TECHNISCHE UNIVERSITÄT DARMSTADT

Applications of multiscale simulation

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Computational Physical Chemistry

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

Outline

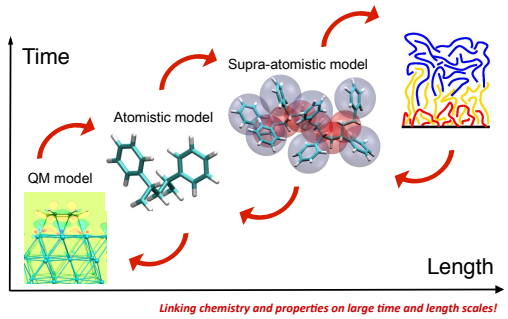
Monday, April 9

- Recap of free energy calculation methods
- Conditional Reversible Work (**CRW**) coarse graining

Tuesday, April 10

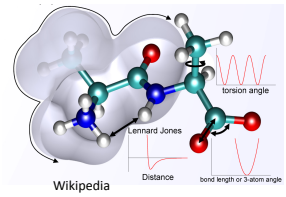
- Applications to soft matter problems
- Dynamically-consistent coarse-grained models

Multiscale simulations of soft matter



Linking chemistry and properties on large time and length scales!

Atomistic force fields



Wikipedia

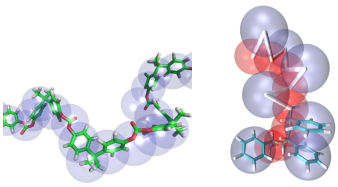
- Quantum chemistry
  - covalent / bonded interactions
  - atomic charges
- Parameterization
  - non-covalent /non-bonded interactions (excluded volume, dispersion)
  - atomic charges

$$U^{AA} = \sum U_B^{AA} + \sum U_{NB}^{AA}$$

Coarse-grained force fields

Transferability

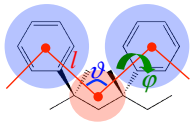
- ❑ State point
- ❑ Chemical ("atom types")



B. Hess et al. *Soft Matter* **2**, 409 (2006) D. Fritz et al. *Macromolecules* **42**, 7579 (2009)

$$U^{CG} = \sum U_B^{CG} + \sum U_{NB}^{CG}$$

Bonded interactions



Coarse-grained configuration

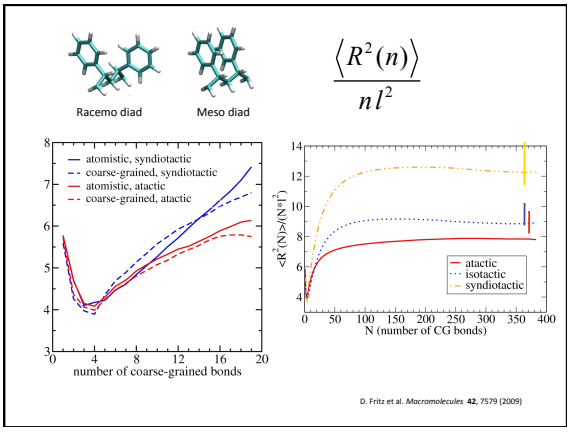
$$\xi = \{l, \vartheta, \varphi\}$$

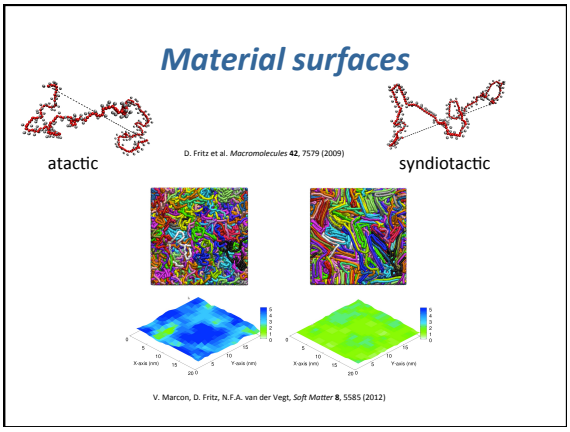
Bonds Angles Torsions

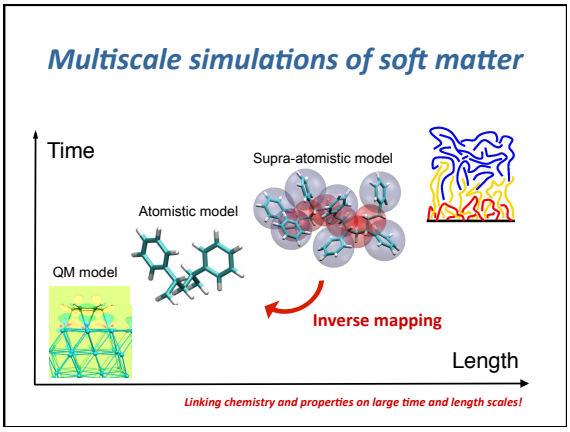
$$\exp\left[-\beta U_B^{CG}(\xi')\right] = \sum_{\Gamma} \exp\left[-\beta U^{at}(\Gamma)\right] \delta\left(\xi(\Gamma) - \xi'\right)$$

Sampling: single chain in free space, local interactions

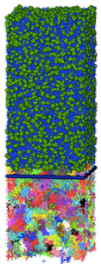
D. Fritz et al. *Macromolecules* **42**, 7579 (2009)

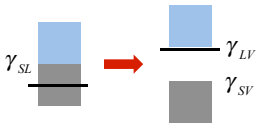

Racemo diad
Meso diad
$\frac{\langle R^2(n)\rangle}{nl^2}$
atomistic, syndiotactic
coarse-grained, syndiotactic
atomistic, atactic
coarse-grained, atactic
number of coarse-grained bonds
atactic
isotactic
syndiotactic
N (number of CG bonds)
D. Fritz et al. Macromolecules 42, 7579 (2009)


Material surfaces
atactic
D. Fritz et al. Macromolecules 42, 7579 (2009)
syndiotactic
V. Marcon, D. Fritz, N.F.A. van der Vegt, Soft Matter 8, 5585 (2012)


Multiscale simulations of soft matter
Time
Supra-atomistic model
Atomistic model
QM model
Inverse mapping
Length
Linking chemistry and properties on large time and length scales!

Solid-liquid work of adhesion

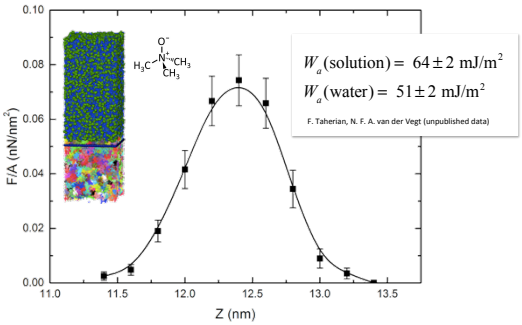




F. Leroy et al. *Macromol. Rapid Commun.* **30**, 864 (2009)

$$W_{ad} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$
$$= \gamma_{LV}\left(1 + \cos\theta\right)$$

Cosolvent effects on wettability

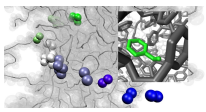


$W_a(\text{solution}) = 64 \pm 2 \text{ mJ/m}^2$

$W_a(\text{water}) = 51 \pm 2 \text{ mJ/m}^2$

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

Solvent swelling



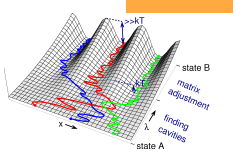
molten polymer (well equilibrated atomistic trajectory obtained through inverse mapping)

State A

+

State B

polymer + solute

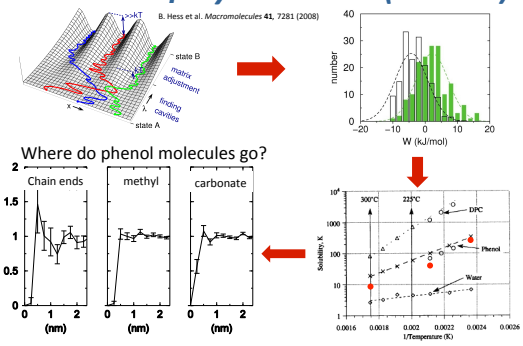


Sample multiple paths and obtain free energy through Jarzynski equality

$$\mu_{ex} = \Delta A_{AB} \le \langle W_{AB} \rangle$$
$$\mu_{ex} = -k_B T \log \left\langle e^{-\beta W_{AB}} \right\rangle_A$$

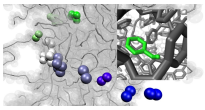
B. Hess et al. *Macromolecules* **41**, 2283-2289 (2008)

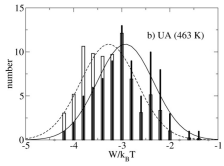
Phenol in polycarbonate (BPA-PC)

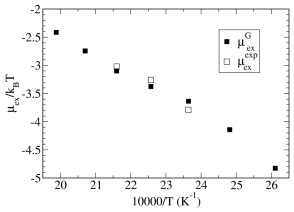


Where do phenol molecules go?

Ethylbenzene in polystyrene





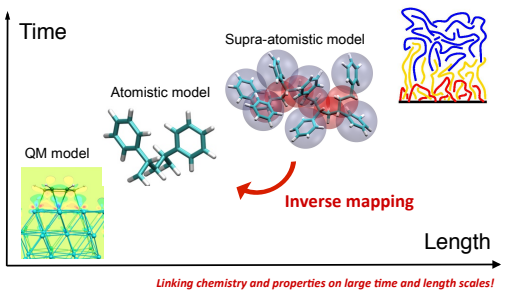


Non-equilibrium free-energy calculations

$$\mu_{ex} = -k_B T \ln\left\langle \exp\left(-W_{AB} / k_B T\right)\right\rangle_A$$

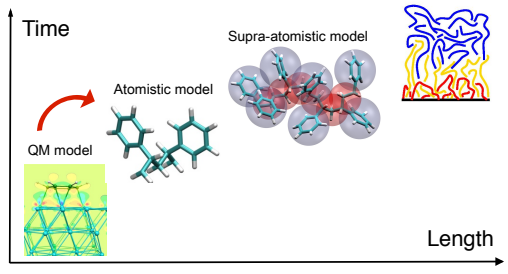
D. Fritz, et al. *Soft Matter* **5**, 4556 (2009)

Multiscale simulations of soft matter



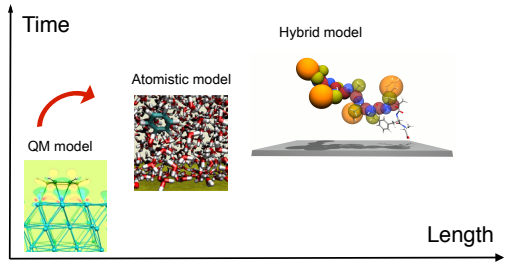
Linking chemistry and properties on large time and length scales!

Multiscale simulations of soft matter



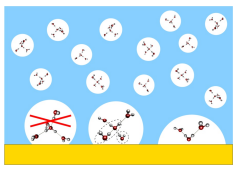
Linking chemistry and properties on large time and length scales!

Multiscale simulations of soft matter



Linking chemistry and properties on large time and length scales!

Water on metals



Stable substructures: use mono-, di-, and tri-mers to calculate E_{ads}

- feasible quantum calculation
- E_{ads} is well defined:

$$E_{ads} = E_{surf+N_{mol}} - \left(E_{surf} + E_{N_{mol}}\right)$$

Ni(111)
Monomer: E_{ads} ~ 0.24 eV
Dimer: E_{ads}/N_{H_2O} ~ 0.24 eV
Trimer: E_{ads}/N_{H_2O} ~ 0.27 eV

Au(111)
E_{ads} ~ 0.1 eV

Pt/Pd(111)
E_{ads} ~ 0.33-0.35 eV

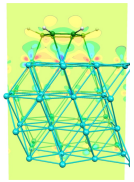
(energy of a H-bond ~ 0.22 eV)

L. Delle Site, D. Sebastiani, *J. Chem. Theory Comp.* **1**, 78 (2005)

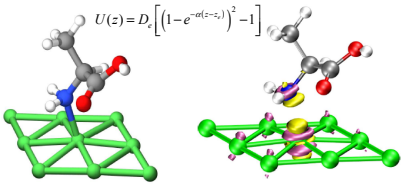
Organic molecules on metal surfaces

Benzene

Alanine



$$U(z) = D_e\left[\left(1 - e^{-\alpha(z-z_e)}\right)^2 - 1\right]$$

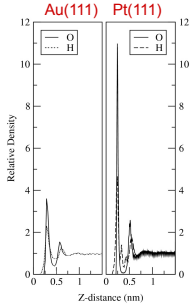


➡ Iterative quantum-statistical modeling

P. Schravendijk et al. *J. Phys. Chem. C* **111**, 2631 (2007)

Wetting of metal surfaces

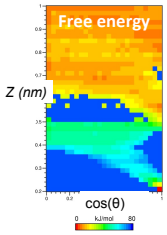
Au(111) Pt(111)

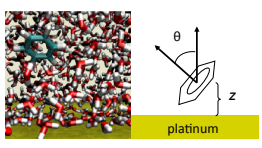


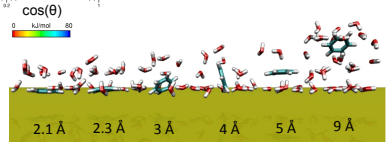
- Clean metal surfaces are hydrophilic
- Pronounced fluid structuring on Pt
- How does that affect the binding of organic solutes?

P. Schravendijk et al. *J. Phys. Chem. C* **111**, 2631 (2007)

Benzene adsorption

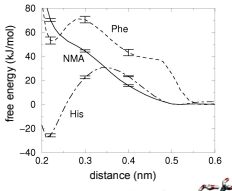




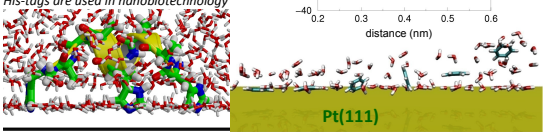


Peptide-surface interaction

- Interactions of organic solutes with metal surfaces under wet conditions
- Understand surface interactions and(macro)molecular conformations



His-tags are used in nanobiotechnology



L. Ghiringhelli et al. *J. Am. Chem. Soc.* **130**, 13460 (2008)