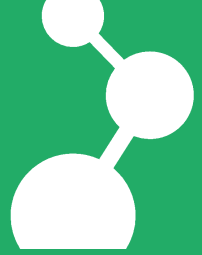
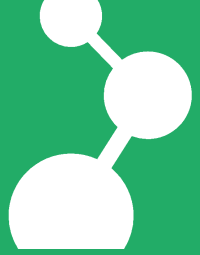


Comparative atomistic and coarse-grained study of water: What do we lose by coarse-graining?

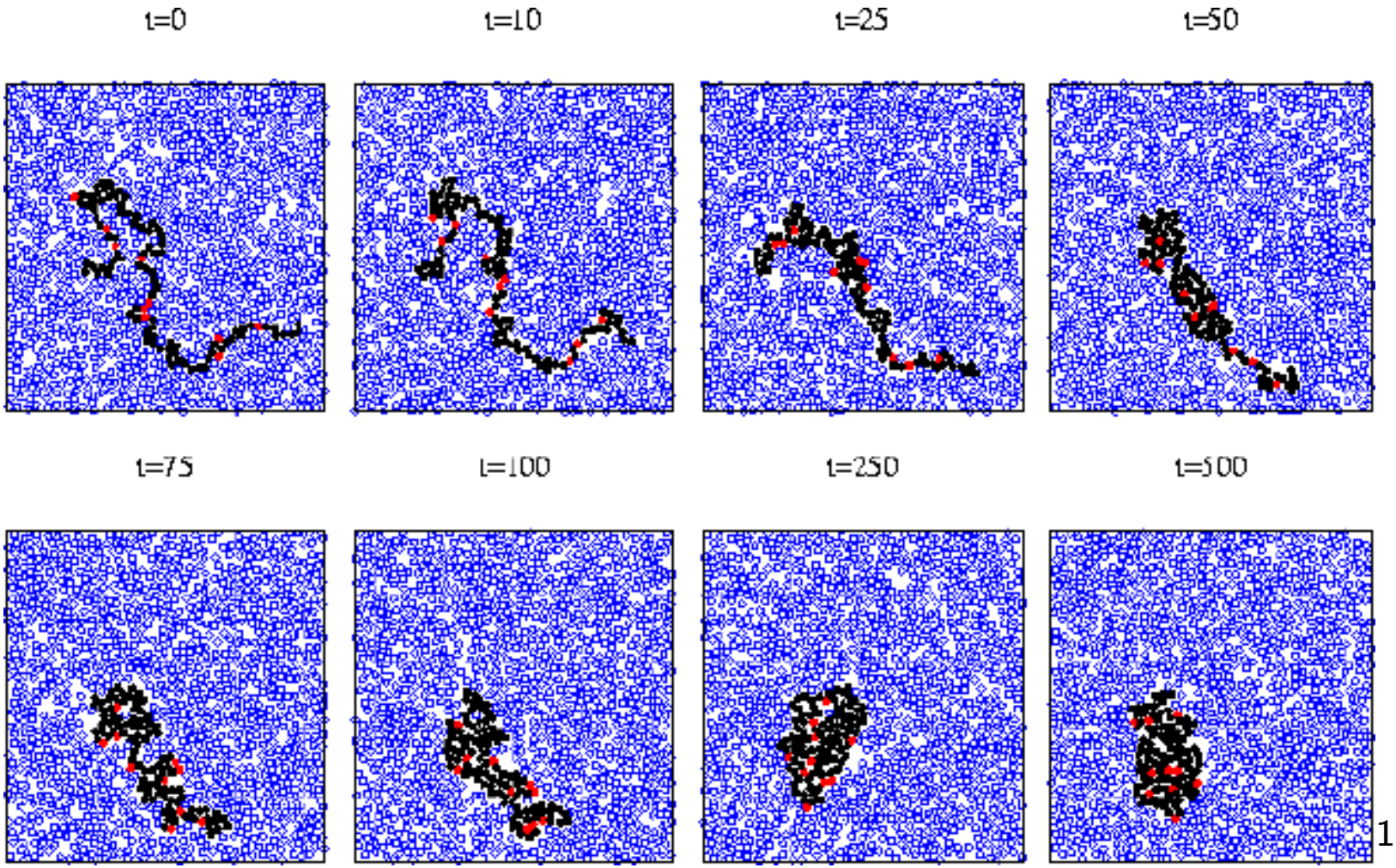
Han Wang, Christoph Junghans and Kurt Kremer

Max Planck Institute for Polymer Research
Mainz

Nov 27, 2008



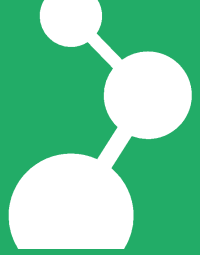
Motivation



[1]

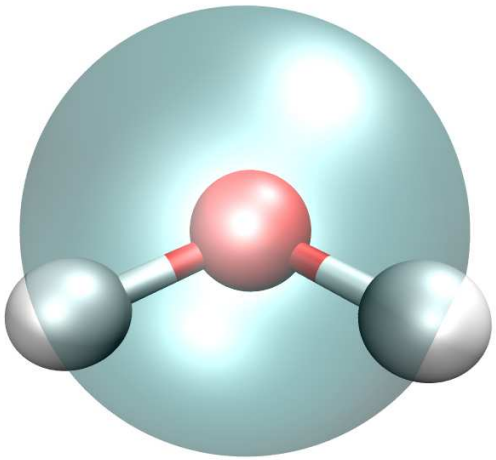
→ What about the solvent?

[1] http://www.upei.ca/ physics/polson/research/research.html



Motivation

Replace every solvent molecule by a coarse-grained bead.

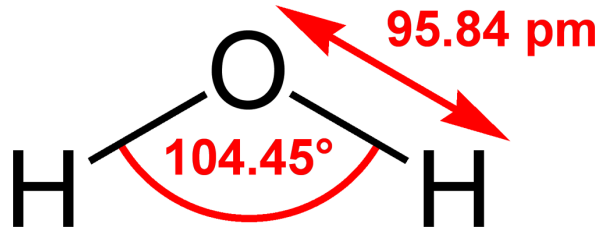


Why?

- Save computer time

  All-Atom 1 Lennard-Jones + 9 Coulomb

  Coarse-Grained 1 Tabulated
- Couple MD to continuum
- Understanding general properties

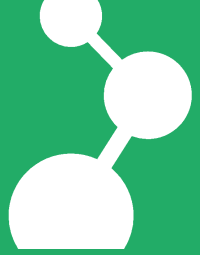


Simplest class of water model:

- Rigid geometry
- Lennard Jones interaction between oxygens
- Coulomb (with partial charges) between all atoms

	TIP3P	SPC	SPC/E
r_{OH} [Å]	0.9572	1.0	1.0
$\angle$HOH [°]	104.52	109.47	109.47
σ [nm]	0.3151	0.3166	0.3166
ϵ [kJ/mol]	0.6364	0.6506	0.6506
q_O [e]	-0.834	-0.820	-0.8476
q_H [e]	$+0.417$	$+0.410$	$+0.4238$

- At ambient conditions, all of them give reasonable results.



Structure based coarse-graining

- Find a pair potential for the coarse-grained system with the equal radial distribution function (RDF,$g(r)$)
- Target RDF $g^{\text{target}}(r)$ is taken from atomistic simulation

Inverse Boltzmann Method[2]

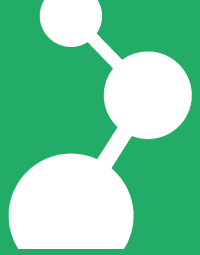
$$V_{i+1}(r) = V_i(r) + \mathrm{k_B}\,T \ln\left[\frac{g_i(r)}{g^{\text{target}}(r)}\right]$$

with potential of mean force as initial guess

$$V_0(r) = -\mathrm{k_B}\,T \ln g^{\text{target}}(r)$$

Neglects higher (> 2) body effects !

[2] D. Reith et al.,J. Comp. Chem. **24**,1624 (2003).



Pressure will change due to removal of all internal degrees of freedom

Pressure-Correction (PC)

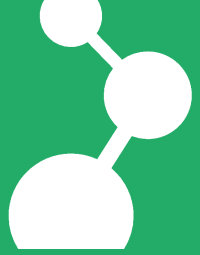
Adding an additional potential of the form

$$\Delta V(r) = A\left(1 - \frac{r}{r_{\text{cut}}}\right) \ ,$$

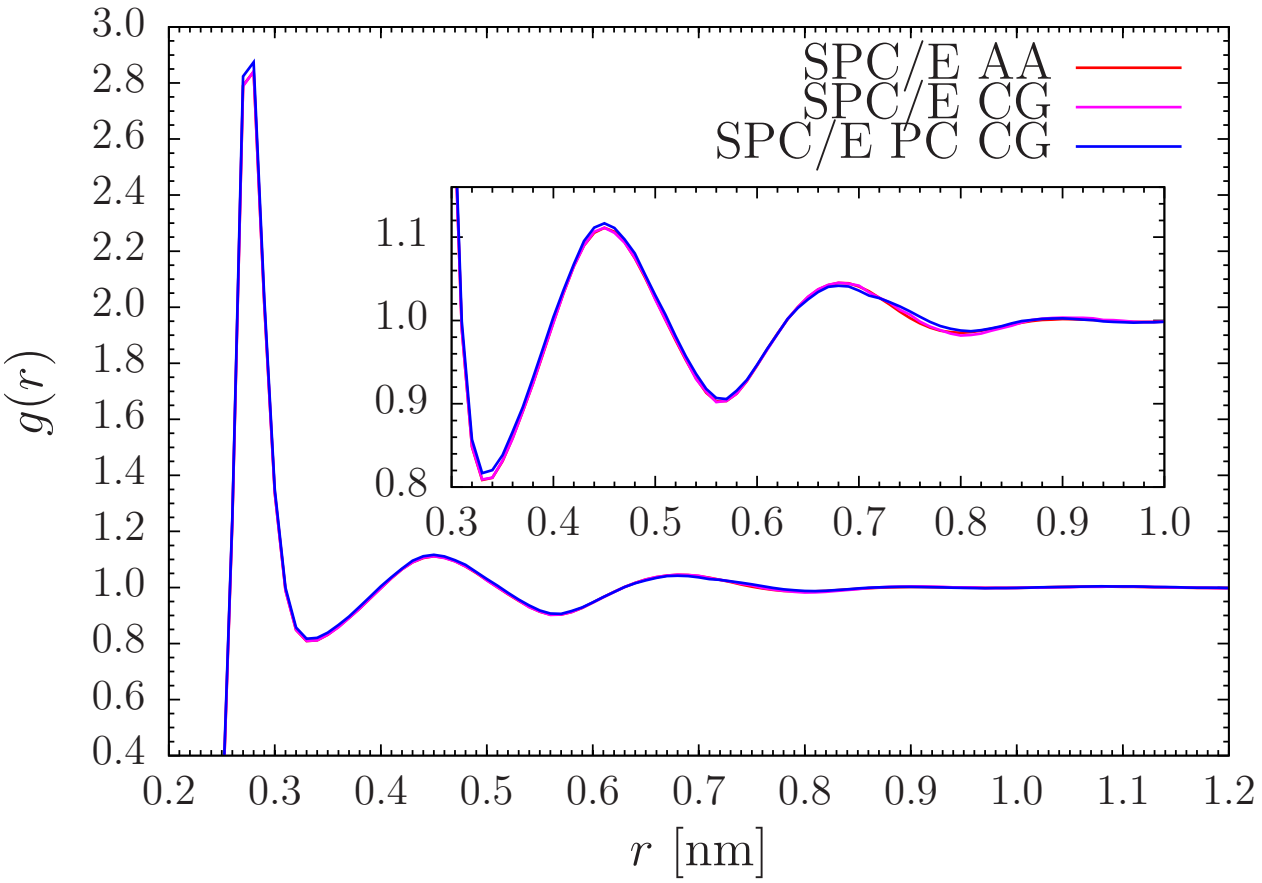
where

$$A_i \approx -(p - p^{\text{target}})V\left[\frac{2\pi N\rho}{3r_{\text{cut}}}\int_0^{r_{\text{cut}}} \mathrm{d}r\ r^3 g_i(r)\right]^{-1}$$

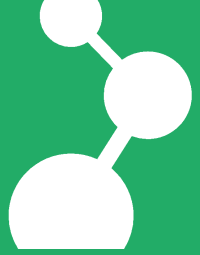
and at maximum $0.1\mathrm{k_B}\,T$



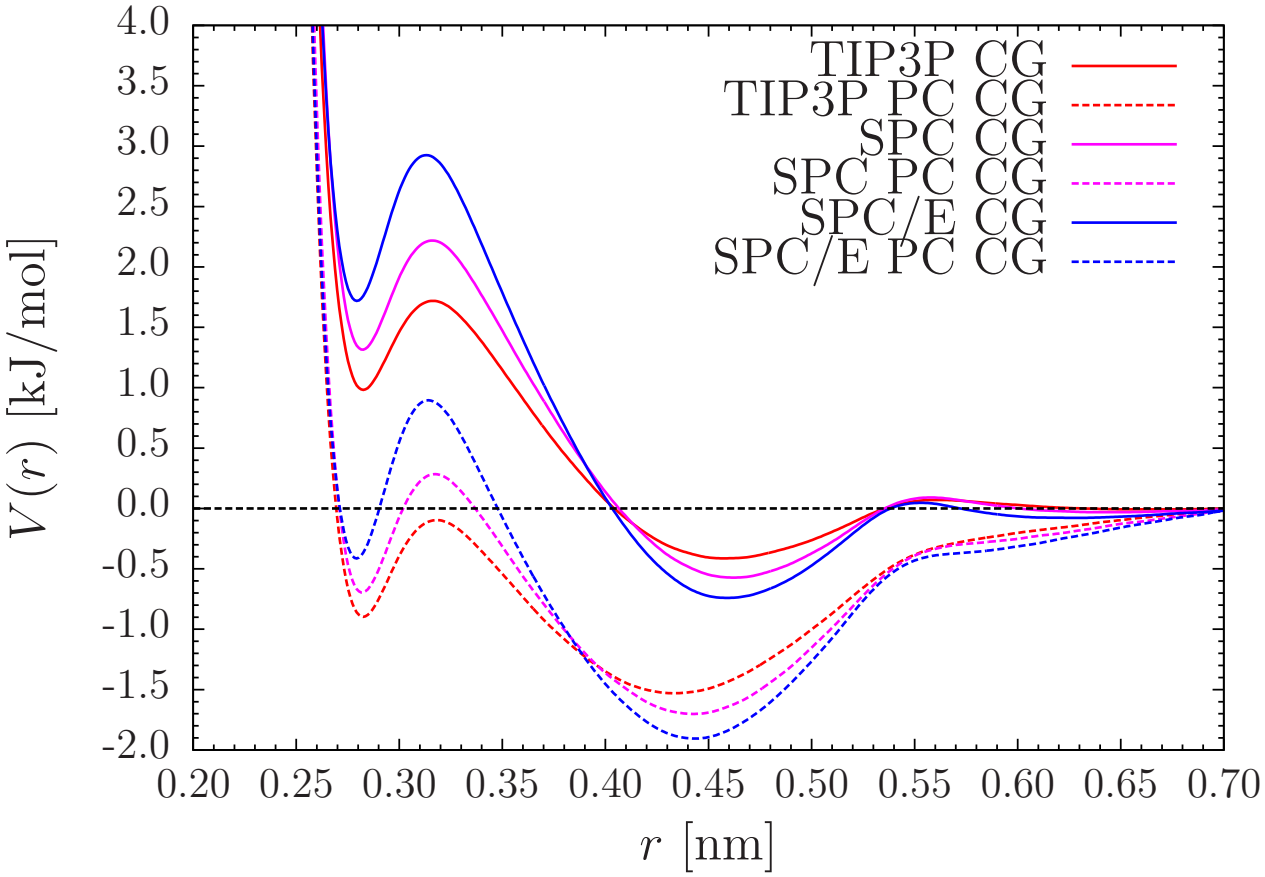
Results
RDF of SPC/E



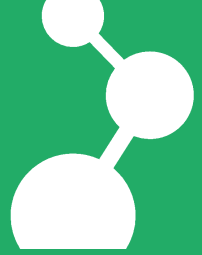
$\longrightarrow$ Pressure correction partly destroys structure



Results
Potentials

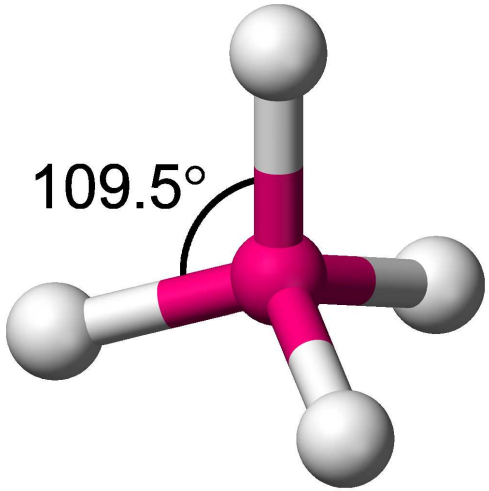


$\longrightarrow$ Behavior is governed by two length ratios



Water likes to pack in a tetrahedral cluster

- 1 center molecule
- 4 neighbor molecules

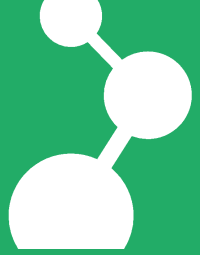


Order parameter[3]

$$q_4 = 1 - C \sqrt{\sum_{i<j} [\theta_{ij} - 109.471^\circ]^2} \ ,$$

- $q_4 = 0$ for randomly distributed particles ($\rightarrow C = 1.8165$)
- $q_4 = 1$ for perfect tetrahedral packing

[3] Other conventions are possible

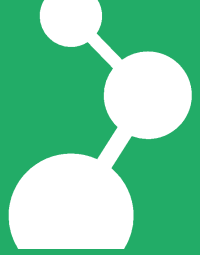


Ratio of the wells

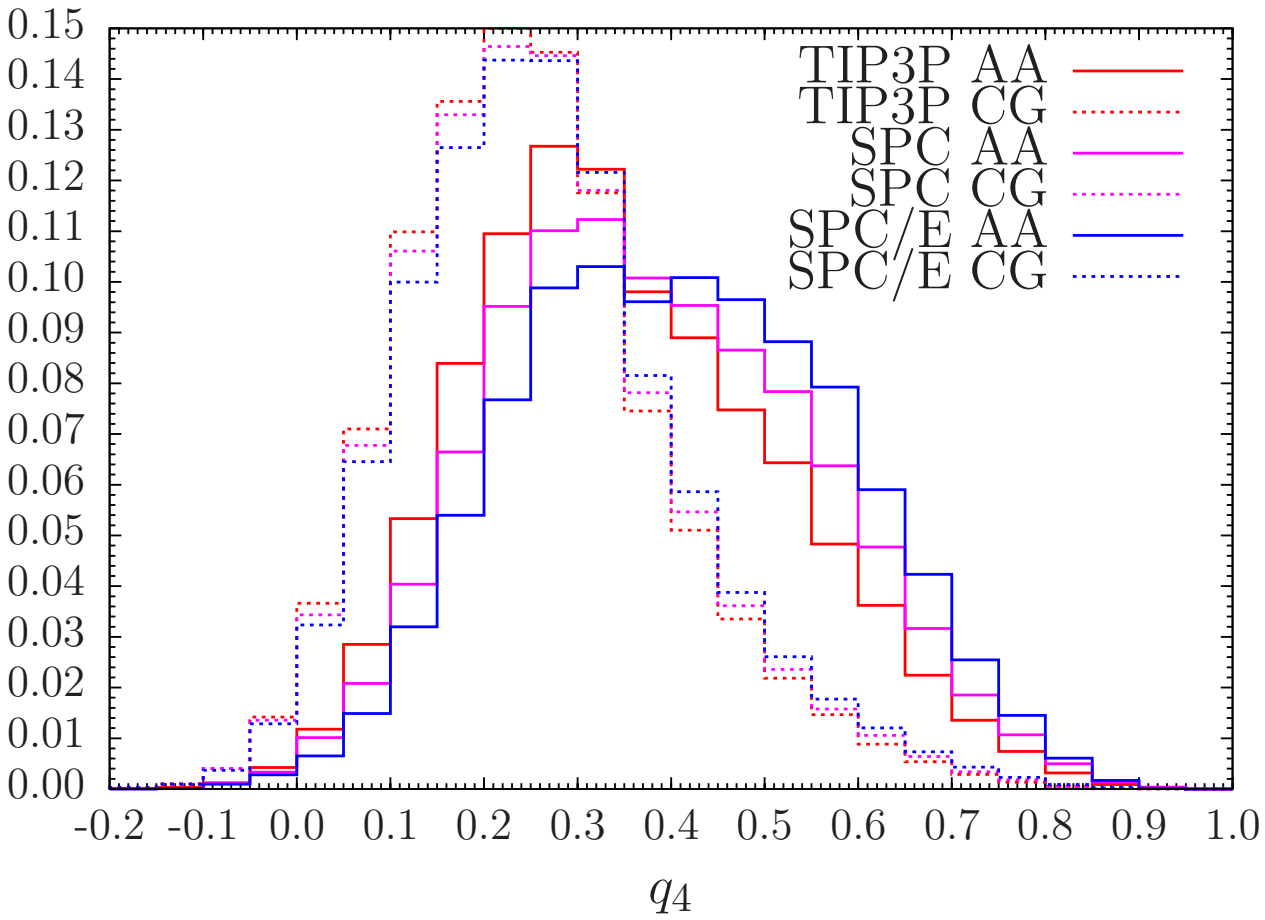
- $\gamma = \frac{\text{second well}}{\text{first well}} \approx \frac{2\sqrt{2}}{3}$
- $\frac{\text{neighbor-neighbor distance}}{\text{center-neighbor distance}} = \frac{2\sqrt{2}}{\sqrt{3}}$
- Need for tetrahedral packing

Ratio of maxima

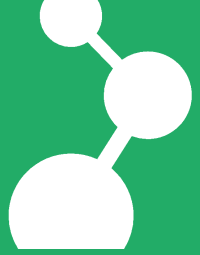
- $\delta = \frac{\text{first well}}{\text{first maxima}} \approx \frac{2}{\sqrt{3}}$
- $\frac{2(\text{center- edge distance})}{\text{center-neighbor distance}} = \frac{2}{\sqrt{3}}$
- Prevents other molecules from entering the cluster



Results
Length Scales

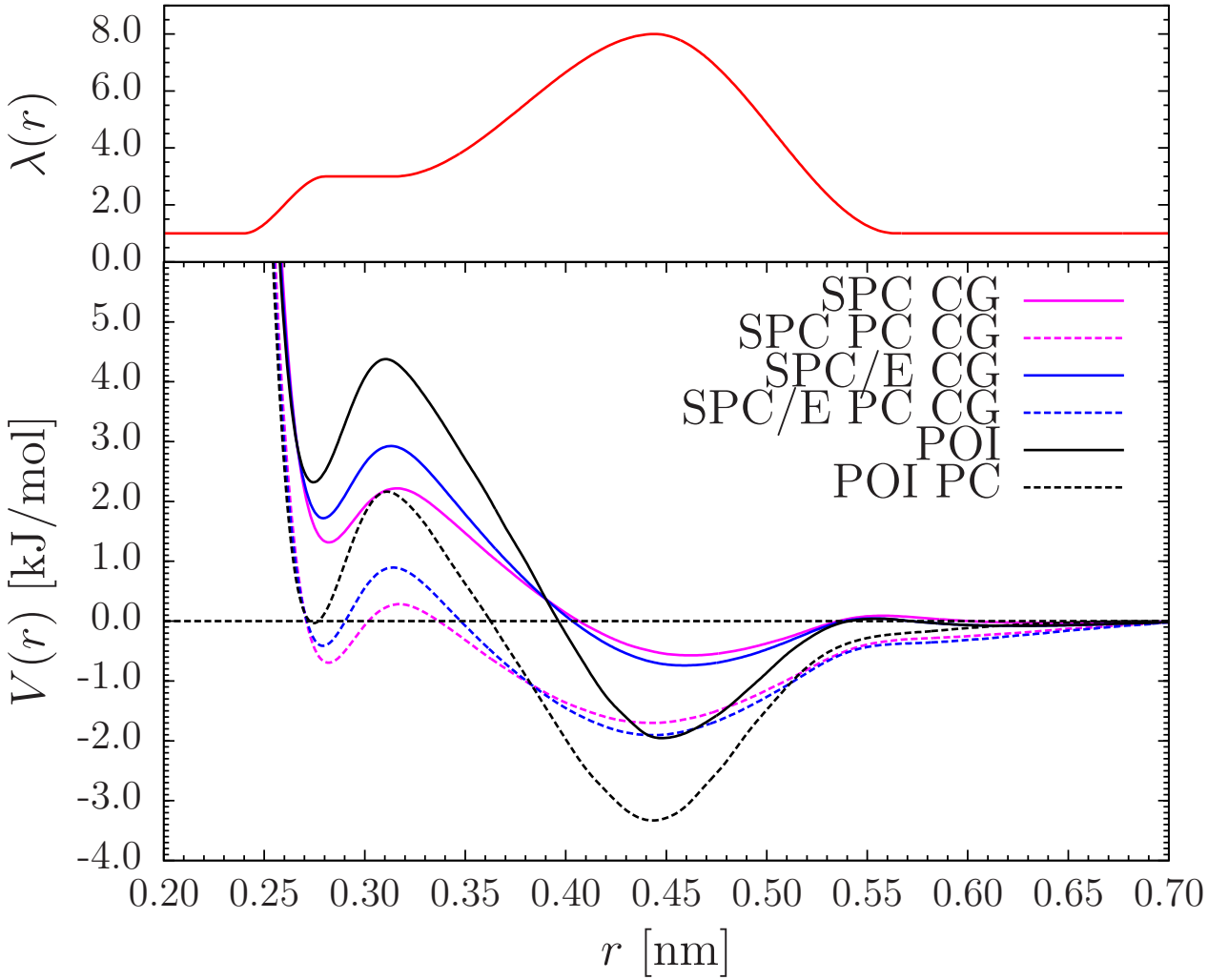


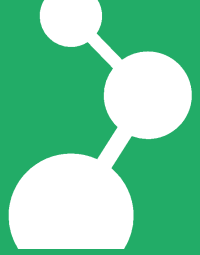
$\longrightarrow$ Coarse-grained models are less packed



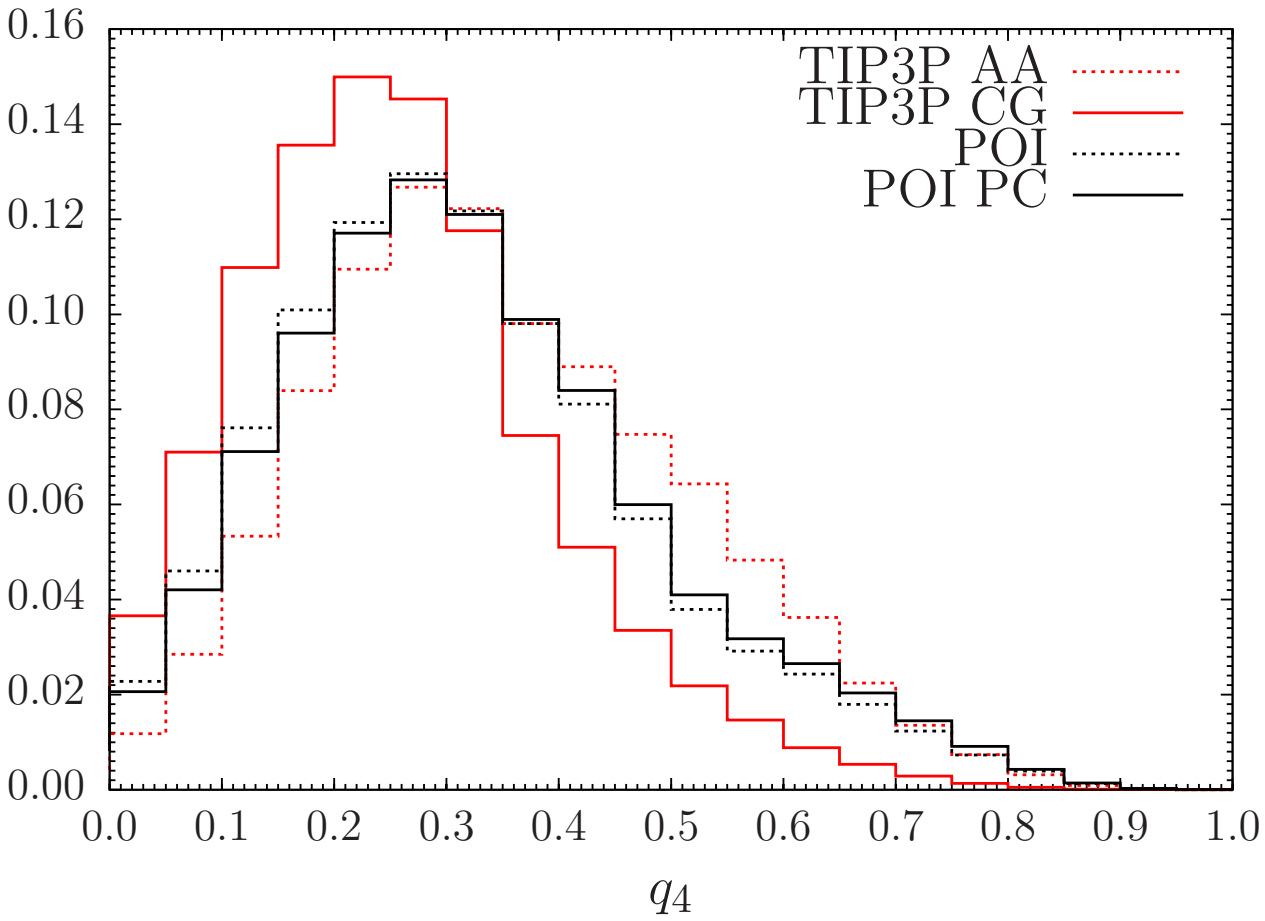
Results
Potential of Extrapolation

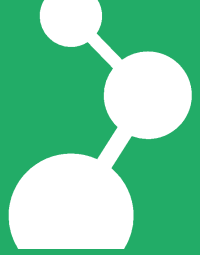
Idea: Add more structure by adding $\lambda \cdot (SPC/E - SPC)$



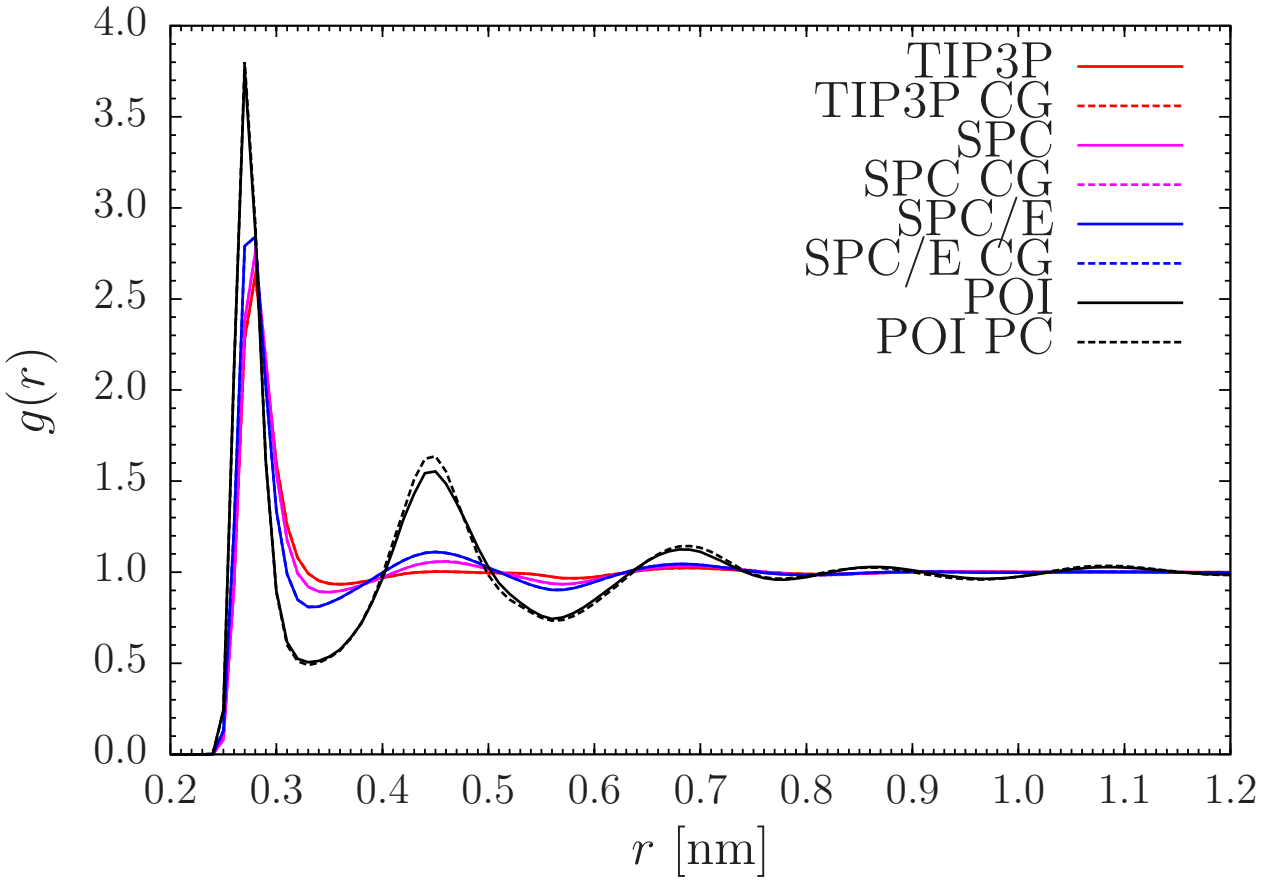


Results
Potential of Extrapolation

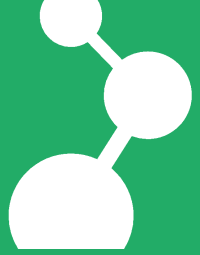




Results
Potential of Extrapolation



→ Price to pay: Structure



Compressibility vs. Pressure

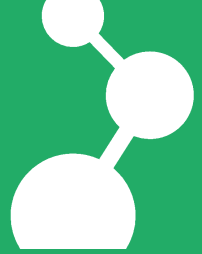
- Want to fit state point (p, V, T) and compressibility κ

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

- Pressure correction destroys compressibility

$$\rho k_B T \kappa_T = 1 + 4\pi\rho \int \mathrm{d}r\, r^2 [g(r) - 1]$$

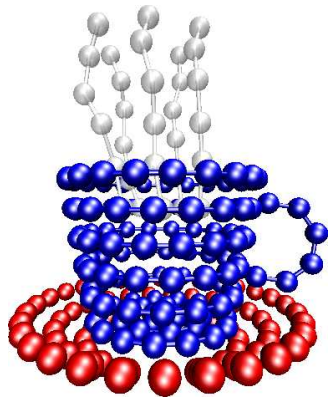
- Can <u>not</u> fit both at the same time (for this models)

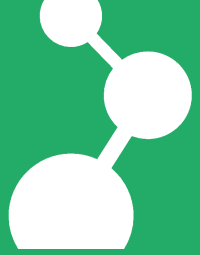


Conclusion

Issues:

- Compressibility vs. pressure
- Decreased tetrahedral packing
- Structure vs. packing
- Not shown: intrinsic speed-up (from self-diffusion ≈ 5)





The End

Thank you for your attention !