Dynamically-consistent coarse-grained models

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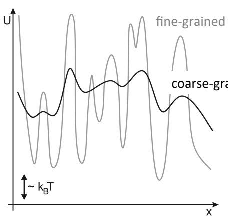
Outline

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



E. Brini *et al. Soft Matter* **9**, 2108 (2013)

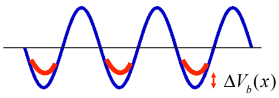
- Energy barriers are smaller
- Faster barrier crossing
- Accelerated dynamics
- Fast equilibration (static properties)

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

Simple model

- One-dimensional barrier crossing

Hyper-MD
A.F. Voter, *JCP* (1997), *PRL* (1997)



- Boosted time step / total boosted time

$$\Delta t_i^b = \Delta t^{MD} \exp\left[\Delta V_b(x(t_i))/k_B T\right] \qquad t^b = \sum_i^{n_{tot}} \Delta t^{MD} \exp\left[\Delta V_b(x(t_i))/k_B T\right]$$

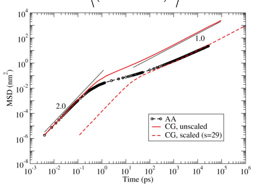
- Average boost factor

$$s(T) \equiv \frac{t^b}{t^{MD}} = \frac{1}{n_{tot}} \sum_i^{n_{tot}} \exp\left[\Delta V_b(x(t_i))/k_B T\right]$$

D. Fritz et al. *PCCP* **13**, 10412 (2011)

A posteriori time mapping

$$MSD(t) = \left\langle \left(\mathbf{r}(t) - \mathbf{r}(0)\right)^2 \right\rangle$$



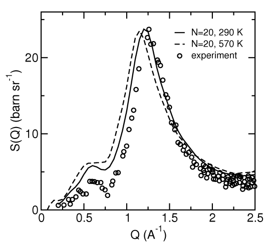
- Dynamic property from short-time fine-grained trajectory
- Same property from the coarse-grained trajectory
- Match for large times

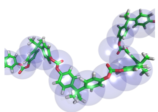
➡ time mapping constant s

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

Inverse mapping (n-scattering)

Coherent n-scattering function



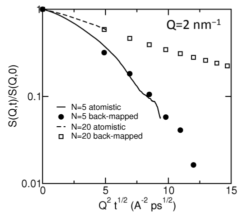


- Structural correlations

B. Hess *et al. Soft Matter* **2**, 409 (2006)

Dynamic n-scattering function

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



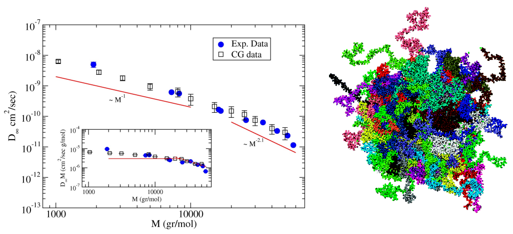
Chain dynamic form factor

$$S(Q,t) = \frac{1}{n}\left\langle \sum_{i,j} l_i l_j \exp\left[i\mathbf{Q}\cdot\left(\mathbf{r}_i(t) - \mathbf{r}_j(0)\right)\right]\right\rangle_{|\mathbf{Q}|}$$

➡ Dynamics reproduced on short and long time scales

B. Hess *et al. Soft Matter* **2**, 409 (2006)

Polymer dynamics

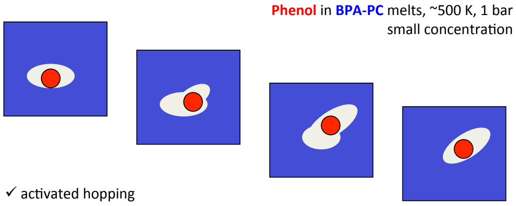


48,000 beads, 10^8 integration time steps, 1 millisecond dynamics

V.A. Harmandaris, K. Kremer, *Macromolecules* **42**, 791 (2009) Experiments: M. Antonietti et al. *Makromol. Chem.* **188**, 2317 (1987)

Polymer permeation

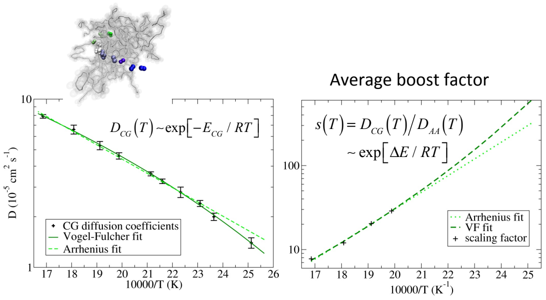
Phenol in **BPA-PC** melts, ~500 K, 1 bar
small concentration



✓ activated hopping
✓ coupling between dynamics of holes and motion of the additive
✓ life time of holes comparable to hopping time of the additive

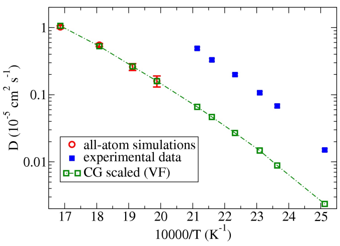
O. Hahn et al. *J. Chem. Phys.* **111**, 6061 (1999)

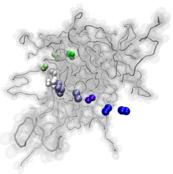
Ethylbenzene diffusion in polystyrene



D. Fritz et al. *Soft Matter* **5**, 4556 (2009)
D. Fritz et al. *PCCP* **13**, 10412 (2011)

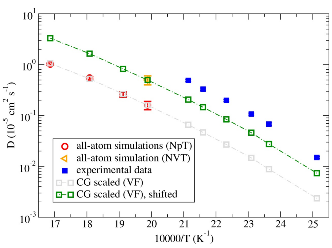
Comparison with PFG-NMR





D. Fritz et al. *Soft Matter* **5**, 4556 (2009)
D. Fritz et al. *PCCP* **13**, 10412 (2011)

Polydispersity and density



D. Fritz et al. *Soft Matter* **5**, 4556 (2009)
D. Fritz et al. *PCCP* **13**, 10412 (2011)

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

R.L.C. Akkermans, W. J. Briels (2000)
H. Lei, B. Caswell, G. E. Karniadakis (2010)
C. Hijón, P. Español, et al. (2010)
S. Izvekov, B.M. Rice, J. Chem. Phys. (2014)

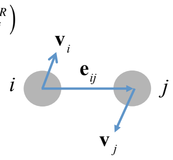
Dissipative Particle Dynamics (DPD)

DPD equation of motion

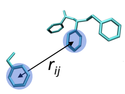
$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}_i = \sum_{j \neq i} \left(\mathbf{F}_{ij}^{CRW} + \mathbf{F}_{ij}^{D} + \mathbf{F}_{ij}^{R} \right)$$

$$\mathbf{F}_{ij,\parallel}^{D} = \gamma_{ij,\parallel}(r_{ij}) \left(\mathbf{e}_{ij} \cdot \mathbf{v}_{ij} \right) \mathbf{e}_{ij}$$

$$\mathbf{F}_{ij,\perp}^{D} = \gamma_{ij,\perp}(r_{ij}) \left(\mathbf{v}_{ij} - (\mathbf{e}_{ij} \cdot \mathbf{v}_{ij}) \mathbf{e}_{ij} \right)$$



Bottom-up calculation of frictions



Assumption: time scale separation
Liquid-phase calculation

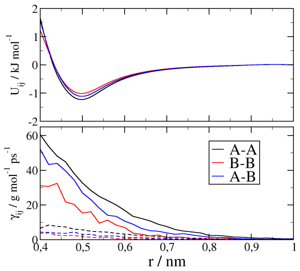
Friction associated with "fast" degrees of freedom

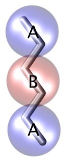
$$\gamma_{ij}(r_{ij}) = \left(k_B T\right)^{-1} \int_0^{\infty} dt \left\langle \delta \mathbf{F}_{ij}(r_{ij}, t) \delta \mathbf{F}_{ij}(r_{ij}, 0) \right\rangle$$

$$\delta \mathbf{F}_{ij}(r_{ij}, t) = \mathbf{F}_{ij}(r_{ij}, t) - \mathbf{F}_{ij}^{CRW}(r_{ij})$$

G. Deichmann, V. Marcon, N. F. A. van der Vegt, *J. Chem. Phys.* **141**, 224109 (2014)

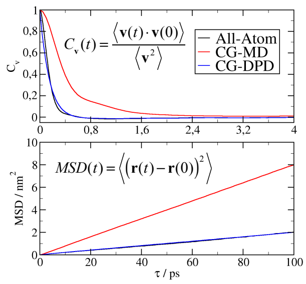
Conservative & dissipative interactions: liquid hexane

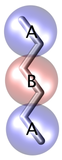




G. Deichmann, N. F. A. van der Vegt (unpublished data)

Coarse-grained dynamics





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Acknowledgements

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