Bottom-up Coarse-graining

Denis Andrienko

Max Planck Institute for Polymer Research
Mainz, Germany

Stuttgart, 8 October 2013

Our dream

Quantum Chemistry

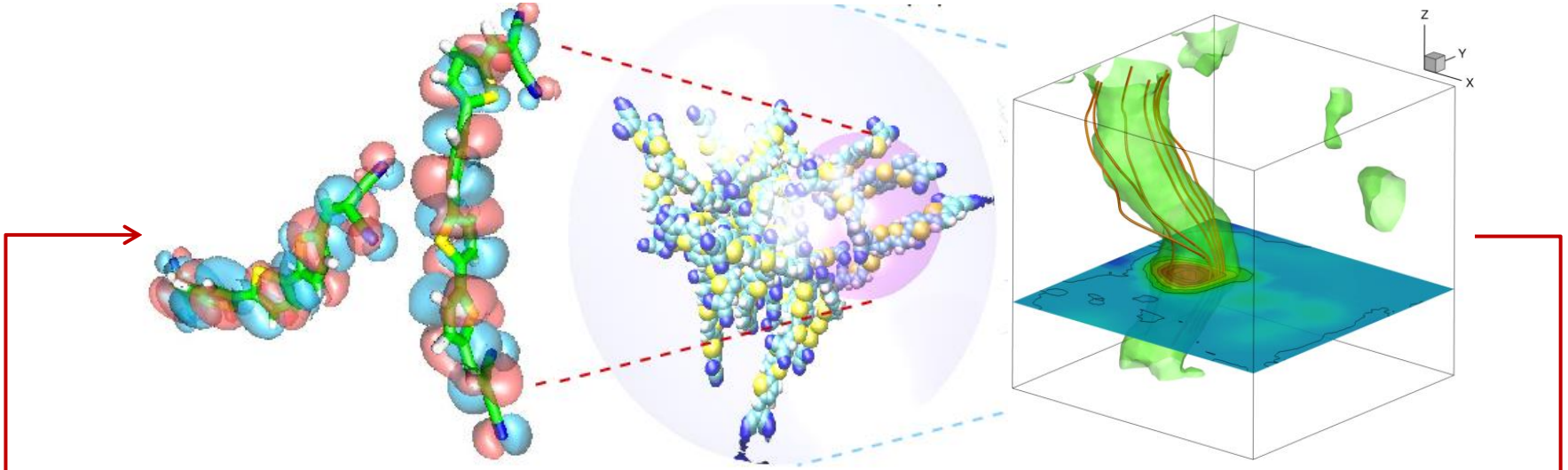
Ground/Excited states
Electrostatic multipoles
Polarizabilities

Statistical Physics

Advanced sampling techniques
Master Equation solvers
Long-range Interactions

Continuous Models

Drift-diffusion solvers
Self-consistent field techniques

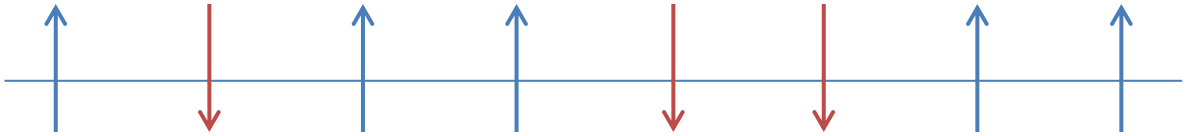


1nm 100nm 1µm

no fitting parameters, quantitative accuracy

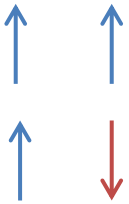
One-dimensional Ising model

1D lattice



$s_i = 1$ (spin up) $s_j = -1$ (spin down)

spins interact



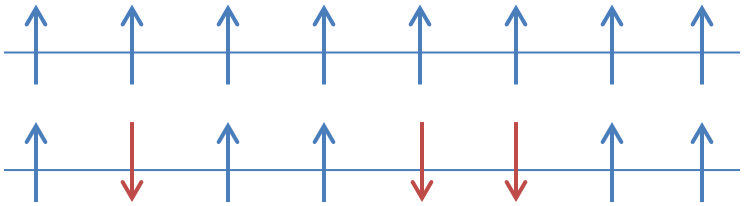
$-J$ (energetically good)

$+J$ (entropically good)

configurations

Low T

High T



Interaction between two neighboring sites only

$$E_{i,i+1} = -J s_i s_{i+1}$$

Hamiltonian

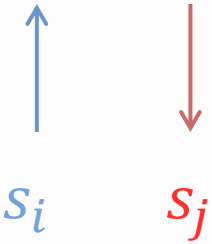
$$H = \sum_i E_{i,i+1}$$

Partition function

$$Z = \sum_{i, s_i = \pm 1} \exp(-\beta H) = \sum_{s_i = \pm 1} \prod_i \exp(\beta J s_i \, s_{i+1})$$

$$\beta = \frac{1}{k_B T}$$

$$F = -k_B T \log Z$$



Can we invent a smart way of evaluating the partition function?

Real space renormalization group: Decimation

Partition function

$$Z = \sum_{s_i=\pm 1} \prod_i \exp \beta J s_i s_{i+1}$$

Decimated partition function

$$Z = \sum_{s_{2n}} \prod_{i=2n} \sum_{s_{2n+1}} \exp \beta J (s_{2n} s_{2n+1} + s_{2n+1}\, s_{2n+2})$$

substitutions

$$\exp \beta J s_i s_{i+1} = \cosh \beta J (1 + u s_i s_{i+1})$$

$$u = \tanh \beta J$$

$$Z = \sum_{s_i} \prod_i \cosh \beta J (1 + u s_i s_{i+1})$$

$$Z = \sum_{s_{2n}} \prod_{i=2n} 2 \cosh^2 \beta J \, (1 + u^2 s_{2n} s_{2n+1})$$

Similar sum but two times less sites. **Repeat!**

Coarse-grained Ising is again Ising!

decimation

$$Z = \sum_{s_i} \prod_{i} \cosh \beta J (1 + u s_i s_{i+1})$$

$$Z = \sum_{s_{2n}} \prod_{i=2n} 2 \cosh^2 \beta J \, (1 + u^2 s_{2n} s_{2n+1})$$

Our first bottom-up coarse-grained model

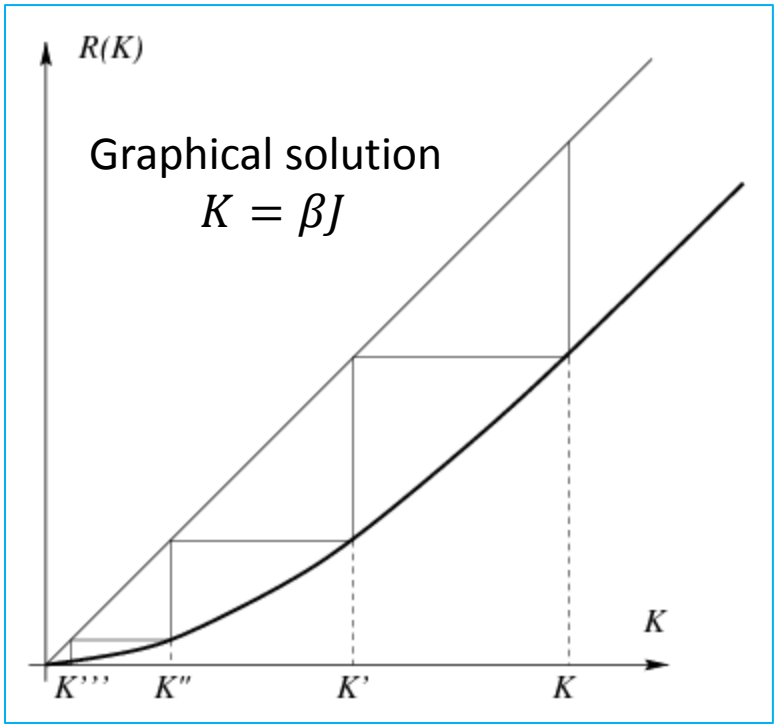
new coupling constants

$$\tanh \beta J' = \tanh^2 \beta J$$

$$\beta J' = \frac{1}{2} \ln \cosh \beta J$$

Check coupling constants when $n \to \infty$

Coupling constants



$$\beta J' = \frac{1}{2} \ln \cosh \beta J$$

Attraction points

$\beta J = 0$ - stable ($T \to \infty$)

$\beta J = \infty$ - unstable

At some length-scale the coupling always becomes small, no matter how strong the microscopic coupling was

1. No long-range order in 1D systems with finite interaction range
2. Fluctuations in 1D always eliminate phase transition

Generalize to more complex systems?

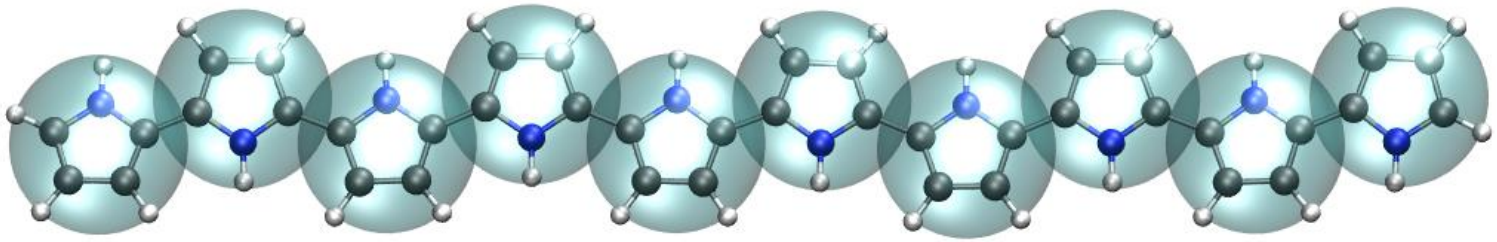
Summary

1. Chose blocks: two spins combined into one
   Mapping operator: Ising -> CG Ising

2. Integrate out “unneeded” degrees of freedom
   Effective CG potential

3. Project effective potential on a CG force-field
   No need, CG Ising has the same $Z(s)$ as Ising $Z(s)$

Coarse-graining of particle-based systems



Atomistic system
polypyrrole chain

$n < N$

Coarse-grained system
10 PPY repeat units

$\boldsymbol{r}^n = \{\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n\}$ coordinates $\boldsymbol{R}^N = \{\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N\}$

$\boldsymbol{p}^n = \{\boldsymbol{p}_1, \ldots, \boldsymbol{p}_n\}$ momenta $\boldsymbol{P}^N = \{\boldsymbol{P}_1, \ldots, \boldsymbol{P}_N\}$

Hamiltonian

$$h(\boldsymbol{r}^n, \boldsymbol{p}^n) = \sum_{i=1}^{n} \frac{1}{2m_i} \boldsymbol{p}_i^2 + u(\boldsymbol{r}^n)$$

$$H(\boldsymbol{R}^N, \boldsymbol{P}^N) = \sum_{I=1}^{N} \frac{1}{2M_I} \boldsymbol{P}_I^2 + U(\boldsymbol{R}^N)$$

Canonical (NVT) ensemble

$$p(\boldsymbol{r}^n) \sim \exp[-\beta u(\boldsymbol{r}^n)]$$

Boltzmann

$$P(\boldsymbol{R}_N) \sim \exp[-\beta U(\boldsymbol{R}^N)]$$

$$p(\boldsymbol{p}^n) \sim \exp\left[-\beta \sum_{i=1}^{n} \frac{\boldsymbol{p}_i^2}{2m_i}\right]$$

Maxwell

$$P(\boldsymbol{P}_N) \sim \exp\left[-\beta \sum_{I=1}^{N} \frac{\boldsymbol{P}_I^2}{2M_I}\right]$$

Total probability

$$p_{rp}(\boldsymbol{r}^n, \boldsymbol{p}^n) = p_r(\boldsymbol{r}^n) p_p(\boldsymbol{p}^n)$$

$$P_{RP}(\boldsymbol{R}^N, \boldsymbol{P}^N) = P_R(\boldsymbol{R}^N) P_P \boldsymbol{P}^N$$

physical intuition

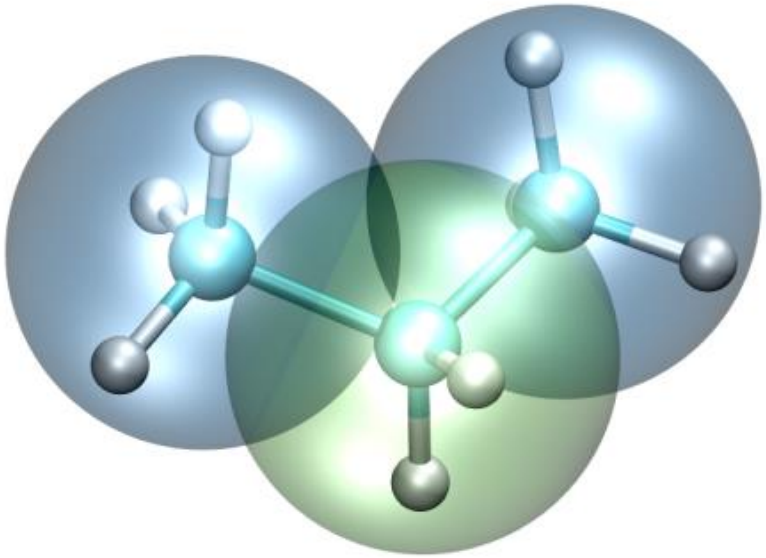
$$p_{rp}(\boldsymbol{r}^n, \boldsymbol{p}^n) = P_{RP}(\boldsymbol{R}^N, \boldsymbol{P}^N)$$

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

Mapping operators

$$\boldsymbol{R}_I = \boldsymbol{M}_{\boldsymbol{RI}}(\boldsymbol{r}^n) = \sum_{i=1}^{n} c_{Ii}\boldsymbol{r}_i$$

$$\boldsymbol{P}_I = \boldsymbol{M}_{\boldsymbol{PI}}(\boldsymbol{p}^n) = M_I \sum_{i=1}^{n} \frac{c_{Ii}\boldsymbol{p}_i}{m_i}$$



c_{Ii} is an $N \times n$ matrix

$\sum_i c_{Ii} = 1$ (translational invariance)

Propane CM:
$4 \times 1, 3 \times 1, 4 \times 1$
block matrix

Here: linear mapping operators only
You will have to specify c_{Ii} in the VOTCA input files!

Conditional probabilities

Equilibrium probability density for CG variables

$$p_R(\boldsymbol{R}^N) = \int d\boldsymbol{r}^n p_r(\boldsymbol{r}^n)\delta\left(\boldsymbol{M}_{\boldsymbol{RI}}^N(\boldsymbol{r}^n) - \boldsymbol{R}^N\right)$$

$$p_P(\boldsymbol{P}^N) = \int d\boldsymbol{p}^n p_p(\boldsymbol{p}^n)\delta(\boldsymbol{M}_{\boldsymbol{PI}}^N(\boldsymbol{p}^n) - \boldsymbol{P}^N)$$

delta function sorts microscopic states in appropriate coarse-grained states

Consistency of the CG and the atomistic models

$$P_{RP}(\boldsymbol{R}^N, \boldsymbol{P}^N) = p_{RP}(\boldsymbol{R}^N, \boldsymbol{P}^N)$$

Potential of Mean Force

$$P_{RP}(\boldsymbol{R}^N, \boldsymbol{P}^N) = p_{RP}(\boldsymbol{R}^N, \boldsymbol{P}^N)$$

is equivalent to

momentum space:

$$M_I = \left(\sum_{i \in \mathrm{I}} \frac{c_{Ii}^2}{m_i} \right)^{-1}$$

coordinate space:

$$\exp[-\beta U(\boldsymbol{R}^N)] \sim \int d\boldsymbol{r}^n \exp[-\beta u\,(\boldsymbol{r}^n)] \delta\left(\boldsymbol{M}_{\boldsymbol{RI}}^N(\boldsymbol{r}^n) - \boldsymbol{R}^N\right)$$

$$\boldsymbol{F}_I(\boldsymbol{R}^N) = \langle \boldsymbol{\mathcal{F}}_I\,(\boldsymbol{r}^n) \rangle_{\boldsymbol{R}^N}$$

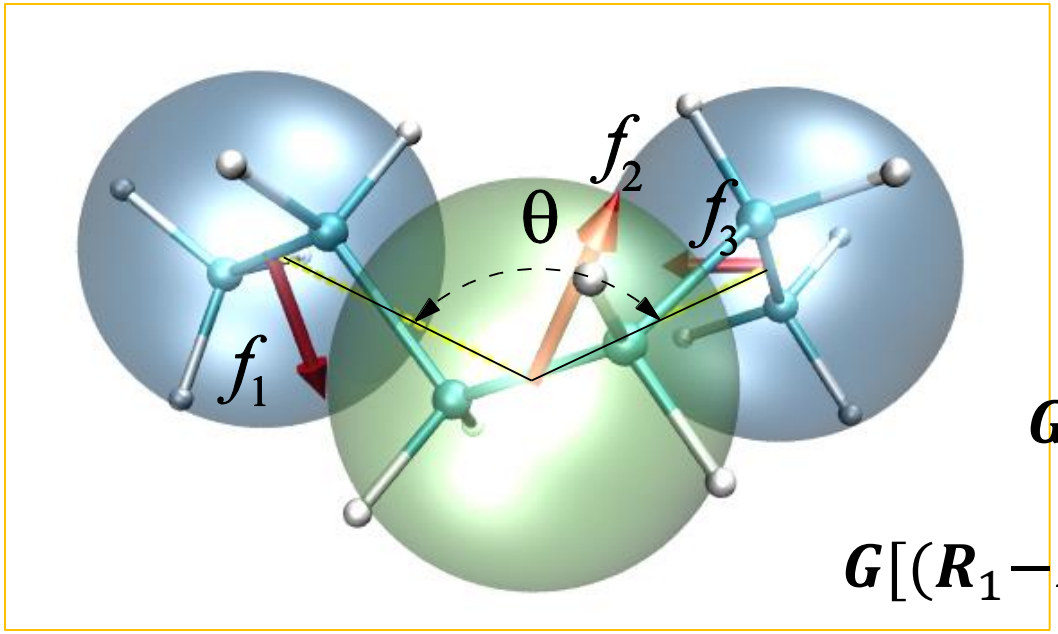
The CG interaction potential is the **potential of mean force**

The CG force is a conditioned expectation value of the atomistic force

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

Force-field basis set functions

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



$$\boldsymbol{G}[\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{R}_3]$$

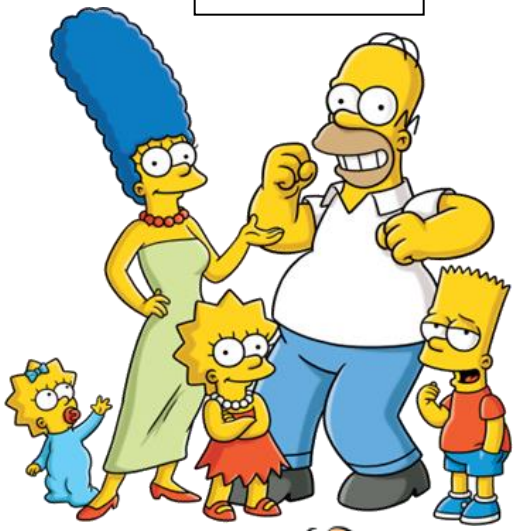
$$\boldsymbol{G}[(\boldsymbol{R}_1 - \boldsymbol{R}_2) \cdot (\boldsymbol{R}_2 - \boldsymbol{R}_3)]$$

PMF requires many-body potential functions $\boldsymbol{G}_I(\boldsymbol{R}^N)$,
MD force-fields provide a **limited** set of many-body potentials
(angles, dihedrals)

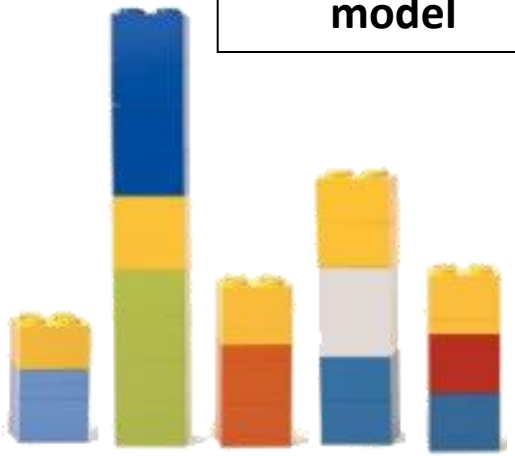
In a nutshell

coarse-graining

Atomistic model



Coarse-grained model



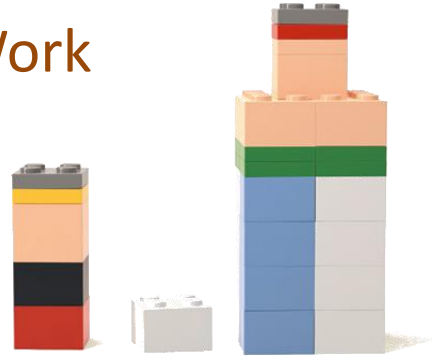
Force Matching

Inverse Monte Carlo

Relative Entropy

Iterative Boltzmann Inversion

Conditional Reversible Work



backmapping

Variational principle

Project the many-body potentials on the functions provided by the force-field

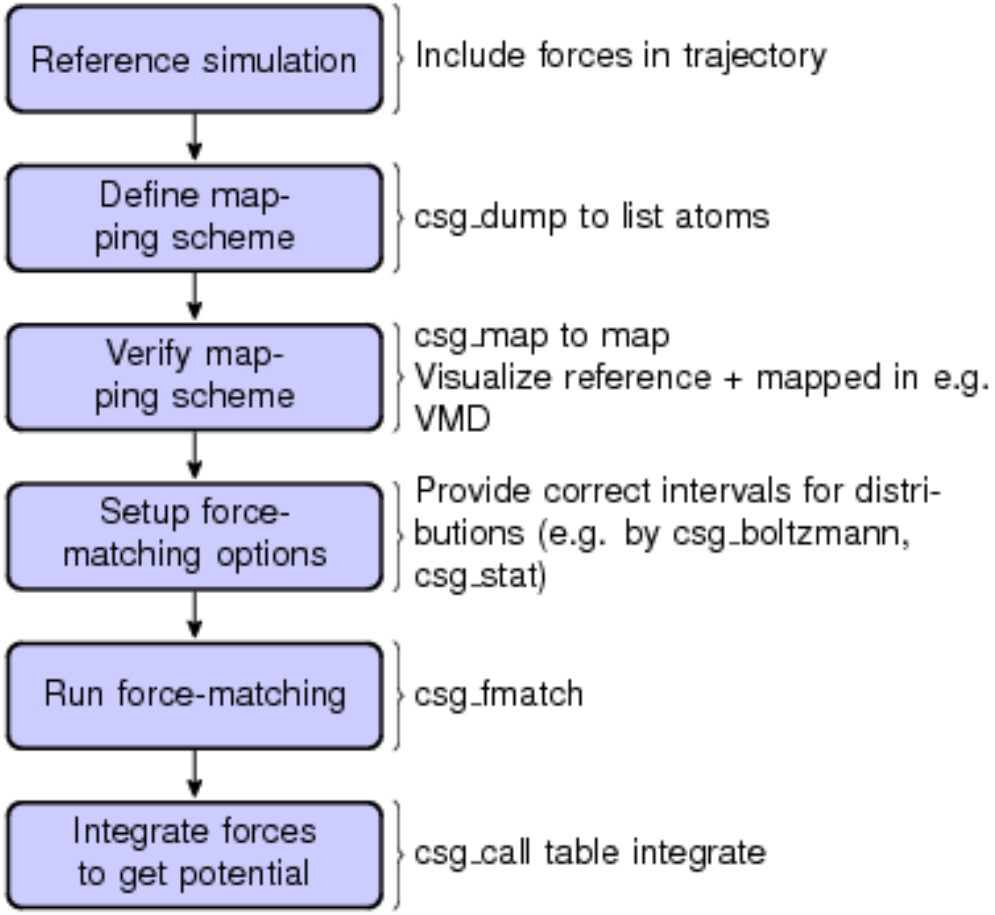
$$\chi^2[\boldsymbol{G}] = \frac{1}{3N}\left\langle \sum_{I=1}^{N} \left| \boldsymbol{\mathcal{F}}_I\left(\boldsymbol{r}^n\right) - \boldsymbol{G}_I\left(\boldsymbol{M}_{\boldsymbol{R}}^{N}(\boldsymbol{r}^n)\right)\right|^2 \right\rangle$$

The global minimum of the functional χ for $\boldsymbol{G}$ in the vector space of CG force fields is achieved when $\boldsymbol{G}$ is $\boldsymbol{F}$

This is exactly what force-matching (MSCG) is doing:
projecting many-body PMF onto the CG force-field basis functions

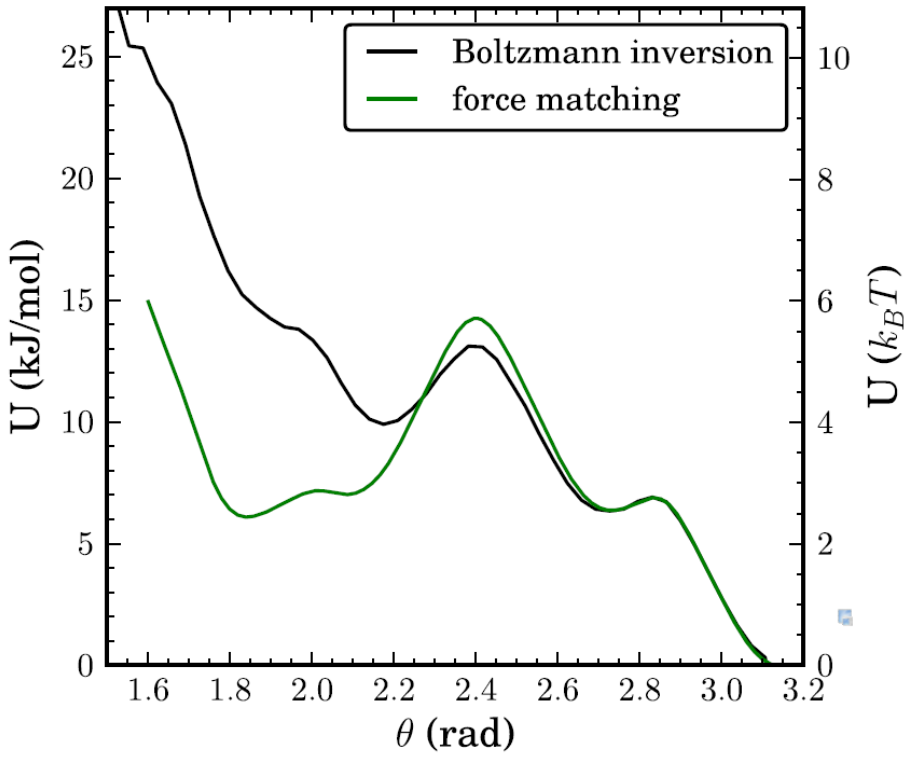
S. Izvekov and G. Voth, J. Chem. Phys. 123, 134105 (2005)
W. Noid et al., J. Chem. Phys. 120, 244114 (2008)

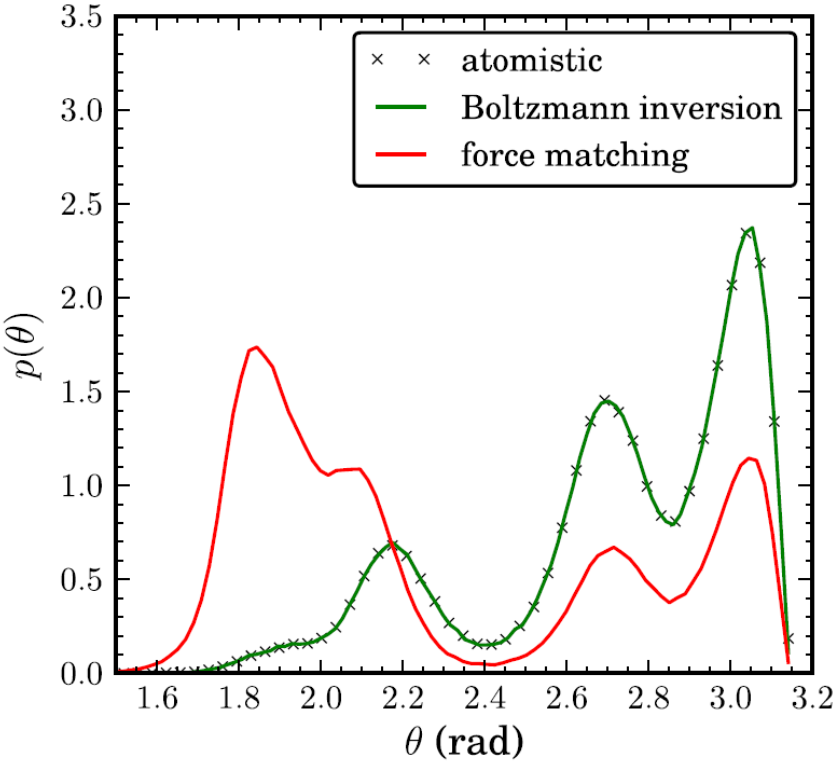
Force matching, **M**ulti**S**cale **C**oarse-**G**raining



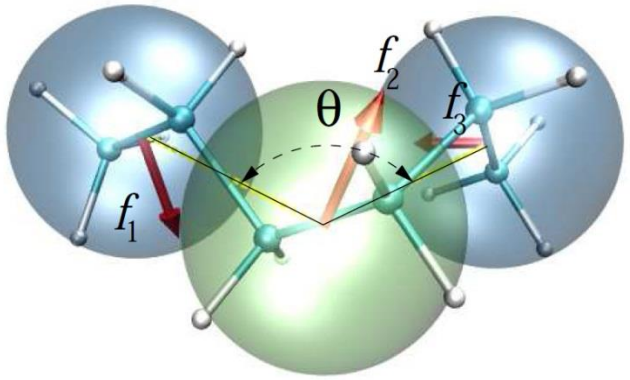
It is a non-iterative method

Example: hexane in vacuum



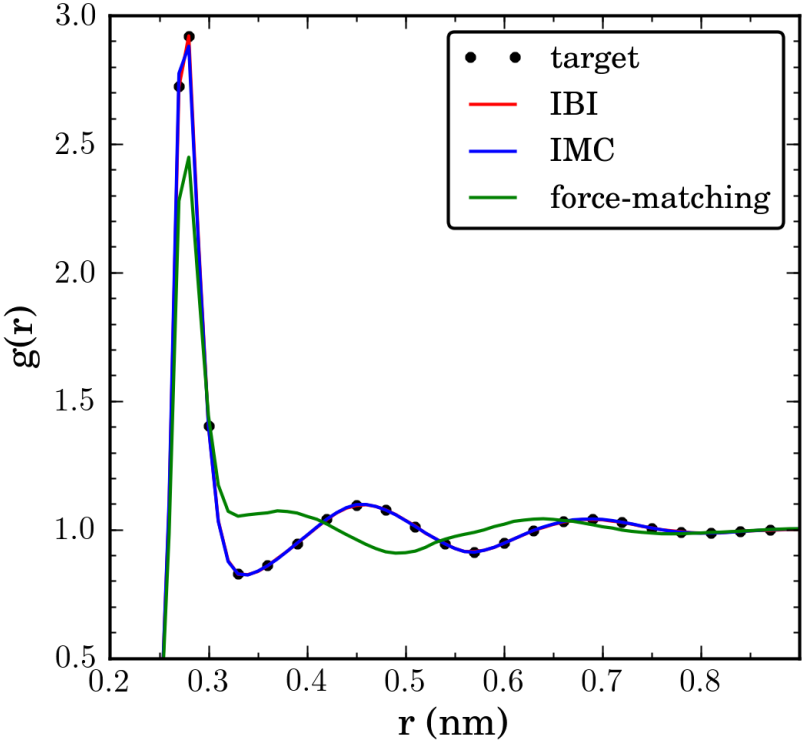


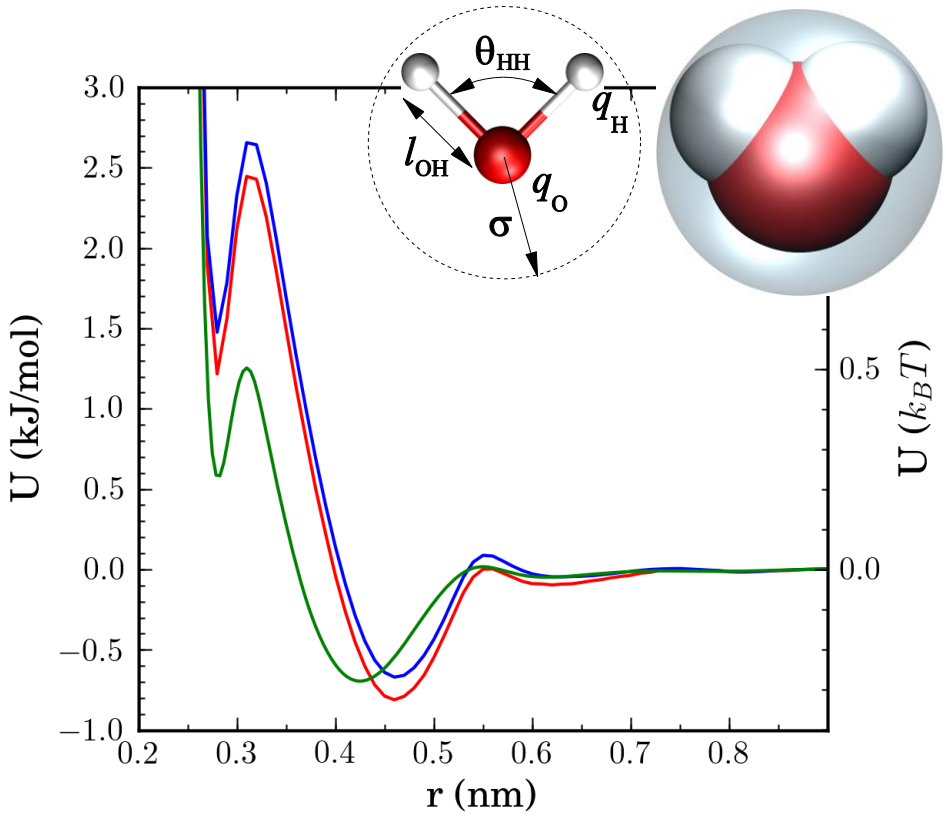
Forces have off-plane components which are not present in the basis set of the coarse-grained force-field



V. Ruehle, et al, J. Chem. Theor. Comp., 5, 3211-3223, 2009

Example: water model (SPC/E)





Pair potential is not reproducing the local tetrahedral structure

Molinero V. & Moore E. B. (2009), J. Phys. Chem. B, 113, 4008-4016

Larini, L.; Lu, L. & Voth, G. A. (2010), J. Chem. Phys. 132, 164107

Structure-based coarse-graining

What if we do not have forces?

(e.g Monte Carlo is used for sampling)

CG procedure can be reformulated in terms of correlation functions

correlation function	simple liquid
$\rho_1(\boldsymbol{r}_1)$	ρ - density
$\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$	$g(r)$ - pair distribution function
$\rho_3(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)$	
…	

Normally ρ and $g(r)$ are used (easy to compute)

Henderson theorem

A classical analogue of the Hohenberg-Kohn theorem in DFT

$$g(r) \equiv U(r)$$

pairwise potential $U(r)$ is unique

All structure-based methods matching ρ and $g(r)$ converge to the same coarse-grained potential

Henderson, R. Phys. Lett. A 1974, A49, 197–198.

Liquid state theory – Yvon-Born-Green equation

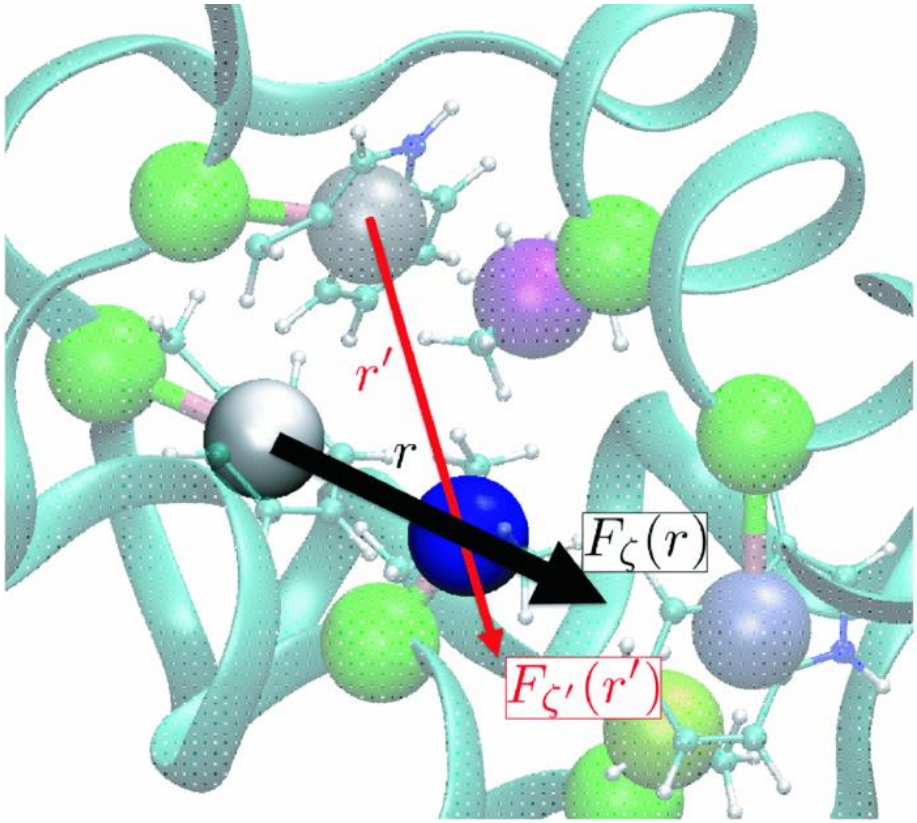
Pair potential of mean force

$$-W_\xi'(r) = F_\xi(r) + \sum_{\xi'} dr' G_{\xi\xi'}(r,r') F_{\xi'}(r')$$

Direct force Correlation function

integrated

$$W_\xi(r) = U_\xi(r) + \sum_{\xi'} W_{\xi\xi'}(r,r')$$



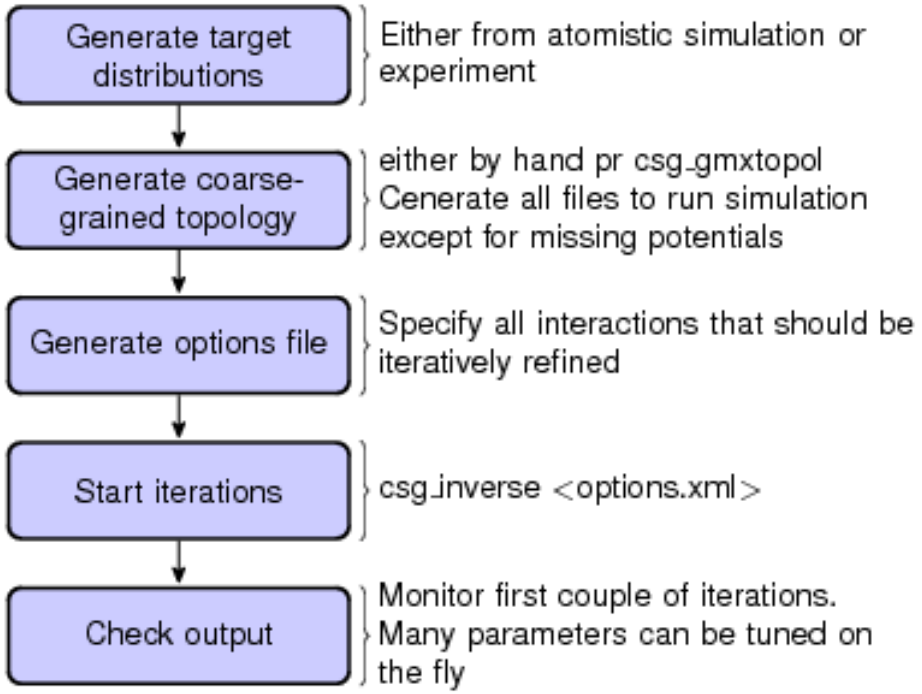
no correlations between DOF

$$\delta U_\xi(r) = w_\xi(r) - W_\xi(r) \sim k_B T \ln [P_\xi(r)/p_\xi(r)]$$

W.G. Noid (2007): J. Phys. Chem. B 111, 4116-4127
J. Chem. Phys. 139, 090901 (2013)

Iterative Boltzmann Inversion

$$\delta U(r) = k_{\mathrm{B}} T \ln \frac{g(r)}{g^{\mathrm{ref}}(r)}$$

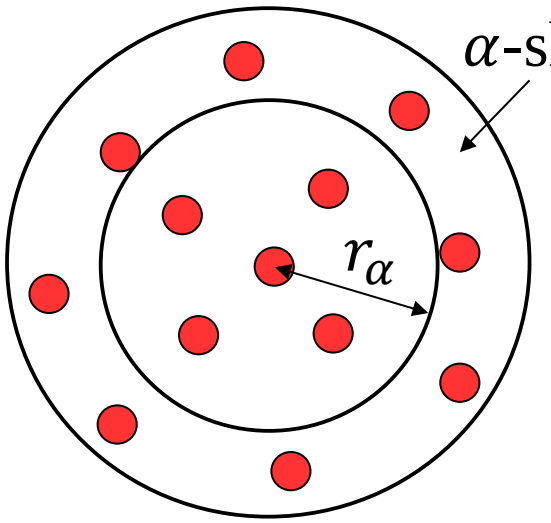


IBI: iterative, local, no correlations.

Robust, but it is not clear if it works for mixtures.

D. Reith et al., J. Comp. Chem. 24 (13), 1624 (2003)
A. K. Soper, Chem. Phys. 202, 295 (1996)

Inverse Monte Carlo



$$S_\alpha = \frac{N(N-1)}{2}\frac{4\pi r_\alpha^2 \Delta r}{V} g(r_\alpha)$$

number of particles in shell Δr at a distance r_α

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

$$\delta\langle S_\alpha\rangle = \langle S_\alpha\rangle - S_\alpha^{\mathrm{ref}} = \sum_\gamma \frac{\partial\langle S_\alpha\rangle}{\delta U_\gamma}\delta U_\gamma + \mathcal{O}(\delta U^2)$$

$$A_{\alpha\gamma} = \frac{\partial\langle S_\alpha\rangle}{\partial U_\gamma} = \frac{\partial}{\partial U_\gamma}\frac{\int dq S_\alpha(q)\exp[-\beta H(q)]}{\int dq \exp[-\beta H(q)]}$$

$$A_{\alpha\gamma} = \beta\left(\langle S_\alpha\rangle\langle S_\gamma\rangle - \langle S_\alpha S_\gamma\rangle\right)$$

In the first order we need only averages (RDF) and correlations

A. Lyubartsev et al., Phys. Rev. E 52 (4), 3730 (1995)
B. R. H. Swendsen, Phys. Rev. Lett. 42, 859 (1979)

Inverse Monte Carlo

$$\langle S_\alpha \rangle - S_\alpha^{\mathrm{ref}} = \sum_\gamma A_{\alpha\gamma} \delta U_\gamma$$

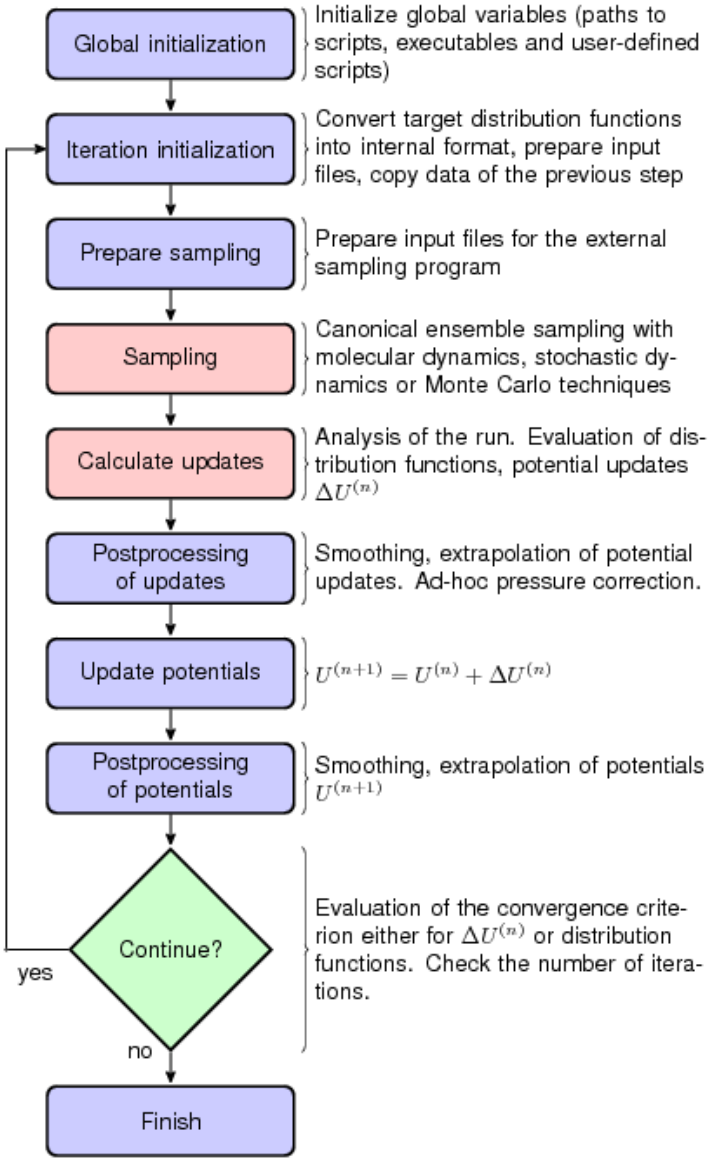
$$A_{\alpha\gamma} = \beta\left(\langle S_\alpha \rangle \langle S_\gamma \rangle - \langle S_\alpha S_\gamma \rangle\right)$$

$$\delta U = A^{-1}[\langle S \rangle - S^{\mathrm{ref}}]$$

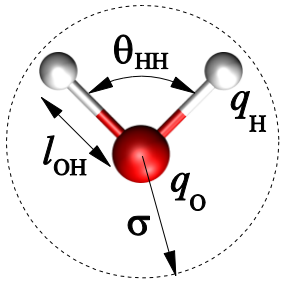
- non-local, iterative, particle-particle correlations are included
- A is tricky to invert

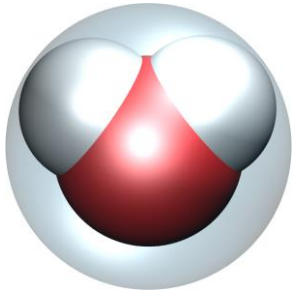
A. Lyubartsev et al., Phys. Rev. E 52 (4), 3730 (1995)

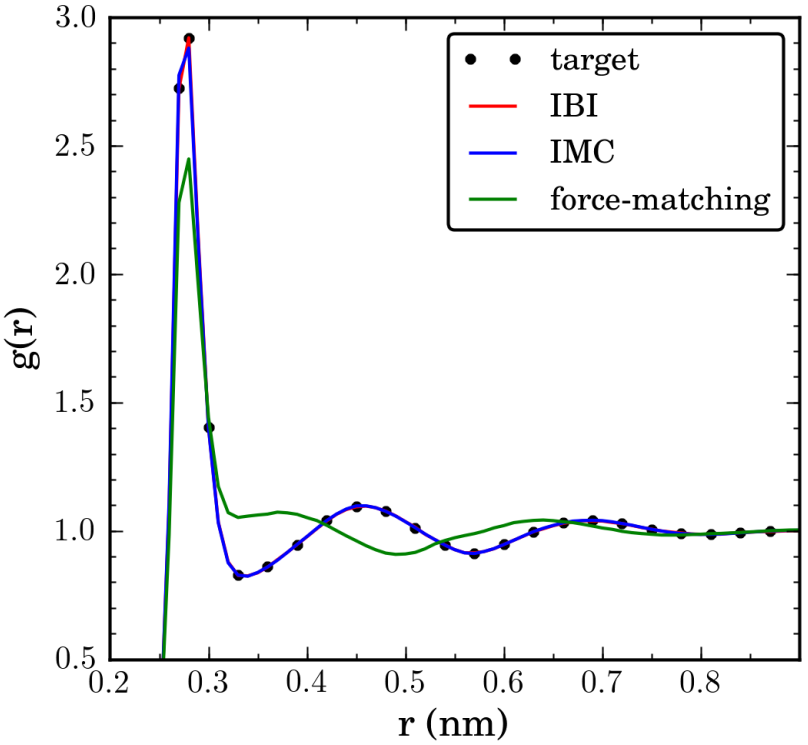
IMC implementation

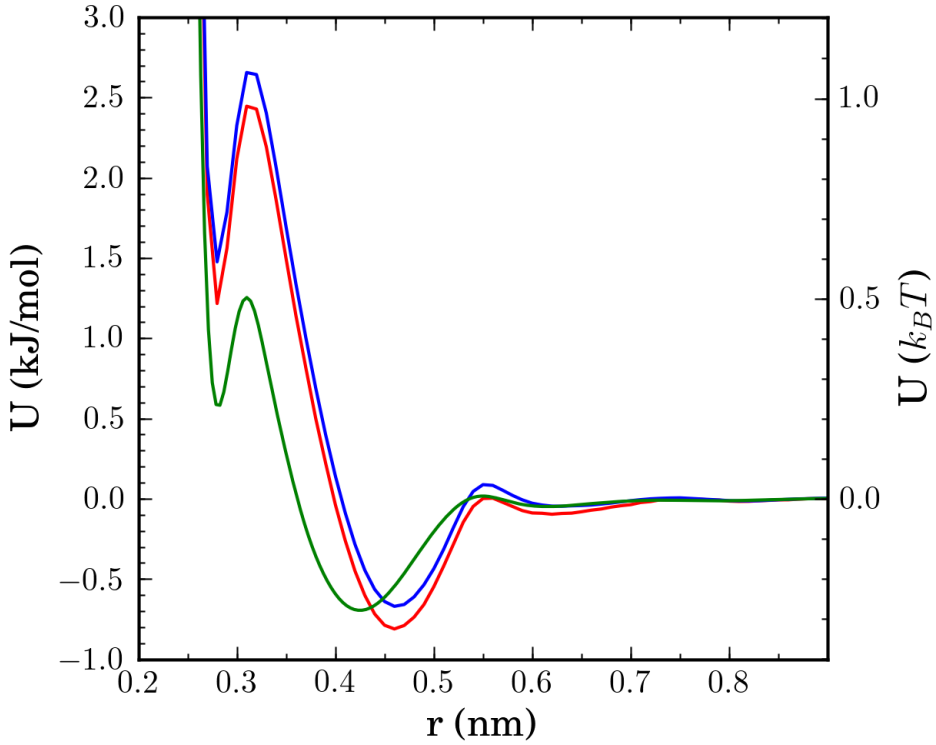


Examples: SPC/E water



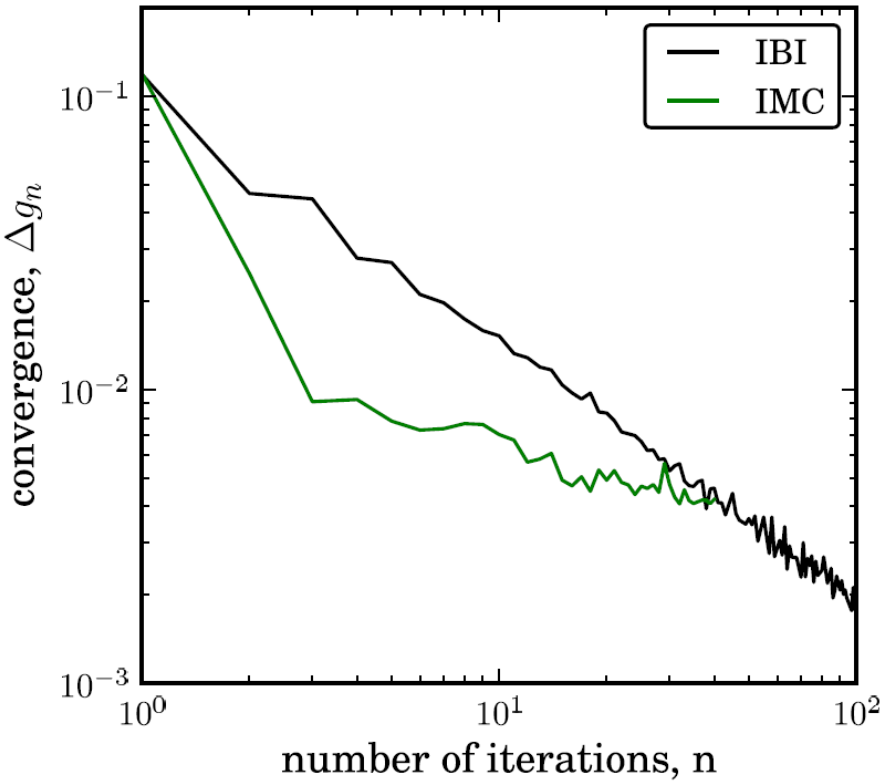


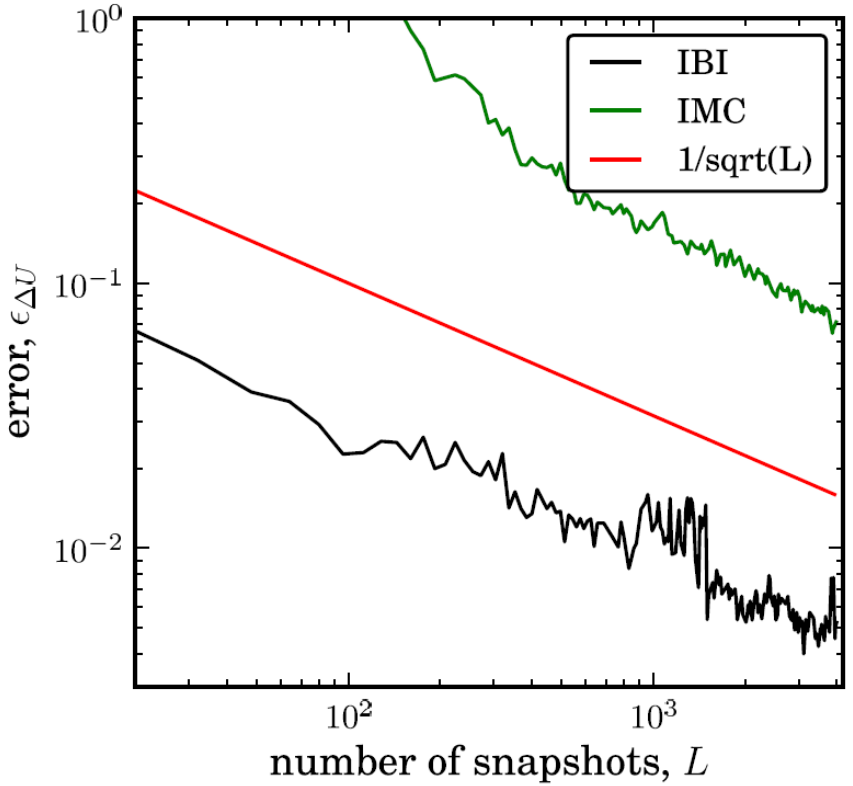




IBI and IMC reproduce RDF and give similar potentials

Examples: Efficiency

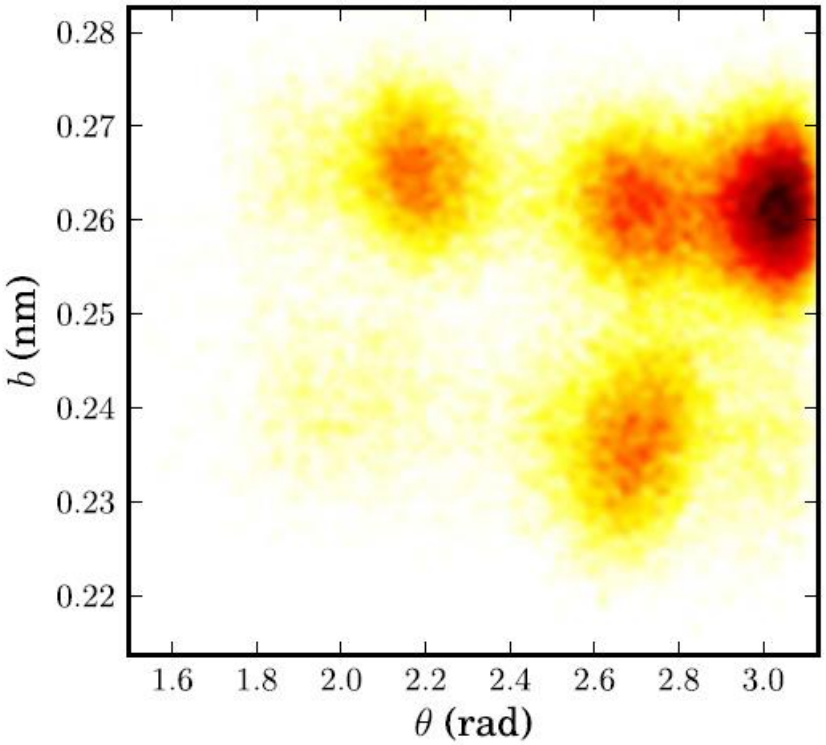


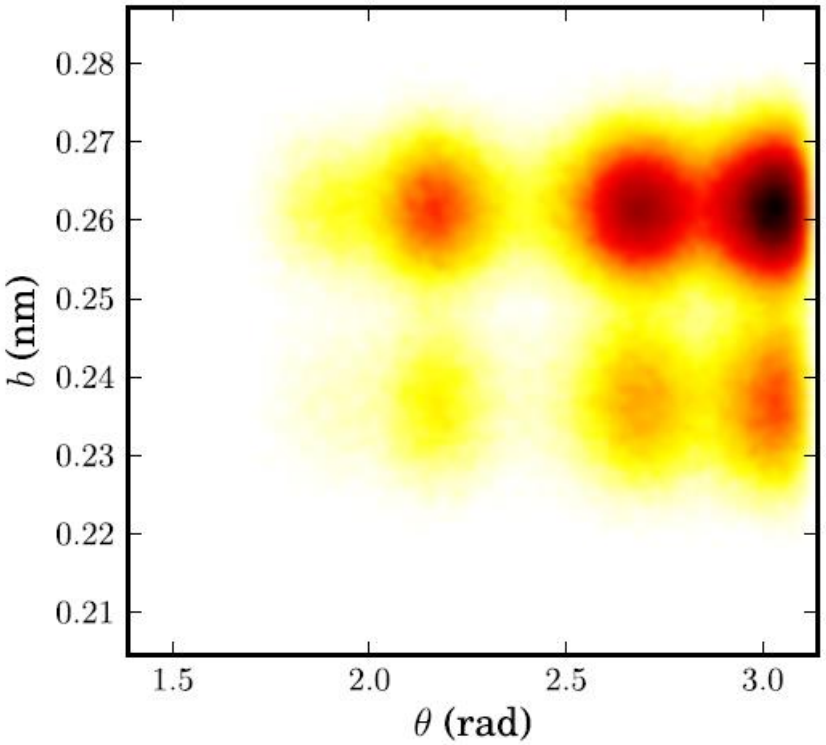


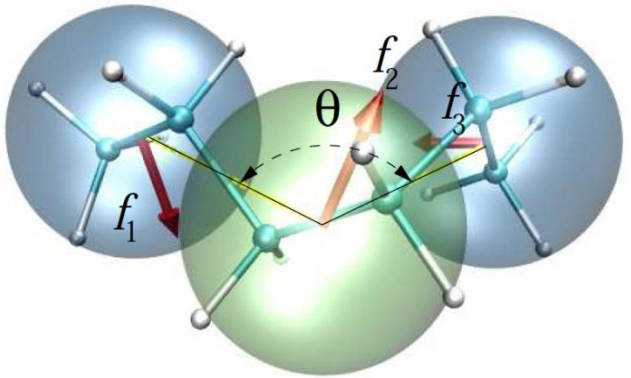
IMC converges faster but needs longer iterations

Less computational costs for IBI

Test your CG model!







Bond-angle correlations are not reproduced

affects chain stiffness, end-to-end distance

Summary

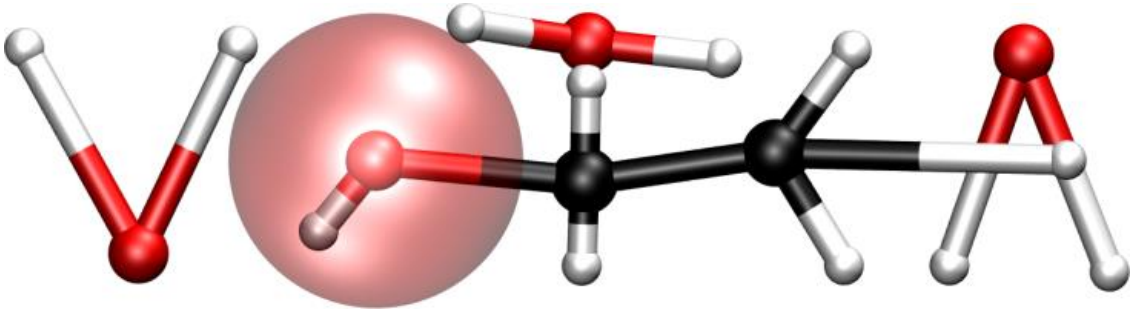
Coarse-graining provides a systematic way to parameterize a force-field based on selected properties of a reference system

Can be based on

- Distribution functions:
  - Boltzmann inversion
  - Iterative Boltzmann Inversion
  - Inverse Monte Carlo
  - Relative Entropy (talk of Sikandar)
- Many-body potential of mean force
  - force matching
  - MSCG
- Desired thermodynamic property
  - Simplex algorithm

Software

Versatile Object-oriented Toolkit for Coarse-graining Applications



votca.org

open source

C++, test suite, hg repository, wiki pages, bug tracker, mailing list

votca-csg modules (coarse-graining)
Google code: votca project

votca-ctp modules (charge transport)
Google code: votca-ctp project

Happy coarse-graining!

charge transport: V. Ruehle, A. Lukyanov, F. May, M. Schrader, T. Vehoff, J. Kirkpatrick, B. Baumeier, D. Andrienko, J. Chem. Theor. Comp., 2011
coarse-graining: V. Ruehle, C. Junghans, A. Lukyanov, K. Kremer, D. Andrienko, J. Chem. Theor. Comp., 5, 3211-3223, 2009