- Dynamic property from short-time fine-grained trajectory
- Same property from the coarse-grained trajectory
- Match for large times

![Plot of MSD vs time](image)

- Accurate for polymer dynamics in melts
- Accurate for polymer permeation
- Not accurate when relative barrier heights are modified ("telescope effect")

**Inverse mapping (n-scattering)**

- Structural correlations

![Graph of scattering function](image)
**Dynamic n-scattering function**

- Short, fine-grained MD simulations (solid/dashed lines)
- Inverse-mapped CG MD trajectories rescaled using a time mapping constant (symbols)

\[ S(Q,t) = \frac{1}{N} \sum_i \exp \{iQ \cdot \langle r_i(t) - r_i(0) \rangle \} \]

Dynamics reproduced on short and long time scales

**Polymer dynamics**

48,000 beads, 10^8 integration time steps, 1 millisecond dynamics

**Polymer permeation**

Phenol in BPA-PC melts, ~500 K, 1 bar, small concentration

- Activated hopping
- Coupling between dynamics of holes and motion of the additive
- Life-time of holes comparable to hopping time of the additive

Ethylbenzene diffusion in polystyrene

\[ D_c(T) \sim \exp \left( \frac{-E_D}{RT_0} \right) \]

Average boost factor

\[ s(T) = \frac{D_c(T)}{D_0(T)} \sim \exp \left( \frac{\Delta E}{RT_0} \right) \]

Comparison with PFG-NMR

Polydispersity and density
Dynamically consistent models

- Fluctuating atomistic forces contribute to friction
- Coarse graining may lead to changes in the relative rates of different dynamic processes
- Bottom-up calculation of "lost" friction
- Dissipative Particle Dynamics model

\[ m \frac{d^2 r_{ij}}{dt^2} = \sum_{\mu} \left( F_{i}^{CRW} + F_{i}^{D} + F_{i}^{R} \right) \]

Dissipative Particle Dynamics (DPD)

DPD equation of motion

\[ F_{i}^{D} = \gamma_{i,j}(r_{ij})(\mathbf{e}_i \cdot \mathbf{v}_i)\mathbf{e}_i \]
\[ F_{i}^{R} = \gamma_{i,j}(r_{ij})\left( \mathbf{v}_i - (\mathbf{e}_i \cdot \mathbf{v}_i)\mathbf{e}_i \right) \]

Bottom-up calculation of frictions

Friction associated with "fast" degrees of freedom

\[ \gamma_{i,j}(r_{ij}) = \left( k_B T \right)^{-1} \int_0^T dr \langle \delta F_i(t, r) \delta F_j(t, 0) \rangle \]
\[ \delta F_i(t, r) = F_i(t, r) - F_i^{CRW}(r, 0) \]

Assumption: time scale separation
Liquid-phase calculation

Conservative & dissipative interactions: liquid hexane

Coarse-grained dynamics

Acknowledgements

Emiliano Brini, Marco Dallavalle, Gregor Deichmann, Dominik Fritz, Vagelis Harmandaris, Kurt Kremer, Valentina Marcon, David Rosenberger, Fereshte Taherian