Systematic Coarse-Graining using VOTCA

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VOTCA Contributors

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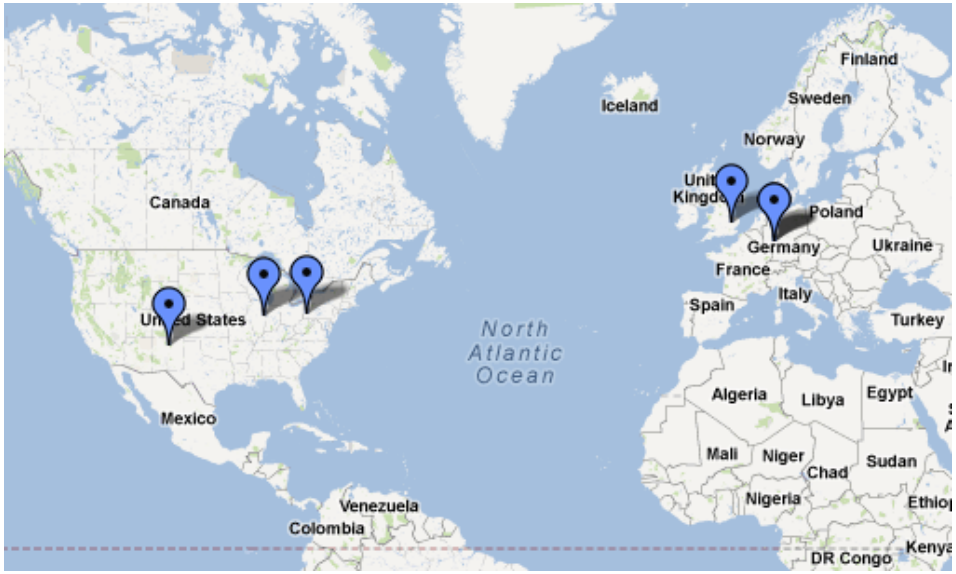


Implementations

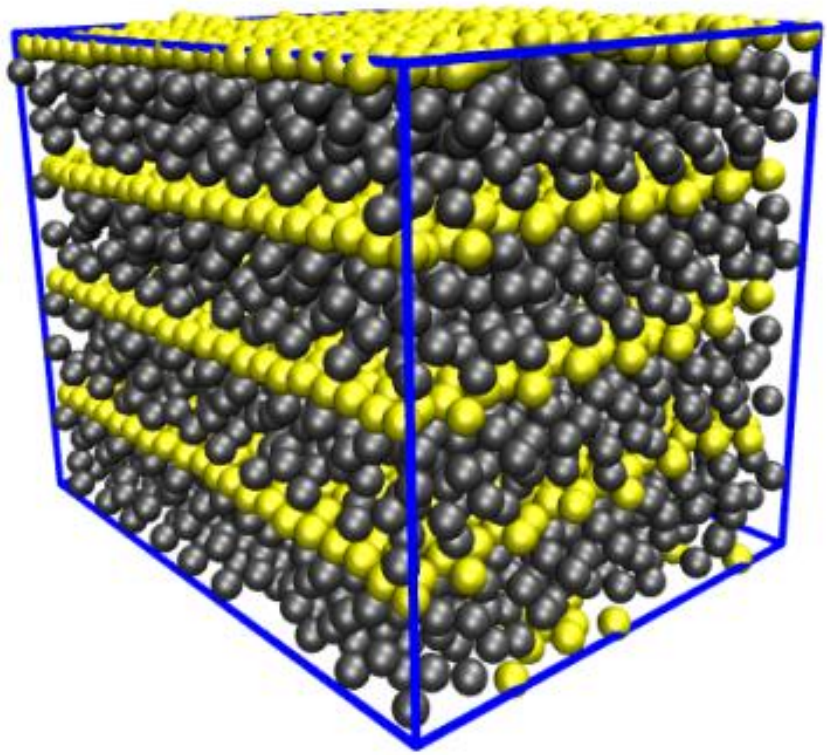
Tristan Bereau	Interface to ESPResSo
Sebastian Fritsch	Interface to AdResS
Mara Jochum	Simplex algorithm
Konstantin Koschke	Parallel analysis engine
Alexander Lukyanov	Force-matching
Sikandar Mashayak	Relative entropy method

Why coarse-graining?

Coarse-graining is an essential part of multiscale simulations:

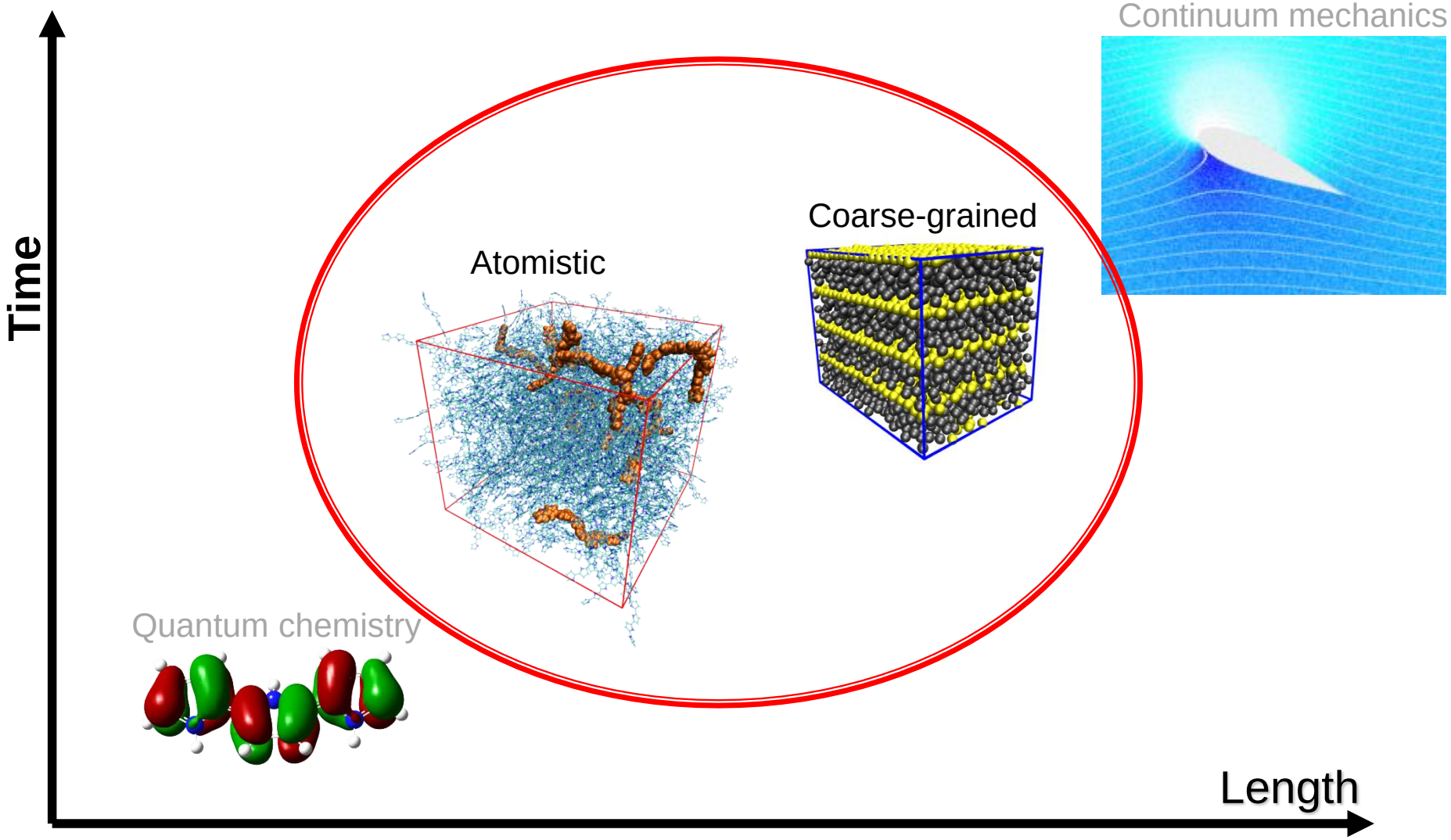
Benefits:

- Less interactions to evaluate
- Less degrees of freedom to integrate
- Intrinsic speedup of dynamics



Enhances accessible range of time- and lengthscales

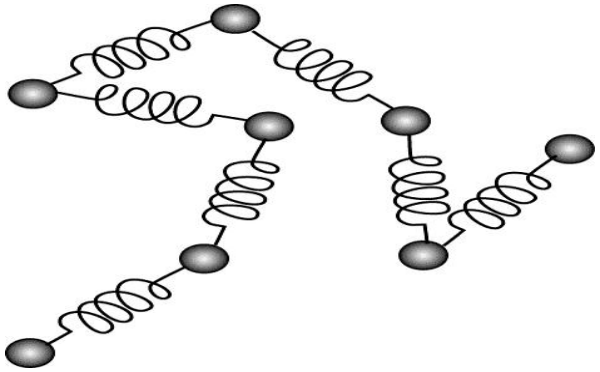
Motivation


Continuum mechanics
Coarse-grained
Atomistic
Quantum chemistry
Time
Length

Polymer models

Example: Gaussian chain

- Represent polymer by beads which are connected by strings



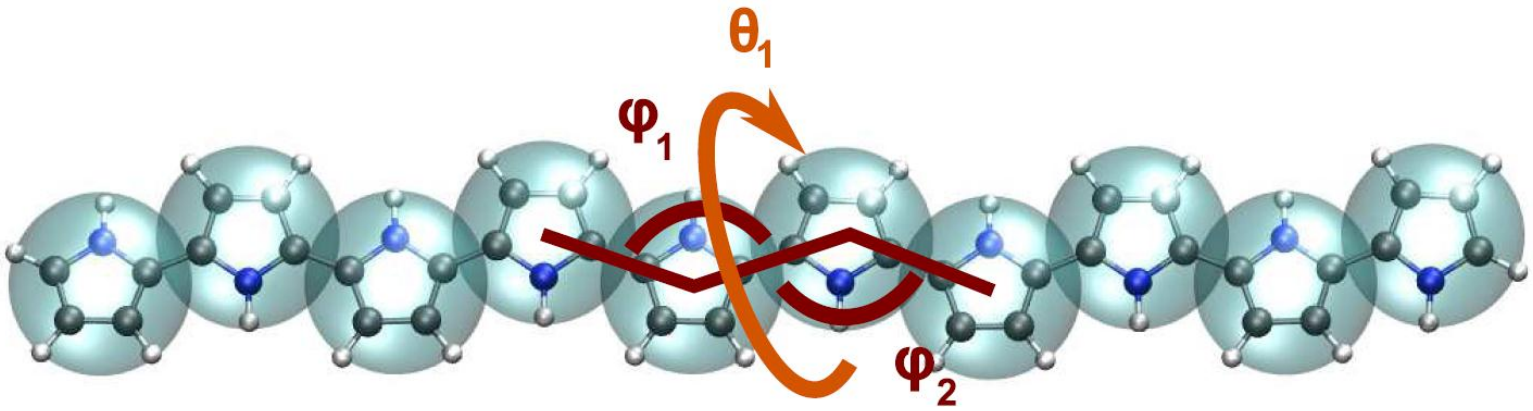
$$H = \frac{1}{2} m_i {p_i}^2 + \frac{3kT}{2b^2} (r_{i+1} - r_i)^2$$

- Works well to obtain scaling laws if $r \gg l_p$
  (end-end distance, …)
- Various modifications / extensions (e.g. add stiffness)
- Often analytical solution available

Problem: No connection to underlying chemistry

Systematic coarse-graining

Is there a coarse-grained model which reproduces selected properties of a given (atomistic) reference system?

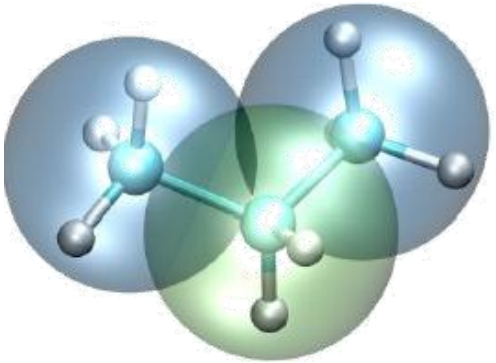


- Mapping from atomistic to coarse-grained system
- Structure based mapping allows to reintroduce atomistic details (back-mapping)

Mapping operator

$$\boldsymbol{r}^n = \{\boldsymbol{r}_1, \dots, \boldsymbol{r}_n\} \longrightarrow \boldsymbol{R}^N = \{\boldsymbol{R}_1, \dots, \boldsymbol{R}_N\}$$

$$R_I = M_I R_I = \sum_i c_{Ii} r_i$$



Equilibrium probability density for mapped CG variables

$$p_R(\boldsymbol{R}^N) = \int d\boldsymbol{r}^n \, p_r(\boldsymbol{r}^n) \delta(M_{\boldsymbol{R}}(\boldsymbol{r}^n) - \boldsymbol{R}^N)$$

Consistency of the coarse-grained and the atomistic models

$$\boldsymbol{p_R}(\boldsymbol{R}^N) = \boldsymbol{P_R}(\boldsymbol{R}^N)$$

Problem: Full multibody distribution function

Bonded interactions: Boltzmann inversion

- Assume that probability distributions for bond, angle, torsion factorize

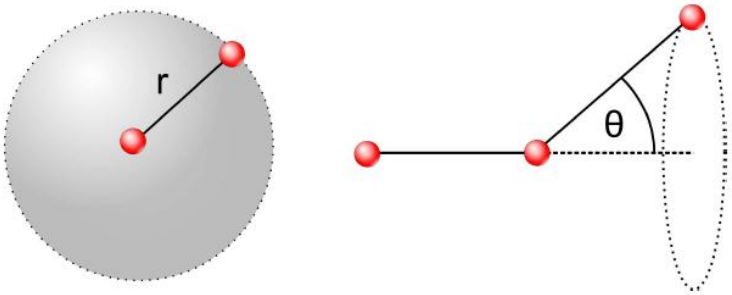
$$P(r, \varphi, \theta) = P(r)P(\varphi)P(\theta)$$

- Invert Boltzmann distribution to obtain potential

$$P(r) = \exp\left(-\frac{U(r)}{k_B T}\right), \qquad U(r) = -k_B T \ln P(r)$$

- Important: use scaled distributions!

$$P(r) = \frac{P'(r)}{r^2}, \qquad P(\varphi) = \frac{P'(\varphi)}{\sin(\varphi)}$$



VOTCA: csg_boltzmann

E. Tschöp et al, Acta Polymer. *49*, 61 – 74 (1998)

Henderson theorem

- Formulate coarse-graining based on correlation functions

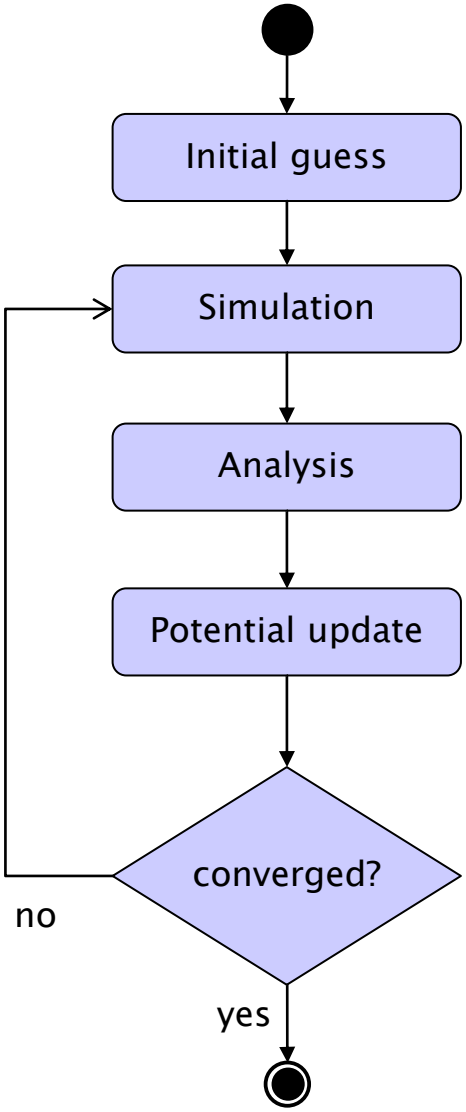
$\rho_1(\boldsymbol{r}_1)$	density
$\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$	radial distribution function (RDF)
$\rho_3(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)$	3-body correlations
…	…

- Truncate after ρ_1, ρ_2 (easy to compute)
- **Henderson theorem:**
  For every $\rho_2(r)$ exists a unique (coarse-grained) pairwise potential $\mathrm{U}(r)$

All structure based iterative method (ρ_1, ρ_2-based) must converge to the same coarse-grained potential

R. Henderson, Phys. Lett. A, A49, 197-198 (1974)

Iterative Boltzmann Inversion (IBI)



- Iteratively fit radial distribution function using tabulated potentials

$$U_0(r) = -k_B T \ln g^{Ref}(r)$$

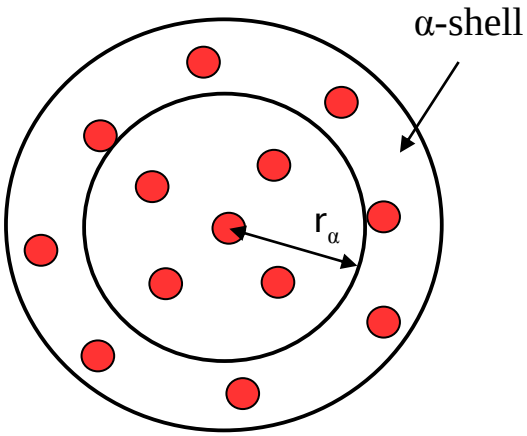
$$\Delta U_n(r) = k_B T \ln \frac{g_n(r)}{g^{Ref}(r)}$$

- Features:
  - Easy to implement
  - no correlations (local update)
  - robust

VOTCA: csg_inverse

D. Reith et al., J. Comp. Chem. 24 (13), 1624 (2003)
A. Lyubartsev et al., Phys. Rev. E 52 (4), 3730 (1995)

Inverse Monte Carlo update



Idea: Tabulate the interaction potential and rewrite all interactions using the number of particles in a shell α

$$H = \sum_{i,j} U(r_{ij}) = \sum_{\alpha} S_\alpha U_\alpha$$

Expand the expectation value of the number of particles in a shell to the change of the potential

$$< S_\alpha > - S_\alpha^{ref} = \sum_{\gamma} \frac{\partial < S_\alpha >}{\partial U_\gamma} \Delta U_\gamma + \mathcal{O}(\Delta U^2)$$

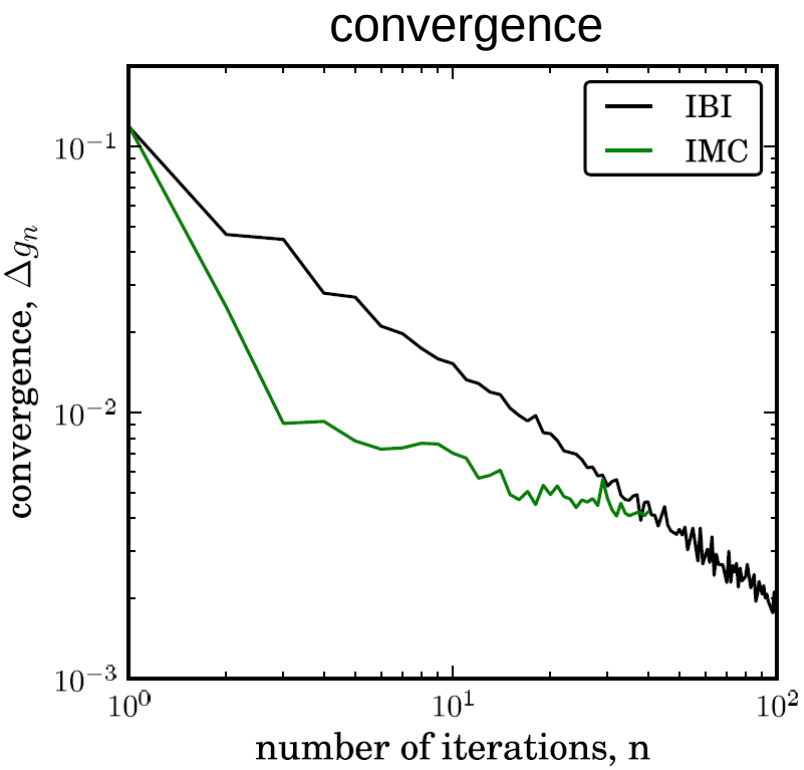
$$\frac{\partial < S_\alpha >}{\partial U_\gamma} = \frac{\partial}{\partial U_\gamma} \frac{\int dq\, S_\alpha(q) \exp[-\beta H(q)]}{\int dq\, \exp[-\beta H(q)]}$$

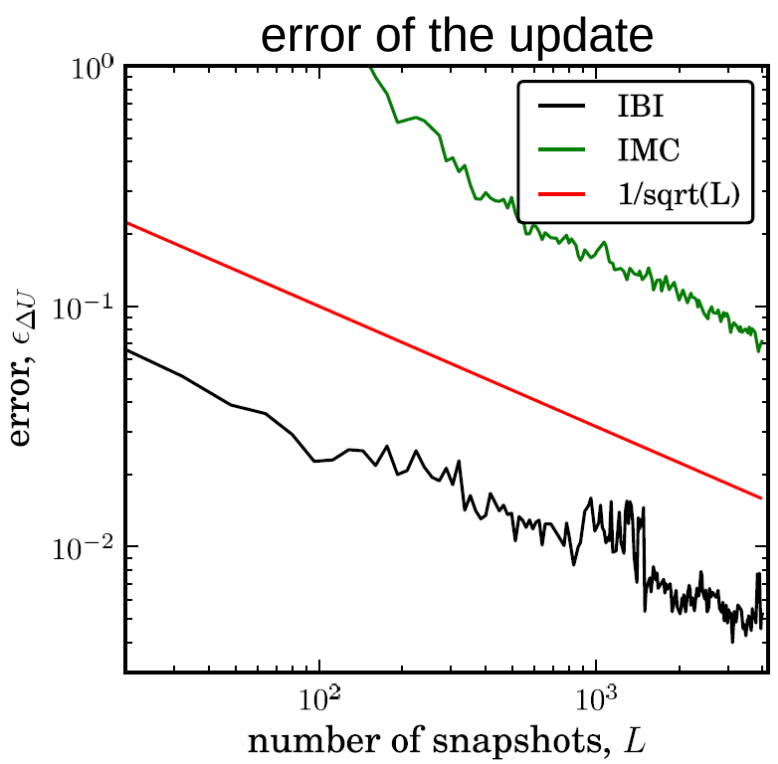
$$\Delta\langle S_\alpha \rangle = \sum_{\gamma} \frac{\langle S_\alpha \rangle \langle S_\gamma \rangle - \langle S_\alpha S_\gamma \rangle}{k_B T} \Delta U_\gamma$$

non-local,
correlations included

A. Lyubartsev et al., Phys. Rev. E 52 (4), 3730 (1995)

Efficiency of the iterative methods





- IMC converges faster but needs longer iterations
- In this example: less computational costs for IBI
- What if correlations are present?

Potential of Mean Force (PMF)

Starting from consistency relation of the coarse-grained and the atomistic models

$$\boldsymbol{p_R(R^N) = P_R(R^N)}$$

$$exp[-\beta U(R^N)] \sim \int dr^n \exp[-\beta u(r^n)]\, \delta(M_{RI}(r^n) - R^N)$$

or

$$F_I(R^N) = < \mathcal{F}_I(r^n) >_{R^N}$$

- The many-body potential of mean force (PMF) is a conditioned free energy surface in the coordinate space of the CG variables
- The CG force-field is F_I a conditioned expectation value of $\mathcal{F}_I$ for an atomistic system

PMF provides **exact** mapping of the atomistic onto CG system

Problem: PMF requires many-body potential functions, while MD force-fields provide a limited set basis set (pair-wise potentials, bonds, angles, dihedrals)

W. Noid et al., J. Chem. Phys. 120, 244114 (2008)

Force matching
(Multiscale coarse-graining)

- Solution: Use variational principle to project the many-body potentials on the functions provided by the force-field

$$x^2 = \left\langle \sum_I \left| F_i^{CG} - \sum_{i \in 1} c_i f_i^{Ref} \right|^2 \right\rangle$$

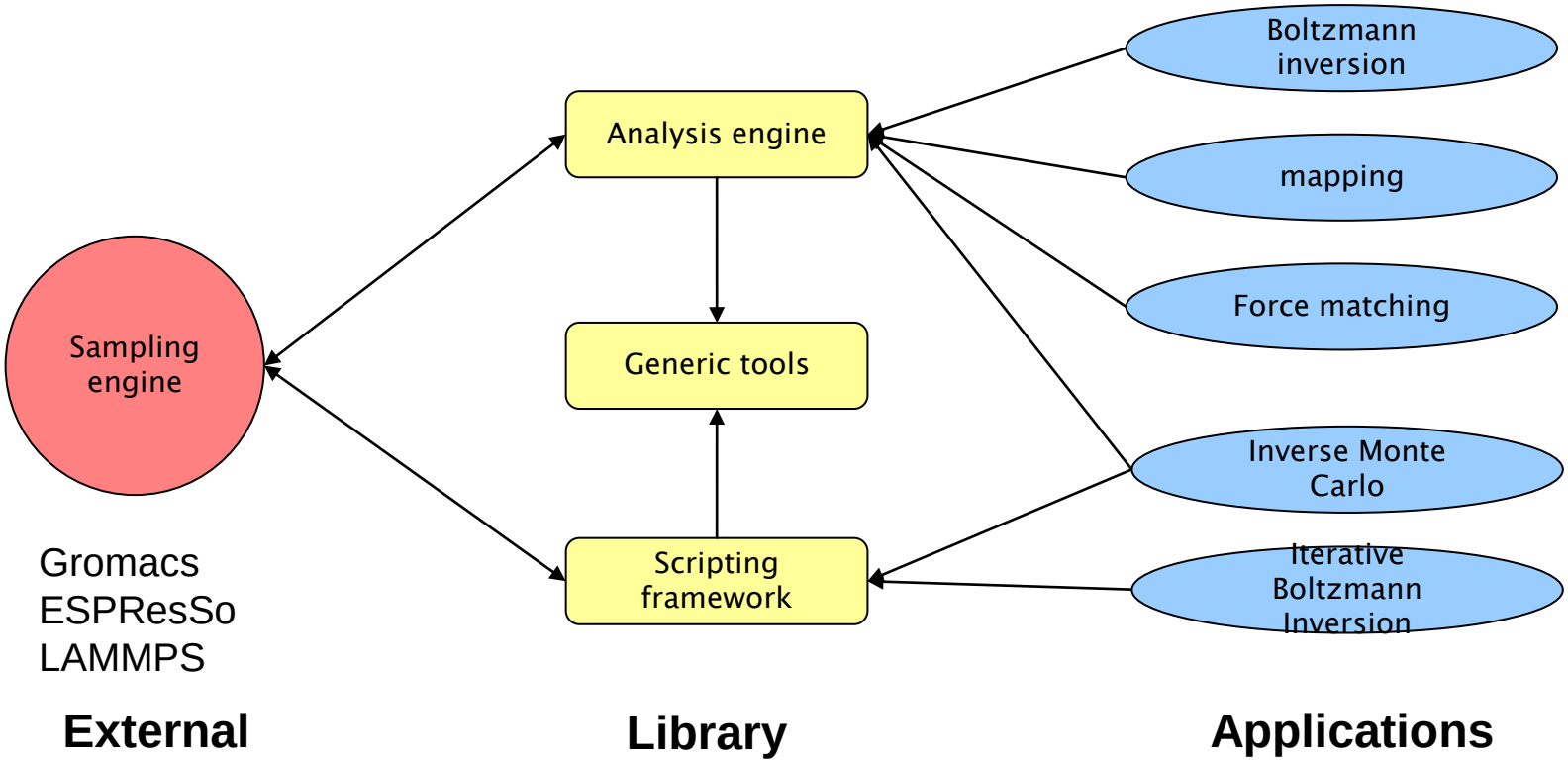
- Splines or step functions → linear least squares fit
- Not iterative → need to add additional terms to the coarse-grained force-field to improve results
- Requires reference forces

VOTCA:
csg_fmatch

S. Izvekov and G. Voth, J. Chem. Phys. 123, 134105 (2005).
W. Noid et al., J. Chem. Phys. 120, 244114 (2008)

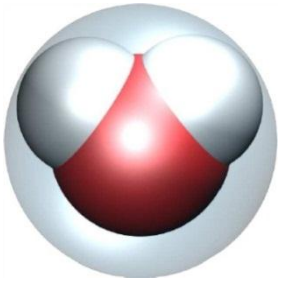
VOTCA

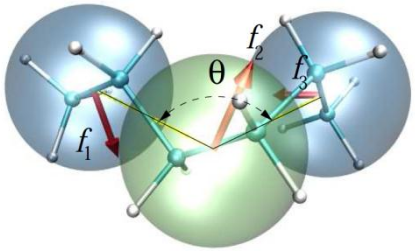
- Consistent implementation of methods
  → allow for direct comparison
- Framework for the implementation of new methods

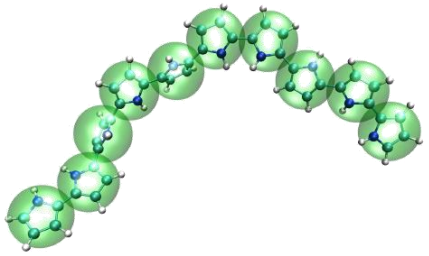


V. Rühle et al, J. Chem. Theo. Comp. 5 (12), 3211 (2009)

Examples







Water

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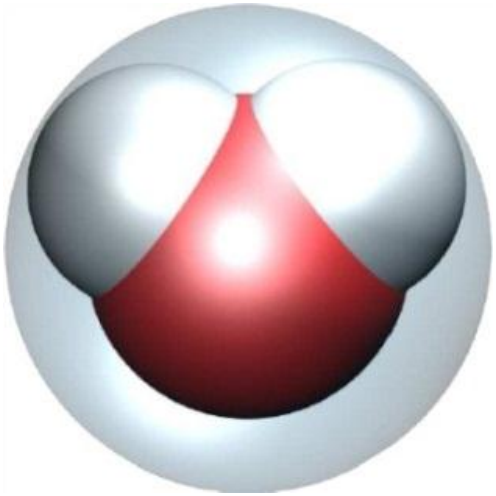
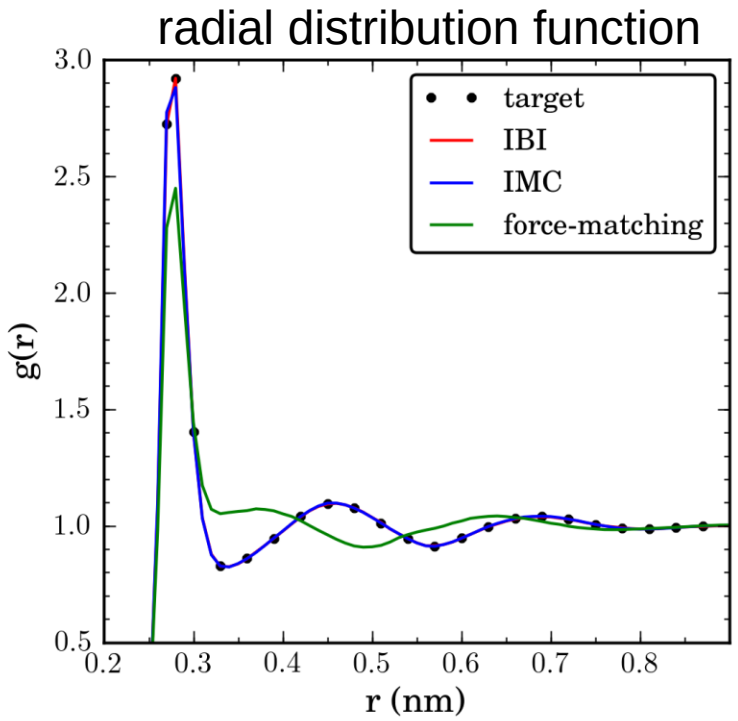
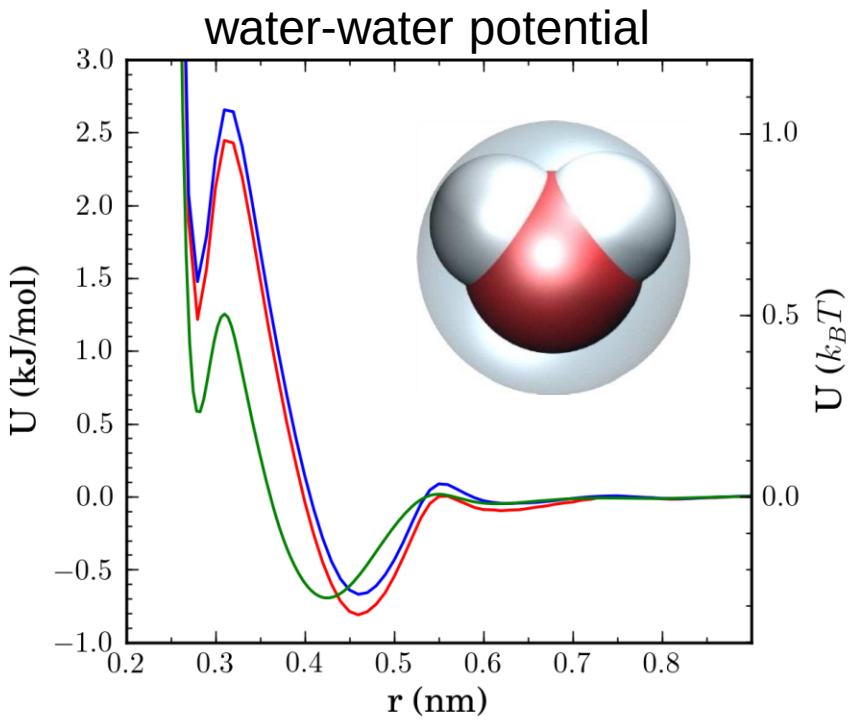
1 cg bead
centre of mass mapping
spherical potential



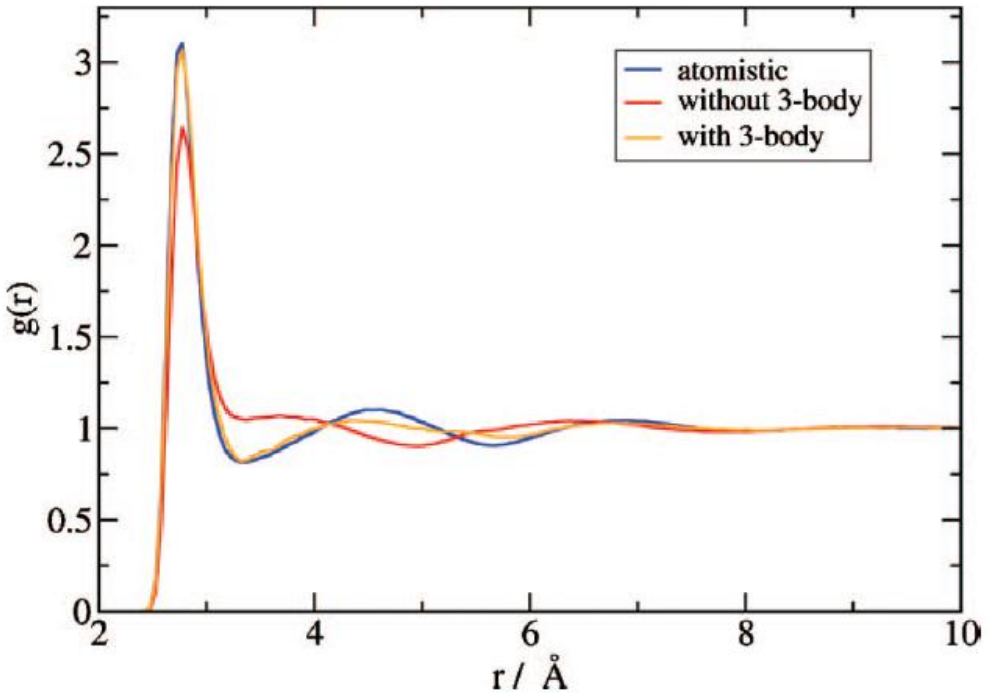
SPC/E water

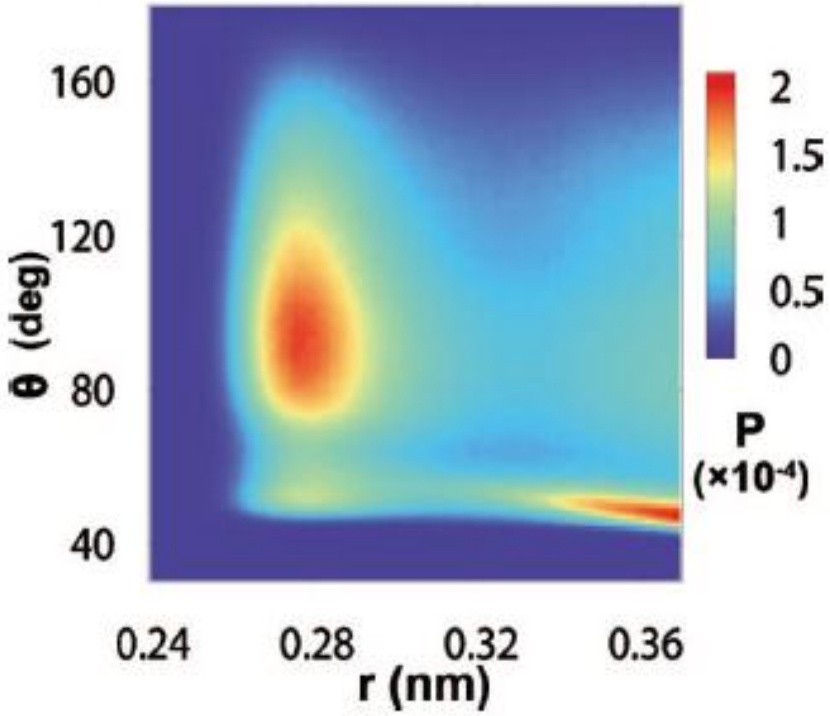




- IBI and IMC reproduce RDF and give similar potentials
- Force matching does not reproduce RDF
  → lack of 3-body term (tetrahedral packing)

SPC/E water: extension of the basis set

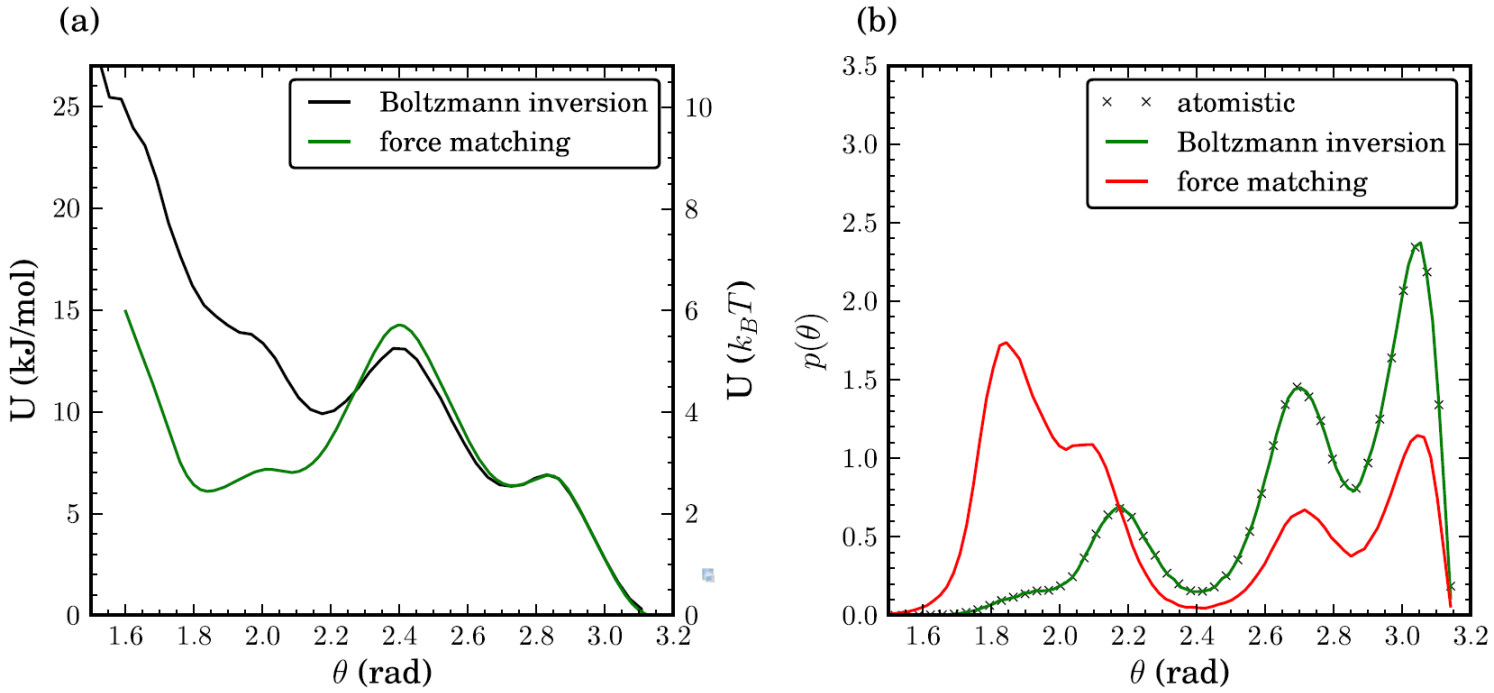




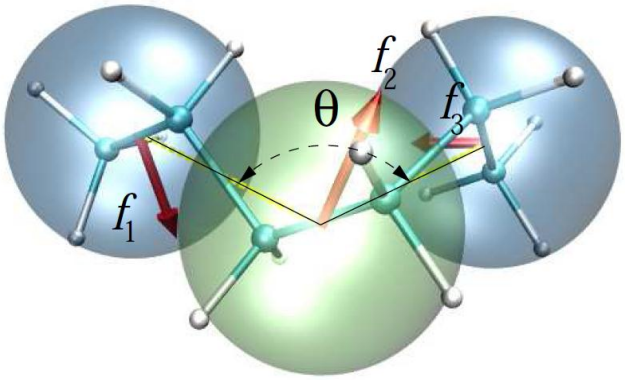
Adding a three-body potential fixes the small basis set problem

Luca Larini, Lanyuan Lu, and Gregory A. Voth, J. Chem. Phys. 132, 164107 (2010)

Force-matching & bonded interactions

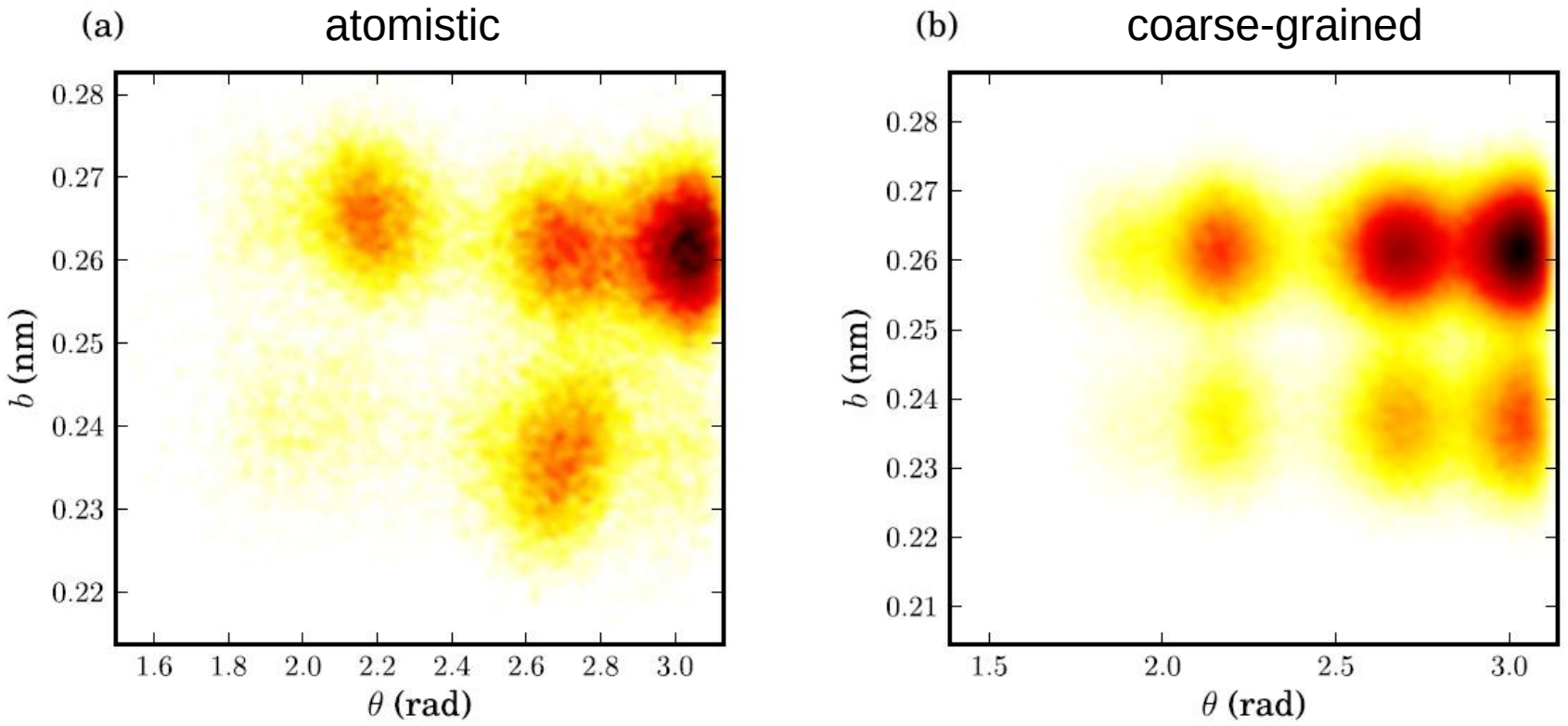


- Hexane: angle distribution not reproduced



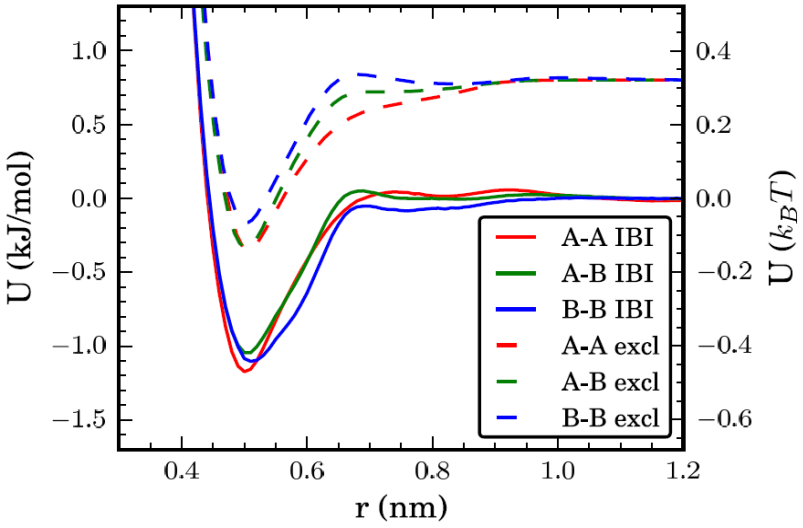
Correlations

- Bond-angle correlations not reproduced
  - affects chain stiffness, end-end distance
  - Problems when backmapping to atomistic details
  - Add further terms to CG force field or adjust mapping

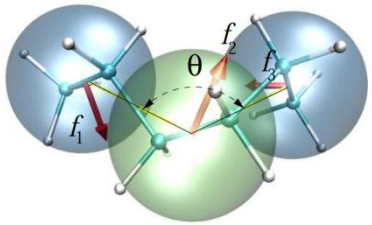


Hybrid approaches

- **Mix force-matching + Boltzmann inversion**
  - apply force matching to derive only those potentials which can be well projected on the basis functions of the CG force-field (typically non-bonded potentials)
  - exclude all forces except those of interest
- **Advantages**
  - can be used for heterogeneous systems where RDF is not well defined



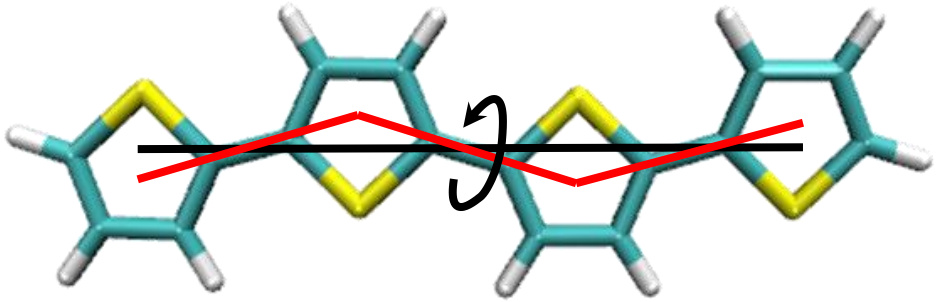
Example: liquid hexane



V. Rühle et. al, Macromol. Theory Simul. **20**, 472–477 (2011)

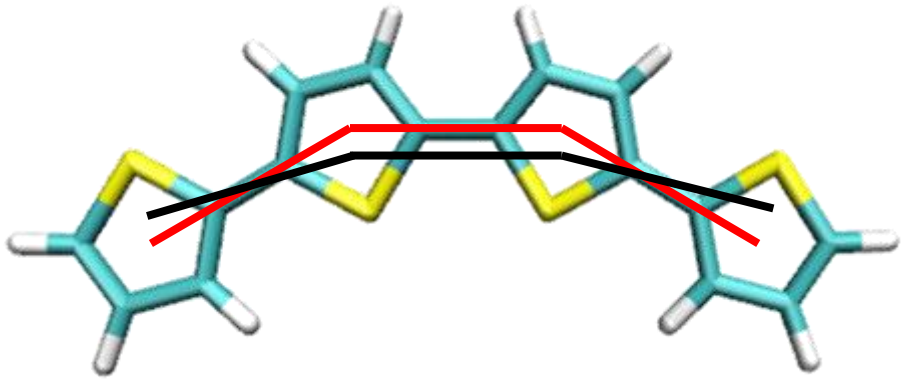
Avoiding correlations

- Adjusting the mapping can avoid correlations.
  - Polythiophene with centre of mass mapping shows correlations due to backbone torsion
  - Use centre of ring mapping avoids correlations since coarse-grained bond corresponds to C-C bond



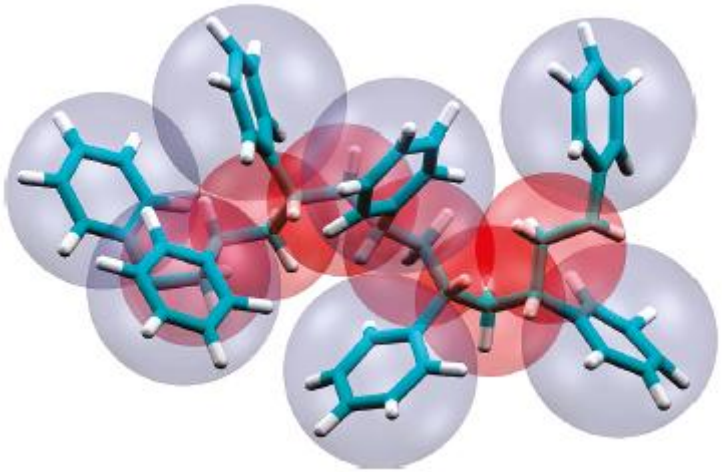
changing backbone bend

constant backbone bend



Successful models (incomplete list)

- Kremer group
  - Polycarbonate
  - Polystyrene
    - Different tacticity, diffusion scaling
    - Fritz et al, Macromolecules **42** (19), 7579–7588 (2009)



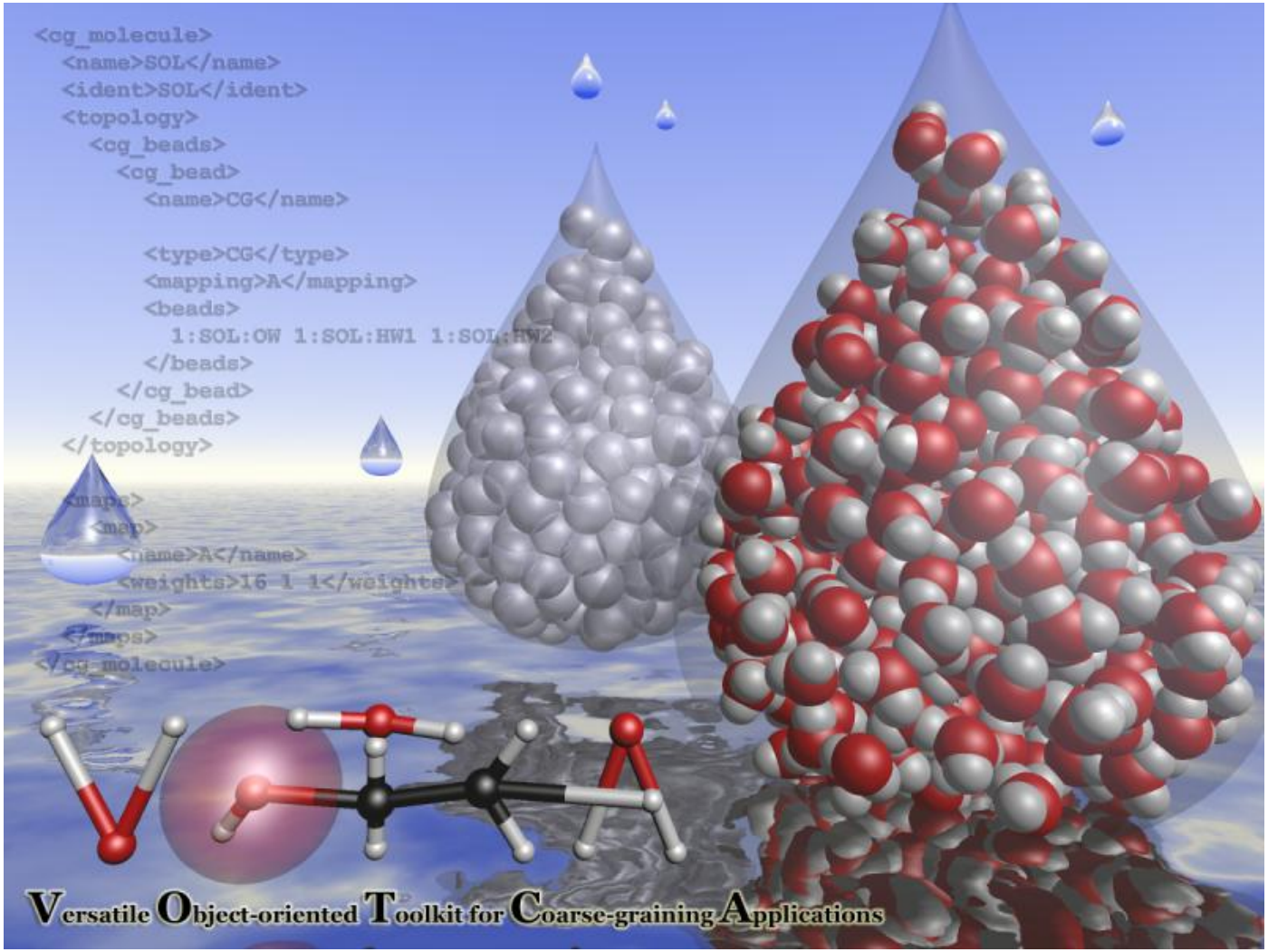
- Voth group, bio systems:
  - Multiscale Coarse-Graining of the Protein Energy Landscape Hills et al, PLoS Comput Biol. 6(6), e1000827 (2010)

Summary

- Coarse-graining provides a systematic way to parameterize a force-field based on selected properties of a reference system. Can be based on
  - Pair distribution functions
    - Boltzmann inversion
    - Iterative Boltzmann Inversion
    - Inverse Monte Carlo
  - Many-body potential of mean force
    - force matching
  - Desired thermodynamic property
    - Simplex algorithm

- Be careful
  - CG models never reproduce all properties
  - CG force-fields parameterized at a specific state point
  - RDF reproduced, but no predictions for other (thermodynamic) properties and higher order correlations (e.g. pressure, tetrahedral packing)

Thank you for your attention!



www.votca.org