TECHNISCHE UNIVERSITÄT DARMSTADT

Systematic coarse graining using reversible work potentials

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

Outline

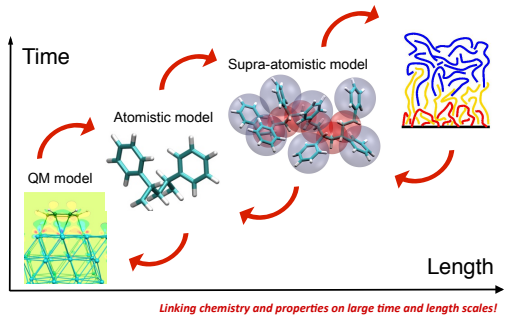
Monday, April 9

- 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



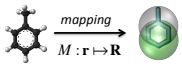
Linking chemistry and properties on large time and length scales!

Systematic coarse graining

Thermodynamic consistency

$$Q^{FG} = Q^{CG} = \int \exp\left[-\beta U^{CG}(\mathbf{R})\right] d\mathbf{R} \qquad \beta = (k_B T)^{-1}$$

$$U^{CG}(\mathbf{R}) = -k_B T \ln\left[\int e^{-\beta U^{FG}(\mathbf{r})} \delta\left(M(\mathbf{r}) - \mathbf{R}\right) d\mathbf{r}\right]$$



$\mathbf{R}$: *coarse DOFs*
$\mathbf{r}$: *atomic DOFs*

- Multi-body potential of mean force
- Prohibitively difficult to calculate and represent

$$U^{CG}(\mathbf{R}) = \sum_i \sum_{j \neq} U_2(\mathbf{R}_i, \mathbf{R}_j) + \sum_i \sum_{j \neq} \sum_{k \neq} U_3(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) + \cdots$$

$$\simeq \sum_i \sum_{j \neq} U_{eff}(\mathbf{R}_{ij})$$

Methods for effective pair potentials

- **Parameterised models** ⟷ **Derived models**
  - **Structure-based**
    - *Iterative Boltzmann Inversion (IBI)*
    - *Kirkwood-Buff IBI (KB-IBI)*
    - *Inverse Monte Carlo (IMC)*
    - *Relative Entropy*
    - *Generalised Yvon-Born-Green*
  - **Force-based**
    - *Force Matching (FM)*
    - *Multiscale Coarse Graining (MSCG)*
  - *pair Potential of Mean Force (pPMF)*
  - *Effective Force Coarse Graining (EFCG)*
  - *Conditional Reversible Work (CRW)*

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

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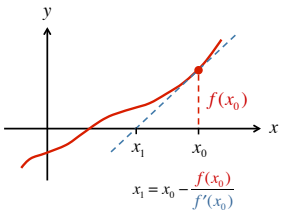
E. Brini *et al. Soft Matter* **9**, 2108 (2013)

Newton's method (Newton-Raphson)

- Finding roots (zeroes) of a function $x : f(x) = 0$
- Initial guess: x_0
- Iterate:

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$$



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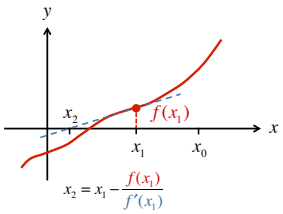

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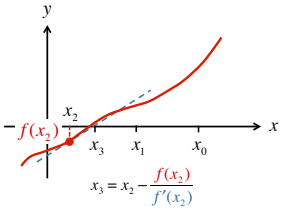


Iterative Boltzmann Inversion (IBI)

$$u_{n+1} = u_n + k_B T \ln\left[g_n / g^{ref} \right] \quad n = 0,1,2,\cdots$$

Reith, Putz, Müller-Plathe, *JCC* (2003)

$F(u_n) = g_n$ Operator F maps u on g

Start with the potential of mean force: $u_0 = -k_B T \ln g^{ref}$

Setting $Y(u) = -k_B T \ln F(u)$ this is equivalent to

$$u_{n+1} = u_n + \left(u_0 - Y(u_n) \right) \quad n = 0,1,2,\cdots$$

For comparison: The classical Newton method would be

$$u_{n+1} = u_n + Y'(u_n)^{-1} \left(u_0 - Y(u_n) \right) \quad n = 0,1,2,\cdots$$

IBI is a modified Newton method

This shows that IBI is a modified Newton method which uses the approximate derivative

$$Y'(u) = -k_B T \frac{1}{F(u)} F'(u) \approx Id$$

i.e.,

$$F'(u) \approx -\beta F(u) Id$$

Becomes exact when $F(u) = e^{-\beta u}$ (low density limit)

Inverse Monte Carlo is an exact Newton method

Another option is the inverse Monte Carlo iteration

$$u_{n+1} = u_n + K^{-1} \left(g^{ref} - F(u_n) \right) \quad n = 0,1,2,\cdots$$

where K is a discretization of the integral operator

$$(Ku)(r) = \int_0^\infty k(r,r') u(r') dr'$$

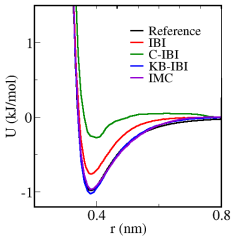
with

$$k(r,r') = -\beta \left(\langle S(r) S(r') \rangle - \langle S(r) \rangle \langle S(r') \rangle \right)$$

Lyubartsev, Laaksonen, 1995

Well-posedness?

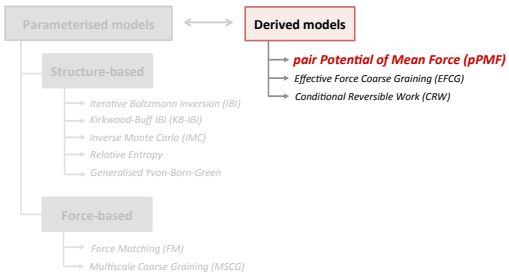
Binary Lennard-Jones mixture, no actual coarse-graining



- All potentials reproduce the RDF within line thickness
- **IBI**: stable, fast and efficient, potential does not converge
- **IMC**: expensive, potential converges

D. Rosenberger, M. Hanke, N. F. A. van der Vegt, *Eur. Phys. J. ST* **225**, 1323 (2016)
M. Hanke, *J. Stat. Phys.* **170**, 536 (2018)

Methods for effective pair potentials



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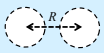
Hydrophobic interaction

atomistic model:
solvent-solvent
solute-solvent
solute-solute

$$U^{eff}(R) = \Delta A_{interaction}(R) + \Delta A_{hydration}(R)$$

single-site CG model:
solvent-solvent (IBI)
solute-solvent (IBI)
solute-solute (not present)

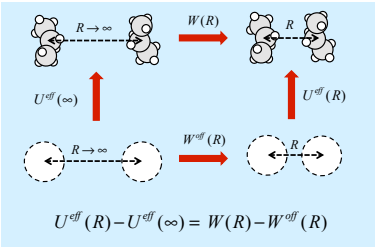


Reproduce the free energy of this pair …

with an appropriate choice of the effective solute-solute pair potential in the CG model

A. Villa, C. Peter, N.F.A. van der Vegt, *JCTC* **6**, 2434 (2010)

Pair potential of mean force



$$U^{eff}(R) - U^{eff}(\infty) = W(R) - W^{eff}(R)$$

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A. Villa, C. Peter, N.F.A. van der Vegt, *JCTC* **6**, 2434 (2010)

The effective potential

$$\begin{aligned} U^{eff}(R) &= W(R) - W^{eff}(R) \\ &= \left[W_{\text{interaction}}(R) + W_{\text{solvent}}(R)\right] - W^{CG}_{\text{solvent}}(R) \\ &= W_{\text{interaction}}(R) + \Delta W_{\text{solvent}}(R) \end{aligned}$$

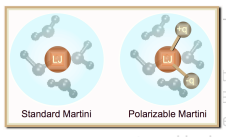
- Can be used in combination with any existing CG solvent model (not necessarily IBI)
- For example: water-water (MARTINI, 4:1 mapping), solute-water (IBI, integral hydration number)
- Tradeoff: structure versus thermodynamics

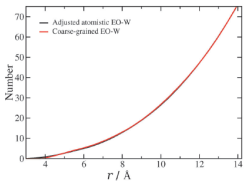
A. Villa, C. Peter, N.F.A. van der Vegt, *JCTC* **6**, 2434 (2010)

The effective potential

$$U^{eff}(R) = W(R) - W^{eff}(R)$$

$$= \left[W_{\text{interaction}}(R) + \right.$$





wa **cgmartini.nl** tegral hydratic

- Tradeoff: structure versus ther

K. Prasitnok, M.R. Wilson *PCCP* **15**, 17093 (2015)

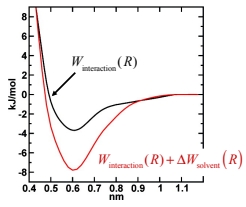
Analogy: single-iteration IBI

$$u_{n+1} = u_n + \left(W - Y(u_n)\right) \quad n = 0,1,2,\cdots$$
$$W = -k_B T \ln g^{ref}$$

- perform a single IBI iteration on the solute-solute interaction using fixed (pre-determined) solute-water and water-water IBI interactions
- choose $u_0 = 0$

$$u_1 = W - Y(u_0) = W - W^{off}$$
$$= W_{\text{interaction}}(R) + \Delta W_{\text{solvent}}(R)$$

Single site benzene/water model



A. Villa, C. Peter, N.F.A. van der Vegt, *JCTC* **6**, 2434 (2010)

Solution thermodynamics

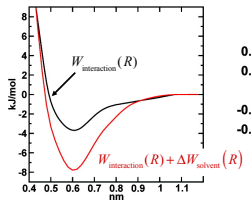
$$\rho_j G_{ij} = \rho_j \int_0^\infty \left[g_{ij}(r) - 1\right] 4\pi r^2 dr$$

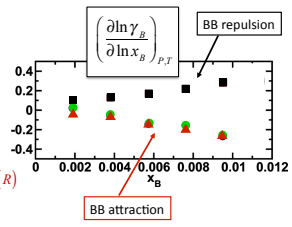
$$\left(\frac{\partial \ln \gamma_B}{\partial \ln x_B}\right)_{P,T} = -\frac{x_B \rho_W \Delta_{BW}}{1 + x_B \rho_W \Delta_{BW}}$$

$$\Delta_{AB} = G_{AA} + G_{BB} - 2G_{AB}$$

J. Milzetti, D. Nayar, N.F.A. van der Vegt, *J. Phys. Chem. B* (2018)
P. Ganguly, N.F.A. van der Vegt, *JCTC* **9**, 1347 (2013)

Single site benzene/water model



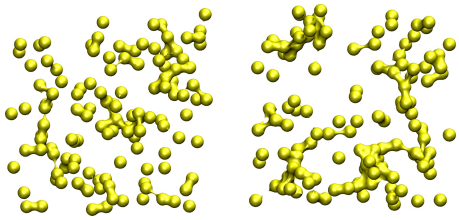


A. Villa, C. Peter, N.F.A. van der Vegt, *JCTC* **6**, 2434 (2010)

Hydrophobic interactions (in this system) are pairwise additive

Liquid structure

0.5 M benzene

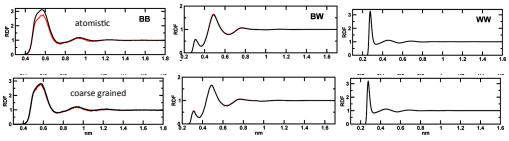


Atomistic Coarse-grained

A. Villa, C. Peter, N.F.A. van der Vegt, *JCTC* **6**, 2434 (2010)

Liquid structure

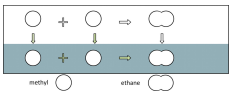
0.2 M and **0.5 M** benzene



- Pair structure and changes of the solute chemical potential are reproduced with a transferable pair potential
- Hydrophobic interactions are pairwise additive

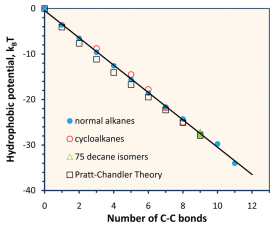
A. Villa, C. Peter, N.F.A. van der Vegt, *JCTC* **6**, 2434 (2010)

Hydrophobic interactions between small molecules are pairwise additive



$$W(r)\big|_{r=b} = F_{s,ethane} - 2F_{s,methane}$$

$$W_n\big|_{bonded} = F_{s,C_n} - nF_{s,methane}$$



J. Wu , J.M. Prausnitz *PNAS* **105**, 9512-9515 (2008)

Methods for effective pair potentials

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  - ***Conditional Reversible Work (CRW)***

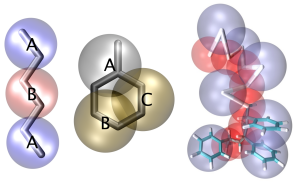
- **Minimize state-point dependent average multibody contributions …**
- **… by deriving the potentials from the atomistic interactions at pair level**
- **Transferable models!**

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

Transferability of intermolecular pair potentials

Transferability

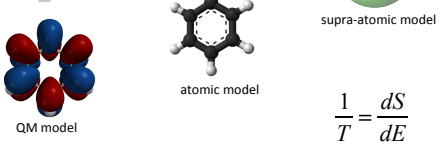
- ❑ State point
- ❑ Chemical ("atom types")



Derived pair potentials

$E_{AA} \neq E_{SA} \quad S_{AA} \neq S_{SA}$

$E_{QM} = E_{AA}$



QM model

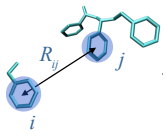
atomic model

supra-atomic model

$$\frac{1}{T} = \frac{dS}{dE}$$

Pair interaction free energy

- No a priori knowledge about the functional dependence on R_{ij}
- Account for entropy of lost degrees of freedom
- Free energy calculations $\Rightarrow \Delta A_{ij}(R_{ij})$
- Use this quantity as a pair potential
- The **Conditional Reversible Work (CRW)** method

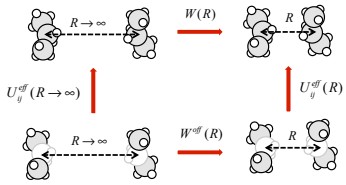


E. Brini *et al. PCCP* (2011); *PCCP* (2012); *J. Chem. Phys.* (2012)
G. Deichmann et al. *JCP* **141**, 224109 (2014)
V. Ardham et al. *JCP* **143**, 243135 (2015)

Y. Wang, W.G. Noid, P. Liu, G.A. Voth, *PCCP* (2009)
D. Fritz, V. Harmandaris, K. Kremer, N.F.A. van der Vegt, *Macromolecules* (2009)
N. Zacharopoulos, N. Vergadou, D.N. Theodorou, *J. Chem. Phys.* (2005)
J.D. McCoy, J.G. Curro, *Macromolecules* (1998)

Conditional Reversible Work (CRW)

Constrained sampling (**Cycle** approach)



Sampling (MD/MC) in:

- ❑ Gas phase
- ❑ Liquid phase
- ❑ Aqueous solvent

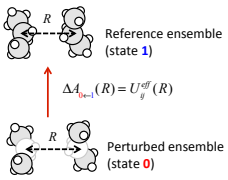
$$U_{ij}^{eff}(R) - U_{ij}^{eff}(R \to \infty) = W(R) - W^{eff}(R)$$

Conditional Reversible Work (CRW)

Unconstrained sampling (**FEP** approach)

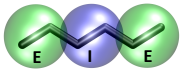
- Simulation of state **1**: liquid phase, full Hamiltonian
- Statistics: Averaging over all pairs

$$\begin{aligned} U_{ij}^{eff}(R) &= \Delta A_{0\leftarrow 1}(R) \\ &= k_B T \ln \left\langle e^{\beta E_{ij}(R)} \right\rangle_1 \\ &= k_B T \ln \left[\int_{-\infty}^{\infty} P_{ij}(E;R) \exp(\beta E) dE \right] \end{aligned}$$

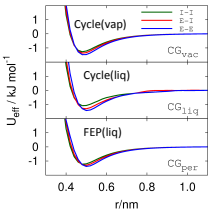


E. Brini, N. F. A. van der Vegt, *J. Chem. Phys.* **137**, 154113 (2012)

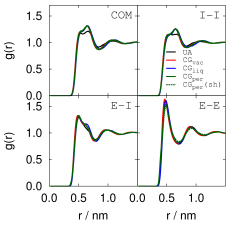
Example: Hexane



CRW models

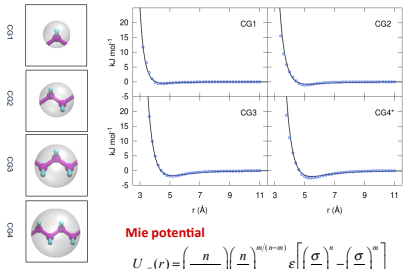


Structural correlations (298 K, 1 atm liquid phase)



E. Brini, N. F. A. van der Vegt, *J. Chem. Phys.* **137**, 154113 (2012)

Alkanes: mapping



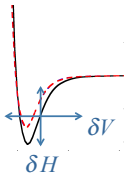
Mie potential

$$U_{eff}(r) = \left(\frac{n}{n-m}\right)\left(\frac{n}{m}\right)^{m/(n-m)} \varepsilon\left[\left(\frac{\sigma}{r}\right)^{n} - \left(\frac{\sigma}{r}\right)^{m}\right]$$

M. Dallavalle, N.F.A. van der Vegt, *PCCP* **19**, 23034 (2017)

State point transferability

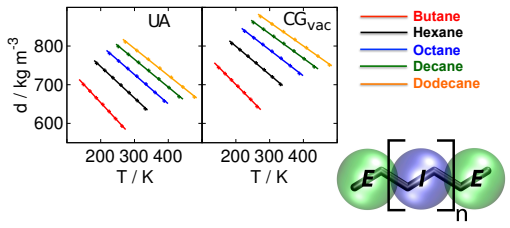
Physical potentials free of state-dependent multi-body contributions show better transferability



$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N} \sim \langle \delta V \delta H \rangle_{NpT}$$

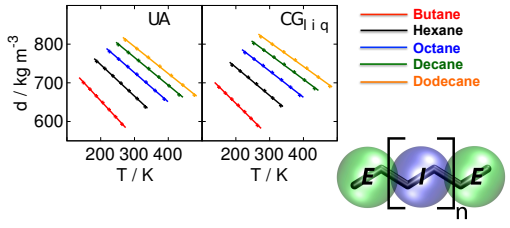
Fluctuations in energy and volume are determined by sampling different regions of the potential

Chemical & state point transferability



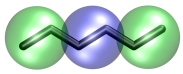
E. Brini, N. F. A. van der Vegt, *J. Chem. Phys.* **137**, 154113 (2012)

Chemical & state point transferability



E. Brini, N. F. A. van der Vegt, *J. Chem. Phys.* **137**, 154113 (2012)

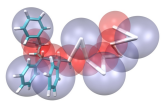
Liquid hexane properties (298 K, 1 atm.)

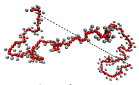


Model	ΔF_{ex} / kJ mol^{-1}	γ_{LV} / mN m^{-1}	α_p / 10^{-9} Pa^{-1}	κ_T / 10^{-3} K^{-1}
Fine-grained	−15.5	17.6	1.7	1.31
Coarse-grained	−6.6	18.5	1.8	1.16

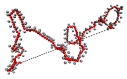
E. Brini, N. F. A. van der Vegt, *J. Chem. Phys.* **137**, 154113 (2012)

Transferability: Material surfaces



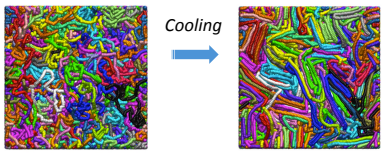


atactic polystyrene



syndiotactic polystyrene

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



V. Marcon, D. Fritz, N.F.A. van der Vegt, *Soft Matter* **8**, 5585 (2012)

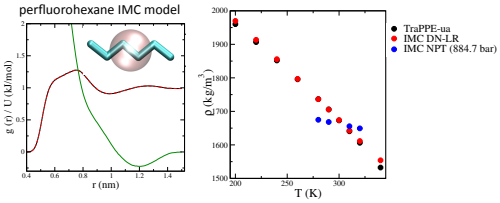
Transferability: Pressure matching

Systems with isotropic volume fluctuations

$$H(\mathbf{r}^N,\mathbf{p}^N,V)=\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i}+U(\mathbf{r}^N)+U_V(V)$$

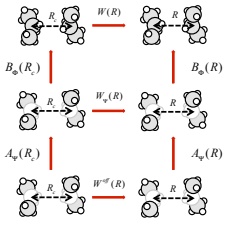
Das, Andersen, *JCP* **132**, 164106 (2010)
Dunn, Noid, *JCP* **143**, 243148 (2015)

perfluorohexane IMC model



D. Rosenberger, N.F.A. van der Vegt, *PCCP* **20**, 6617 (2018)

Polar fluids: electrostatics



G. Deichmann, N. F. A. van der Vegt, *JCTC* **13**, 6158 (2017)

Interaction components: Ψ,Φ

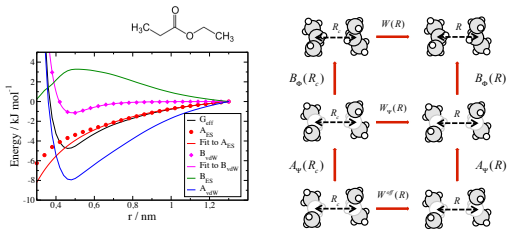
$$U_{ij}^{eff}(R)=A_\Psi(R)+B_\Phi(R)$$

$$\Psi,\Phi=\begin{cases}ES,VdW\\VdW,ES\end{cases}$$

Free energy components: Order/ sequence matters!

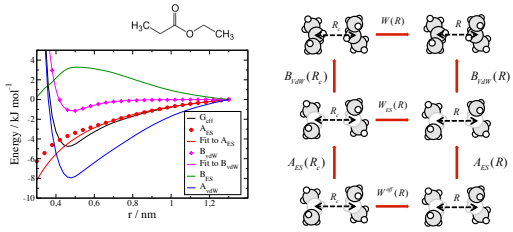
$$A_\Psi \neq B_\Psi$$

Polar fluids: electrostatics



G. Deichmann, N. F. A. van der Vegt, *JCTC* **13**, 6158 (2017)

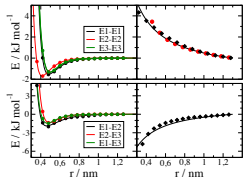
Polar fluids: electrostatics

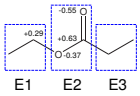


G. Deichmann, N. F. A. van der Vegt, *JCTC* **13**, 6158 (2017)

Polar fluids: electrostatics

CRW-ES model for ethyl proprionate





G. Deichmann, N. F. A. van der Vegt, *JCTC* **13**, 6158 (2017)