Towards a Unified Framework for Coarse-graining Particle-based Simulations

Christoph Junghans

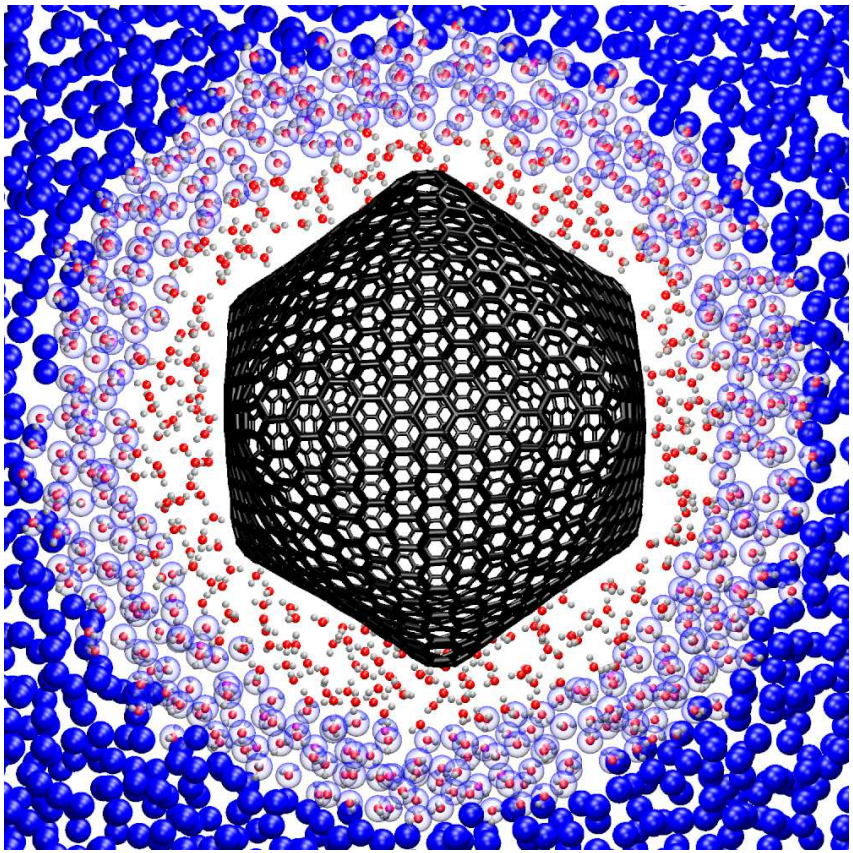
Los Alamos National Laboratory
NM, USA

Jun 5, 2012

Introduction

Coarse-graining is an essential part of multi-scale simulations!

- Reduces number of degrees of freedom
- Enhances accessible range of time- and length-scales
- Links atomistic and coarse-grained representations



Introduction

Systematic Coarse-Graining

Is there a force-field for the coarse-grained model which reproduces a certain property?

- Structure (e.g. bond distribution or two-body correlations):
  - Boltzmann inversion
  - Iterative Boltzmann inversion
  - Inverse "Monte Carlo"
  - Relative Entropy Method
- Forces $\rightarrow$ Force matching (multi-body PMF)
- Free energy (MARTINI force-field)
- Further properties:
  - Pressure $\rightarrow$ Pressure correction
  - Diffusion $\rightarrow$ Thermostat (friction constant fitting)

Incomplete list, many more methods and variations available!

Introduction
VOTCA Framework

- Consistent implementation of most of these methods → Allows for direct comparison
- Platform for the implementation of new methods
- Integrates existing sampling programs (e.g. MD codes)

Parts of VOTCA[1]- www.votca.org

- Mapping engine
- Parallel analysis framework
- Automated iterative coarse-graining
- Charge transport modules

- Ohloh: 10 Person Years / 39.8k Lines / $ 528.4K
- 15 Developers
- Packages in Fedora, OpenSuse, Gentoo

[1] JCTC 5, 3211 (2009) & Macromol. Theo. Simul. 20, 472 (2011)

Kirkwood-Buff Models

Introduction

Find a coarse-grained model that reproduces the Kirkwood-Buff Integrals:

$$G_{ij} = 4\pi \int_0^\infty [g_{ij}^{\mu VT}(r) - 1] r^2 \, \mathrm{d}r$$

Motivation

Describe salting-in/salting-out of Biomolecules on a coarse-grained level:

$$f_{cc} = \left(\frac{\partial \ln \gamma_c}{\partial \ln \rho_c} \right)_{p,T} = -\frac{\rho_c \left(\mathrm{G}_{cc} - \mathrm{G}_{cw} \right)}{1 + \rho_c \left(\mathrm{G}_{cc} - \mathrm{G}_{cw} \right)},$$

$k_B T \ln \gamma_c$: co-solvent solvation free energy
γ_c: co-solvent molar scale activity coefficient
ρ_c: co-solvent number density

Assumption: large systems ($g^{\mu VT} \approx g^{NVT}$)

Los Alamos NATIONAL LABORATORY EST. 1943

Kirkwood-Buff Models

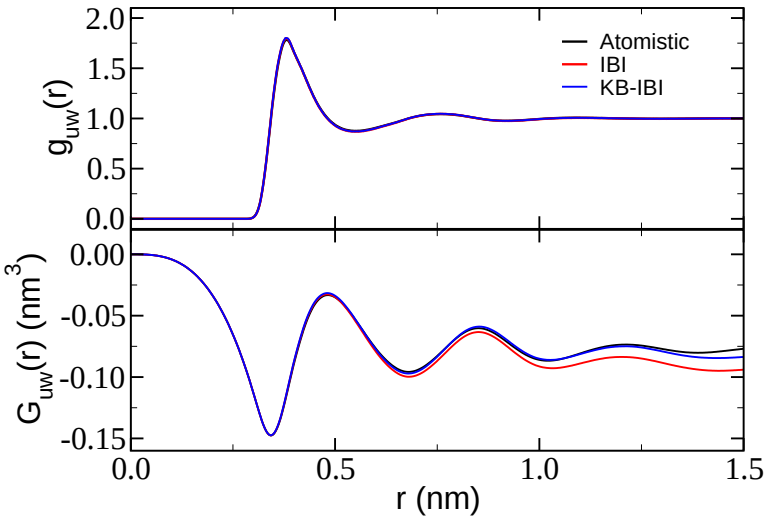
Aqueous Urea Mixture

Algorithms

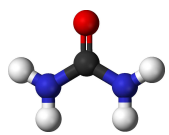
- Infinitely long iterative Boltzmann inversion $\rightarrow$ fails

$$\Delta U_{ij}(r) = \mathrm{k_B}\, T \ln \frac{g_{ij}(r)}{g^{\mathrm{Ref}}(r)}$$

- Ramp correction [2]



(aqueous urea mixture at 4.7 M urea)



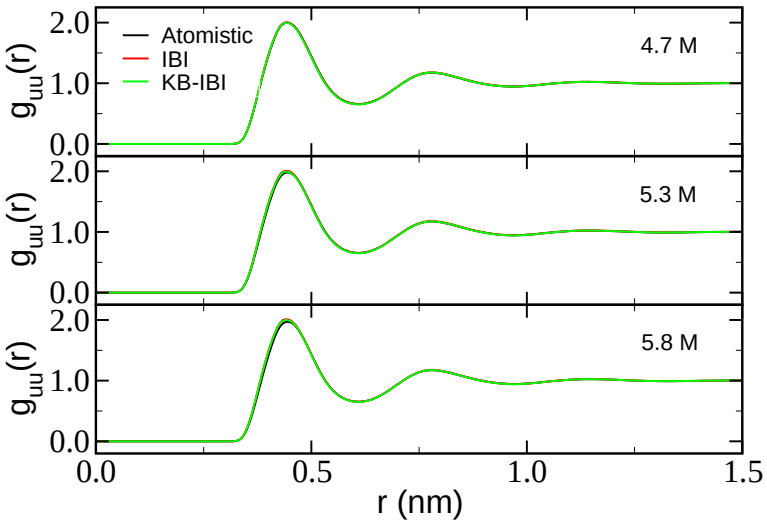
$$\Delta U_{ij}(r) = A(\mathrm{G}_{ij}^{(n)} - \mathrm{G}_{ij}^{(ref)}) \left(1 - \frac{r}{r_{\mathrm{cut}}}\right)$$

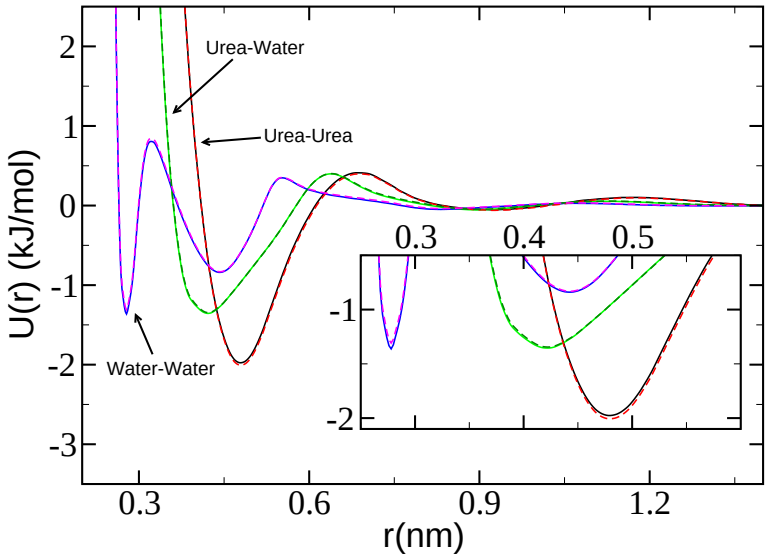
Problem: A is difficult to determine.

[2] Ganguly et al., JCTC 8, 1802 (2012)

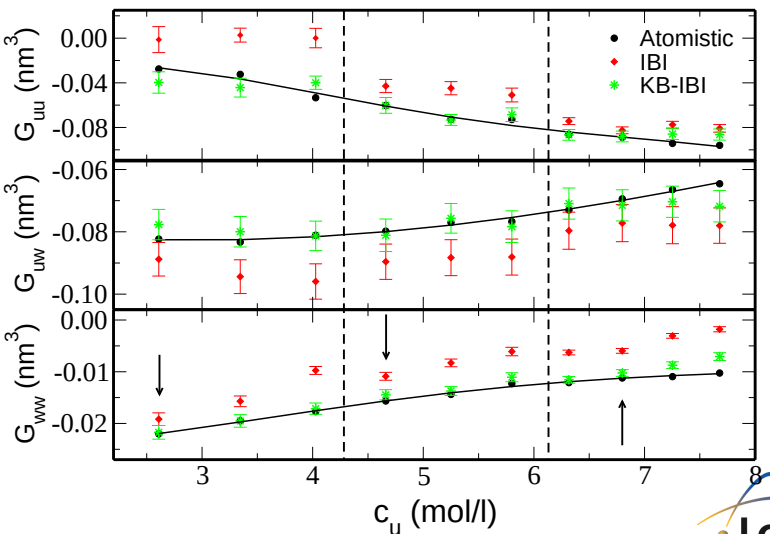
Kirkwood-Buff Models

Aqueous Urea Mixture





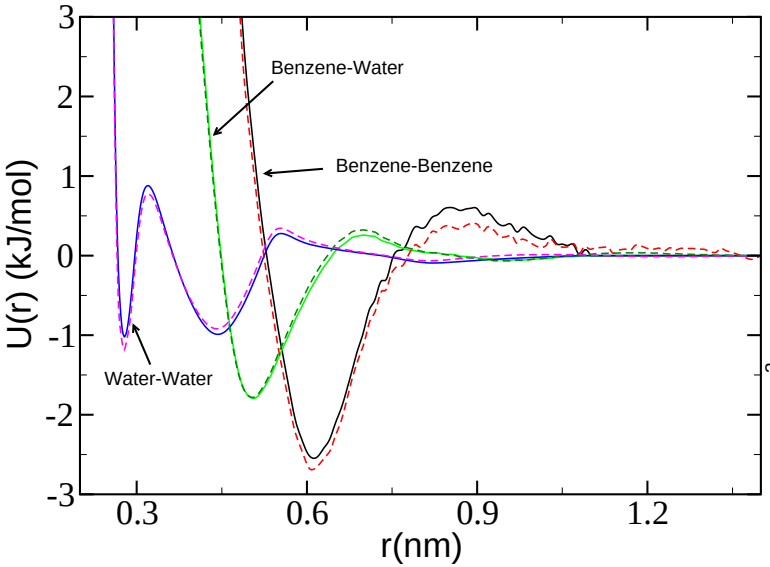
- Minimal differences in the potential
- Potentials are transferable in a small concentration interval
- Does it work for other systems?

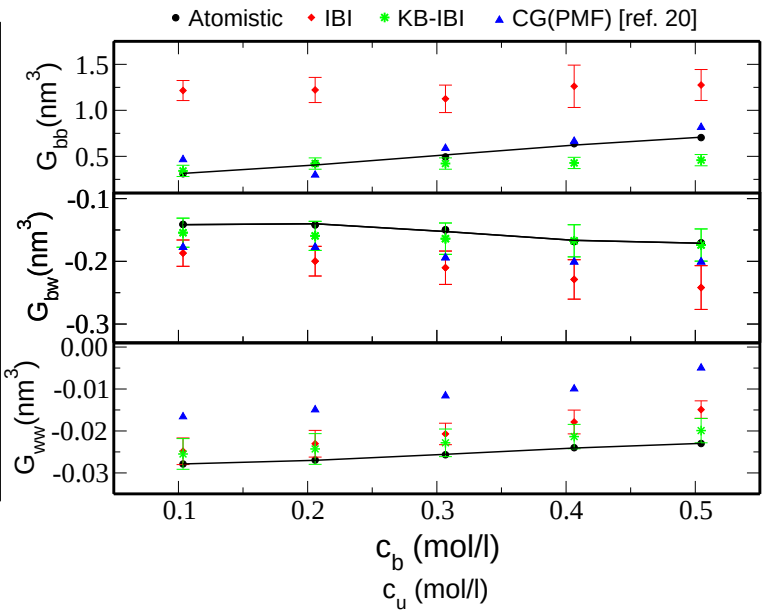


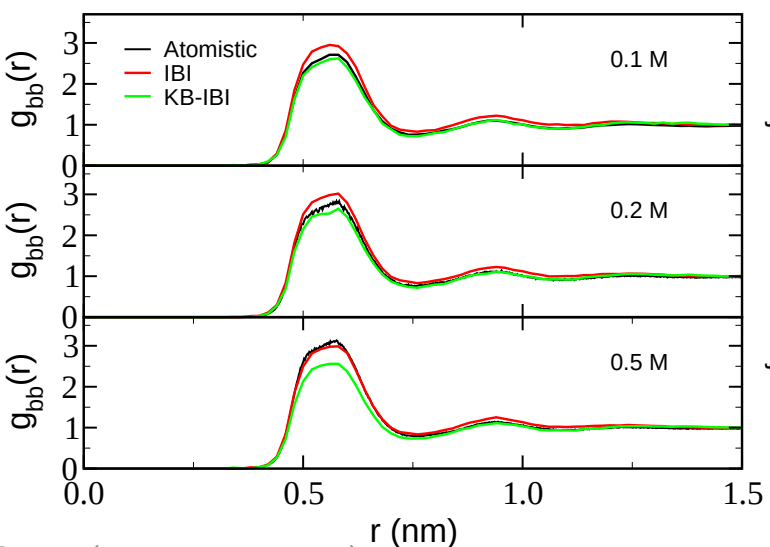
Los Alamos NATIONAL LABORATORY EST. 1943

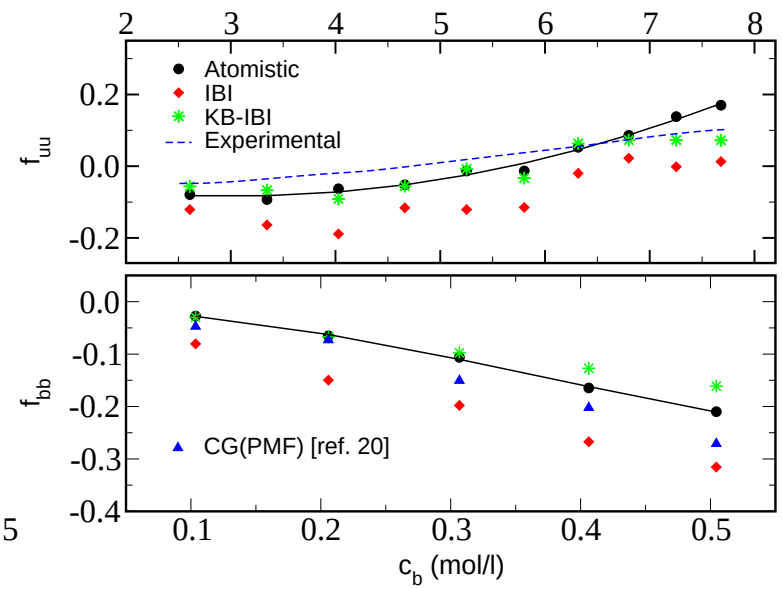
Kirkwood-Buff Models

Benzene in Water









Kirkwood-Buff Models

Conclusion

What did we learn?

- Iterative Boltzmann inversion alone is not enough
- Transferable potentials over different concentrations
- Useful method to develop models to study salting-in and salting-out

Open questions:

- Are there less arbitrary ways of correcting?
- Is it possible to incorporate the correction in an inversion scheme?

Targeted Coarse-Graining
Introduction

Find a coarse-grained model, which reproduces other non-structural related property.

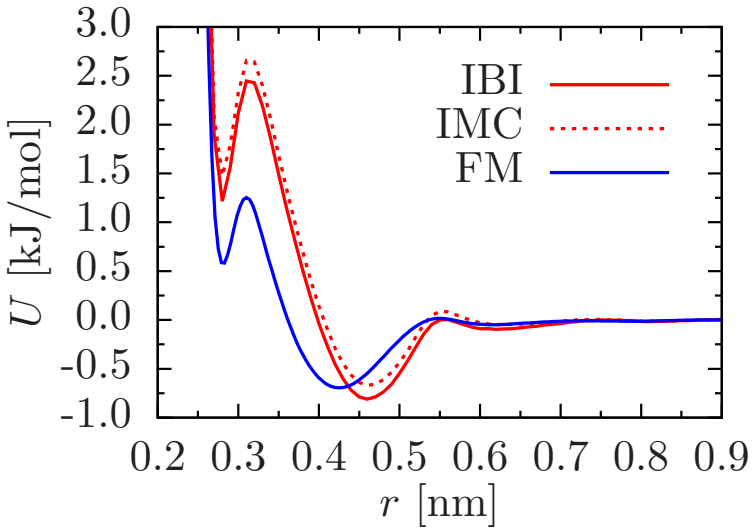
Reformulation

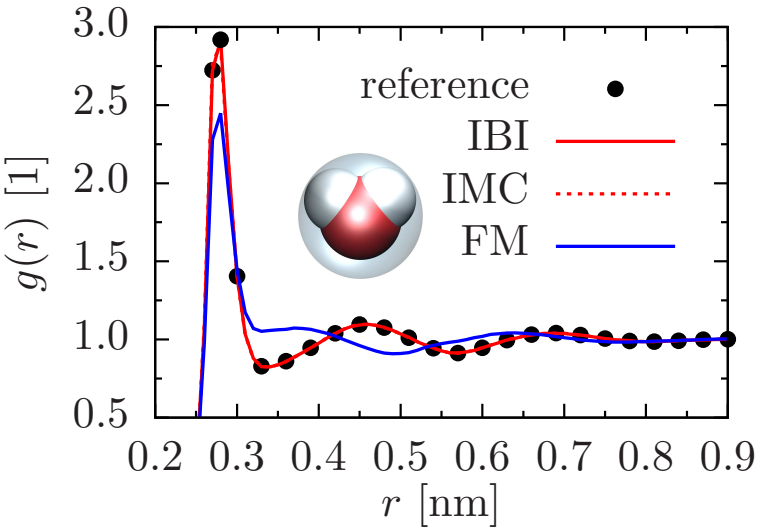
Use n ($\sim$5000) input parameters (potential tables) to generate m output parameters (properties measured in the MD simulation) and rank their quality.

- The problem is overdetermined $\rightarrow$ use $\sim$10 essential parameters
- Equivalent to a standard optimization problem
- Minimization would be possible if all ∂input/∂output exist

Targeted Coarse-Graining

Example: Water



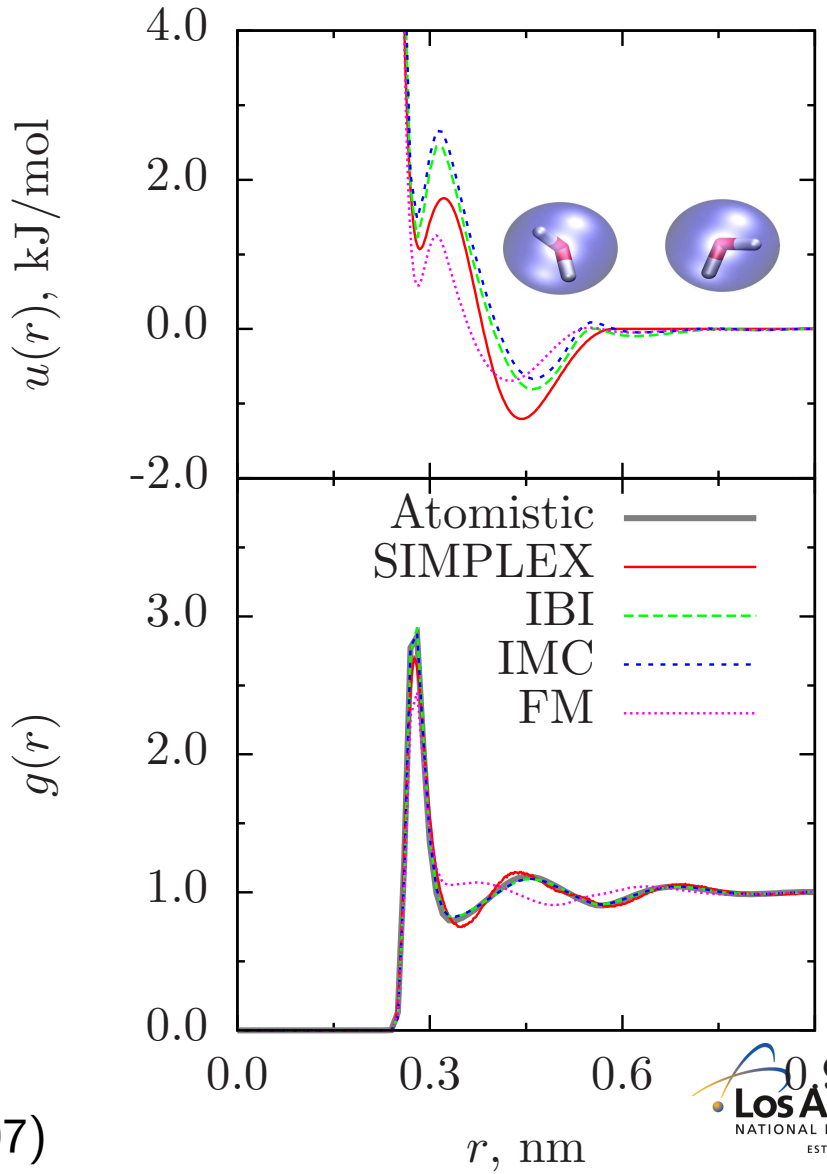


Potential should have 2 minima.

Targeted Coarse-Graining

Example: Water

- Center of mass mapping
- CKD (= WCA + $\cos^2$ attraction) + Gaussian (6 parameters)[3]
- Optimize parameters with Nelder-Mead method (Simplex)[4]



[3] Idea: M. Jochum, Phd Thesis

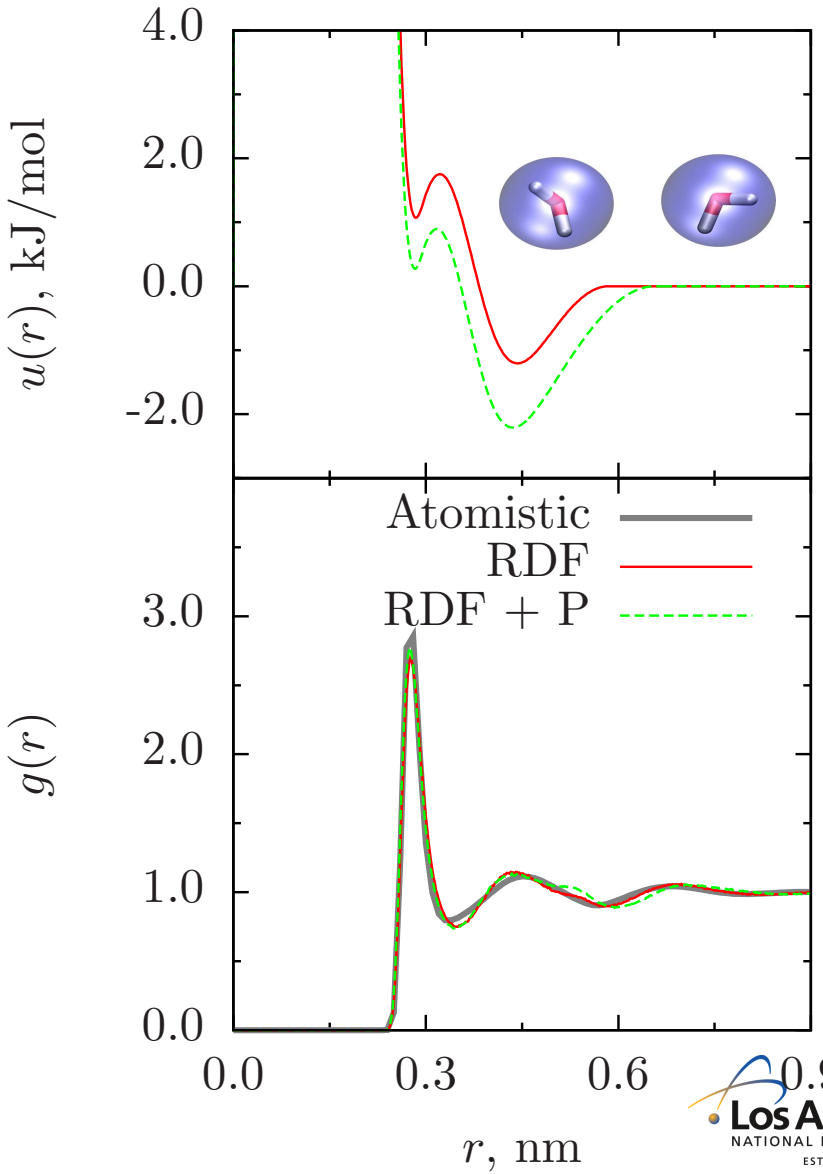
[4] Shinoda et al., Mol. Sim. 33, 27 (2007)

Targeted Coarse-Graining

Example: Water

What about the pressure?

- Can easily be incorporated
- Objective (penalty) function needs modification



Targeted Coarse-Graining

Example: Water

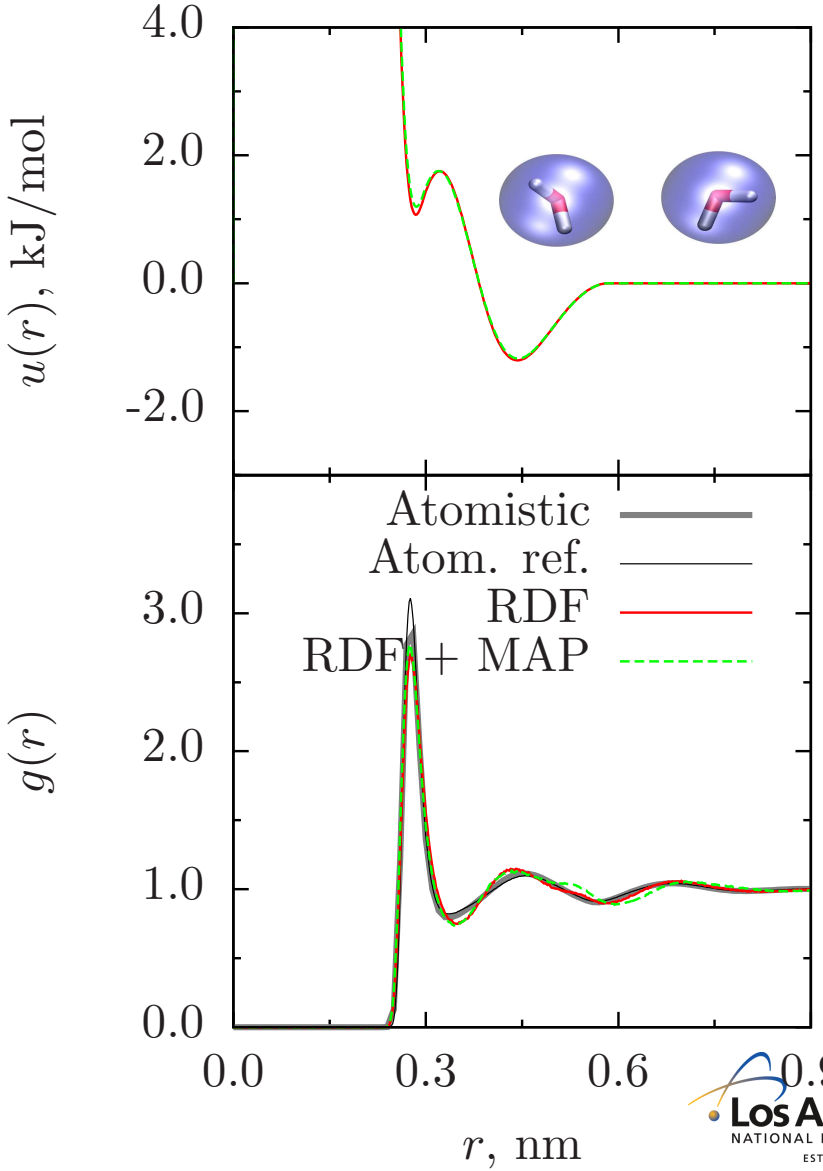
What about the mapping?

$$\vec{R} = \sum_i \lambda_i \vec{r}_i$$

with

$$\sum_i \lambda_i = 1$$

- Can easily be incorporated
- adds 1 extra parameter for symmetric mappings
- Objective (penalty) function needs no modification
- Reference rdf changes



Conclusion
Example: Water

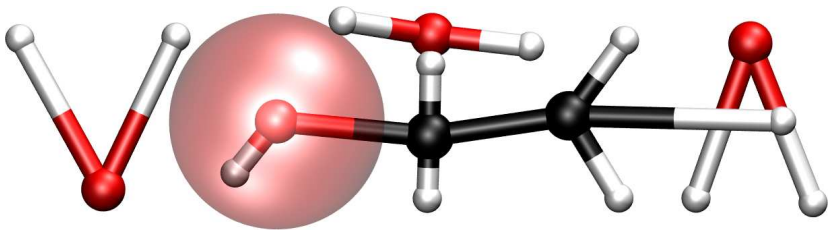
What did we learn?

- 6 parameters are enough, but simple LJ (2) is not
- Potential is short ranged
- Other target properties can be incorporated
- Simplex is fast, but can be trapped, inefficient for $\geq$10 parameters
- Use of learning optimizers (e.g. CMA Evolution Strategy or genetic algorithms) possible
- Functional potential can speed up the simulations
- Mapping can be optimized as well

The optimization view provides a framework to aim for a broader class of coarse-grained models.

Conclusion
VOTCA Team

Core developers
- Victor Rühle
- Christoph Junghans



Versatile **O**bject-oriented **T**oolkit for **C**oarse-graining **A**pplications

Modular C++ kernel
Scripting for iterative workflow
Simple integration of other simulation packages

Iterative Boltzmann inversion
Inverse Monte Carlo
Force matching

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

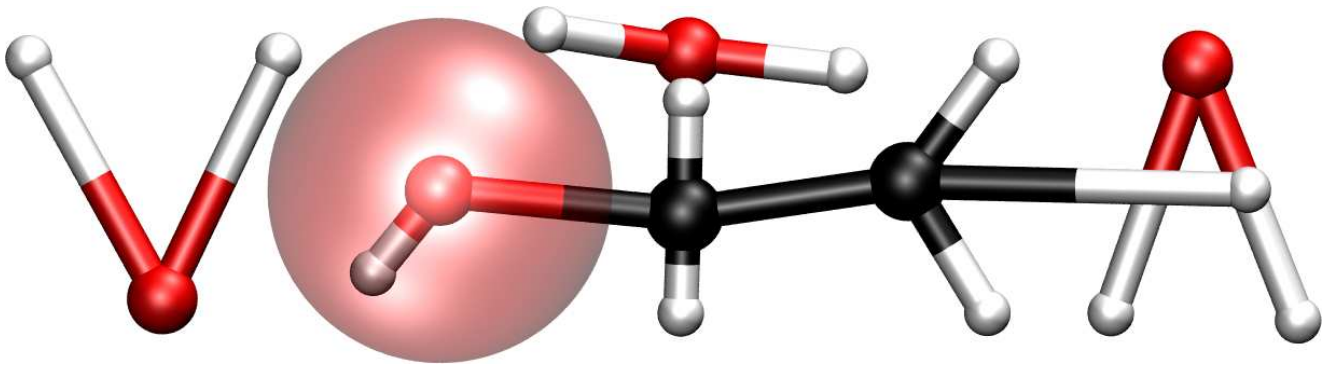
Project supervisor
- Denis Andrienko
- Kurt Kremer

Los Alamos NATIONAL LABORATORY EST. 1943

Conclusion
VOTCA Package

Linus Torvalds:

Talk is cheap, show me the code.



Versatile **O**bject-oriented **T**oolkit for **C**oarse-graining **A**pplications

Modular C++ kernel
Scripting for iterative workflow
Simple integration of other simulation packages

Iterative Boltzmann inversion
Inverse Monte Carlo
Force matching

- It's free
- All examples are in the tutorial
- It's flexible and expandable

Visit us at www.votca.org

Los Alamos NATIONAL LABORATORY EST. 1943

Conclusion
Acknowledgments

$$$

- Max Planck Society
- SFB 625 – “From Single Molecules to Nanoscopically Structured Materials”
- Department of Energy

The End

Thank you for your attention !