Performing coarse-grained molecular dynamics simulations in the isothermal, isobaric ensemble

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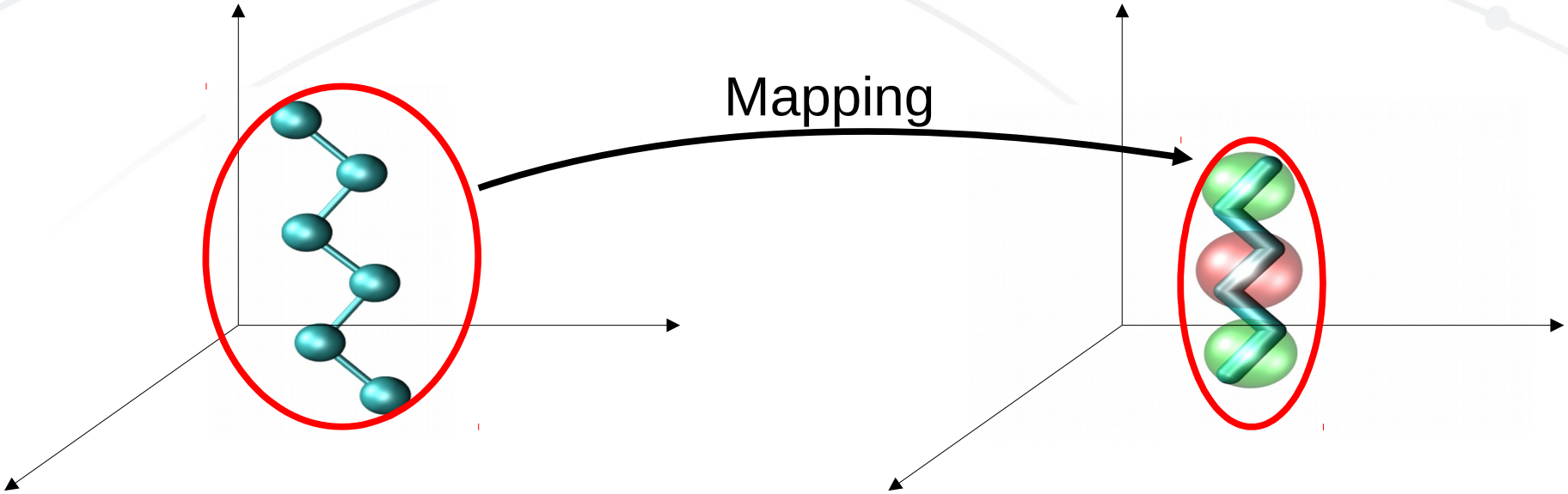
LA-UR-19-28089

Bottom-up coarse graining



1. Mapping configurations

2. Mapping potential energy surface

Bottom-up coarse graining

$$U\left(R^N\right)=\sum_{n_{bonds}} U\left(l,\theta,\phi\right)+\sum_{i<j} U\left(r_{ij}\right)$$

U (l, θ, Φ): intramolecular interactions

- l: bond length
- θ: bond angle
- Φ: dihedral angle

Bottom-up coarse graining

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U (l, θ, Φ): intramolecular interactions

$$U^{(PMF)}\left(q\right)=-k_B T \ln P^0\left(q\right)+C_q$$

Bottom-up coarse graining

$$U\left(R^N\right)=\sum_{n_{bonds}} U\left(l,\theta,\phi\right)+\sum_{i<j} U\left(r_{ij}\right)$$

U (r_{ij}): intermolecular interactions

$$U^{(PMF)}\left(r_{ij}\right)=-k_B T \ln g^0\left(r_{ij}\right)+C_q$$

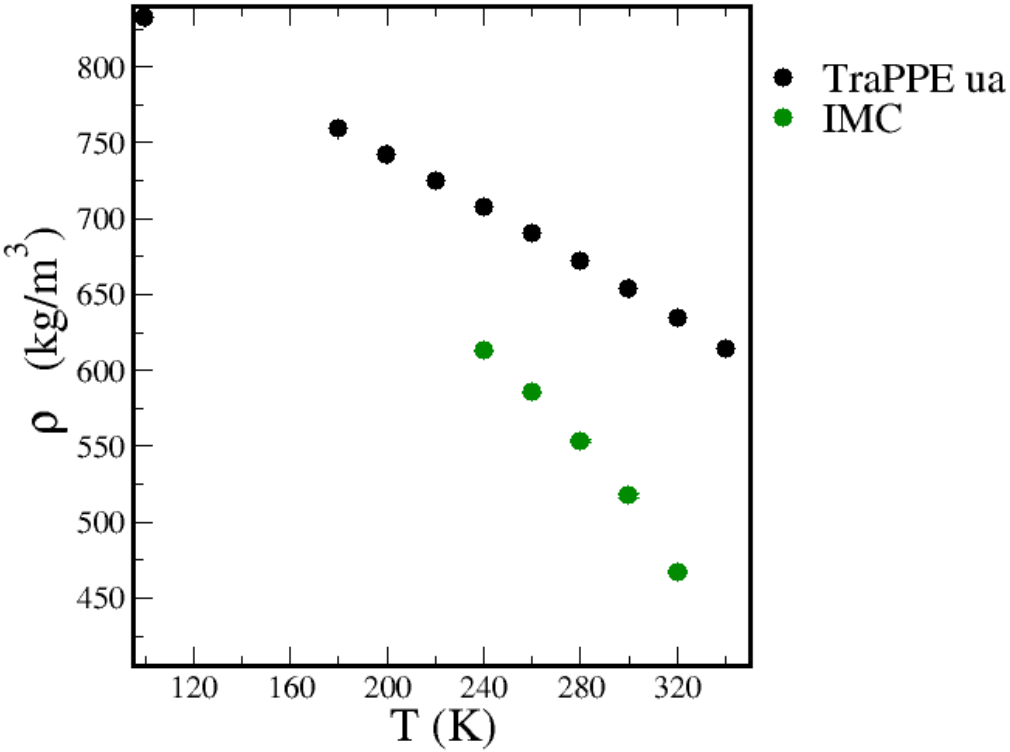
Structure based coarse-graining via Inverse Monte Carlo (IMC):[1]

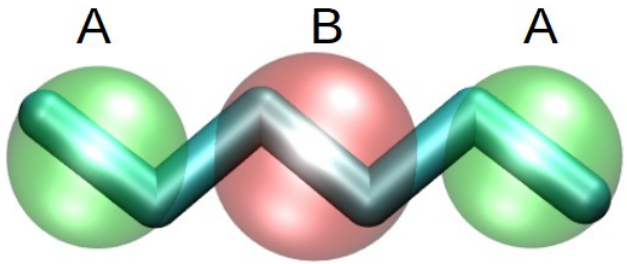
$$U^n\left(r_{ij}\right) = U^{PMF}\left(r_{ij}\right) + \Delta U\left(r_{ij}\right)$$

$$\left\langle N_\alpha \right\rangle - N_\alpha^{ref} = \beta\left(\left\langle N_\alpha \right\rangle\left\langle N_\gamma \right\rangle - \left\langle N_\alpha N_\gamma \right\rangle\right)\Delta U_\gamma$$

[1]: Lyubartsev, Laaksonen: Phys. Rev. E., 52, 3730 (1995)

Coarse-grained simulations of hexane at 1 bar (NPT)





D.R. and N. F. A. van der Vegt: Phys. Chem. Chem. Phys, 20, 6617 (2018)

Extended Hamiltonian to describe CG system[1]

$$H_{CG} = \sum_{i=1}^{N} \frac{P_i^2}{2m_i} + U\left(R^N\right) + U_v\left(V\right)$$

$$U_V\left(V\right) = N\left(\frac{V}{\bar{v}}\right)\psi_1 + N\left(\frac{V-\bar{v}}{\bar{v}}\right)^2\psi_2$$

[1]: Das, Andersen: J. Chem. Phys. 132,164106 (2010)

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N = Number of CG beads

V = Volume

$\bar{v}$ = Average volume of the fine grained system

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$$U_V(V) = N\left(\frac{V}{\bar{v}}\right)\psi_1 + N\left(\frac{V-\bar{v}}{\bar{v}}\right)^2\psi_2$$

- **Variational principle to determine ψ_1, ψ_2:**

  [1]: Das, Andersen: J. Chem. Phys. 132, 164106 (2010)

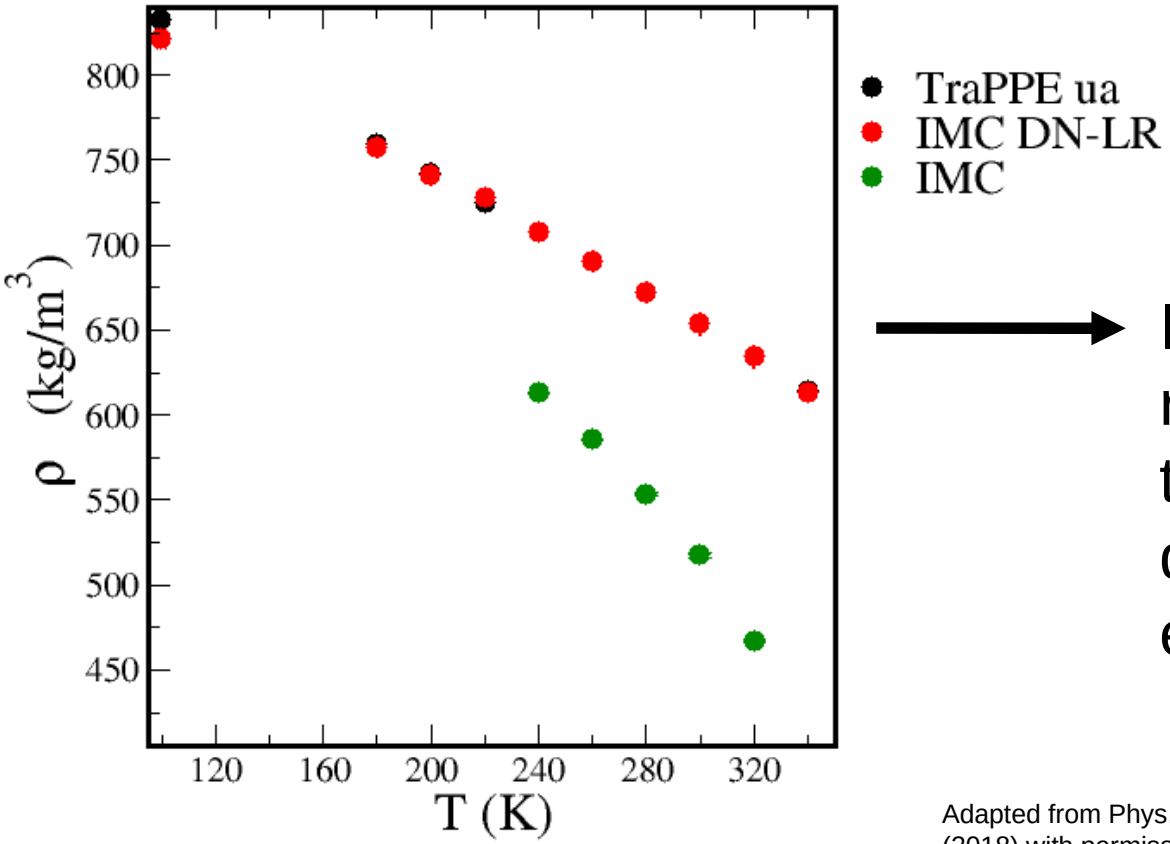
- **Self-consistent correction:**

  [2]: Dunn, Noid: J.Chem. Phys. 143, 243148 (2015)

- **Linear regression approach:**

  [3]: **D.R.,** van der Vegt: Phys. Chem. Chem. Phys, 20, 6617 (2018)

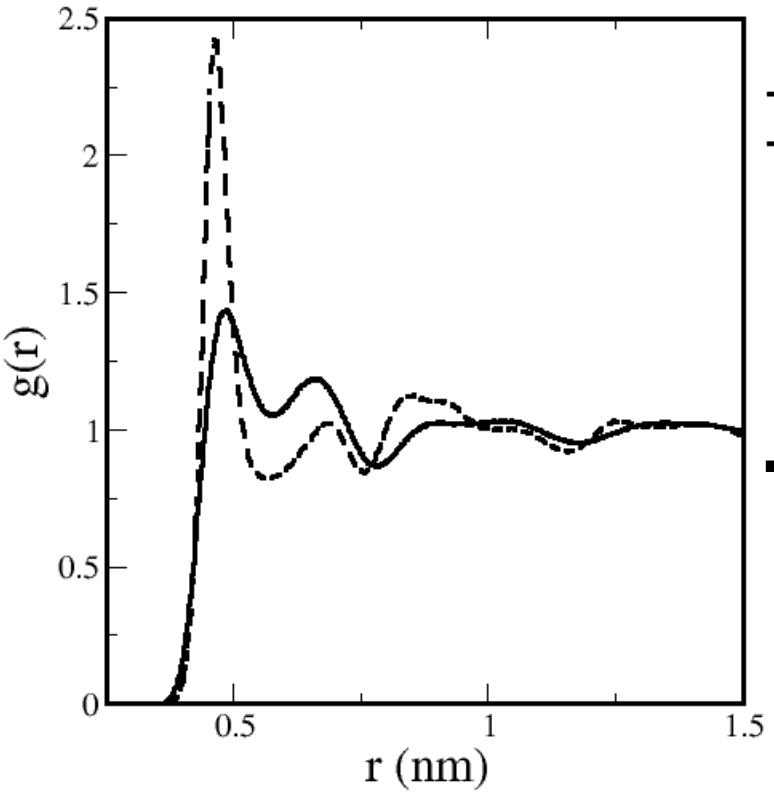
Influence of U_v on the bulk density of hexane

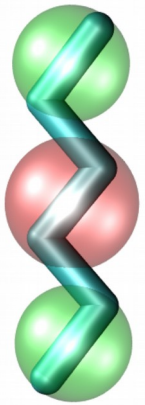


→ Improved representability and transferability for bulk density and thermal expansion behavior

Adapted from Phys. Chem. Chem. Phys, DOI: 10.1039/C7CP08246K (2018) with permission from the PCCP Owner Societies.

Transferability: Center of mass RDF





→ Particle interactions are not transferable

Conclusion

- Volume dependent potential enables simulations in N, P, T ensemble at same pressure as during reference simulations
- Linear regression approach provides a computational less expensive way to derive transferable CG potentials for alkanes
- Recently applied for concentration transferability:

  D. R. and N. F. A. van der Vegt, Phys. Rev. E 99, 053308 (2019)

- Matching structure not equal matching thermodynamics

Prof. Dr. Nico van der Vegt

Computational Physical Chemistry

TECHNISCHE UNIVERSITÄT DARMSTADT

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Multiscale Simulation Methods for Soft Matter Systems

DFG Deutsche Forschungsgemeinschaft

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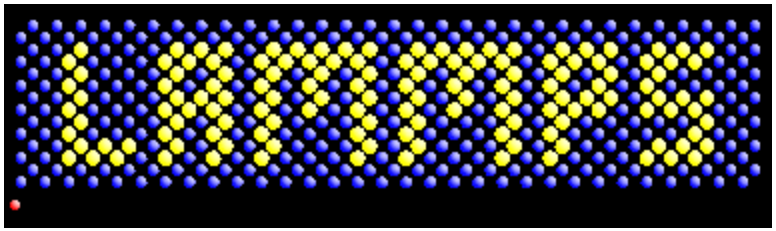
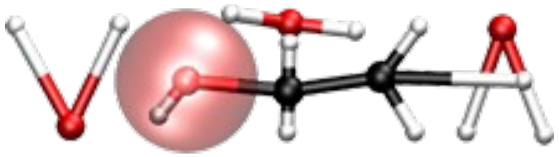


Bottom-up **O**pen-source
Coarse-graining **S**oftware
https://github.com/noid-group/BOCS



https://github.com/votca/csg