Multiscale Simulations of Quantum Fluids

KAVLI informal talk - April 19, 2012

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in collaboration with

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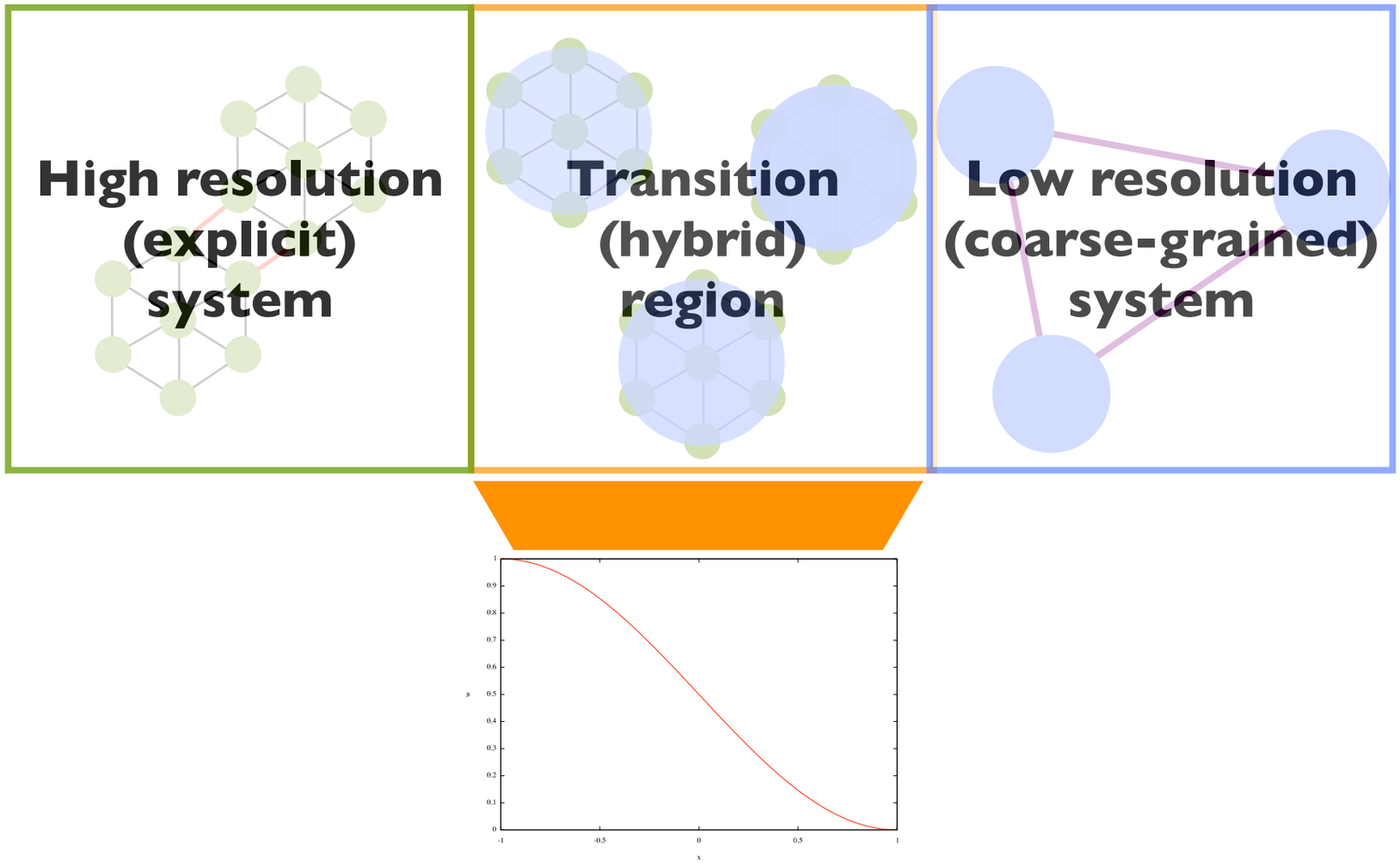
Sebastian Fritsch
Davide Donadio
Kurt Kremer

The AdResS multiscale simulation method

The two regions at different resolution are coupled by a transition (hybrid) region

Force-based method: forces change smoothly from high-res to CG

$$\mathbf{F}_{\alpha\beta} = w(X_\alpha)w(X_\beta)\mathbf{F}^{expl}_{\alpha\beta} + [1 - w(X_\alpha)w(X_\beta)]\mathbf{F}^{cg}_{\alpha\beta}$$



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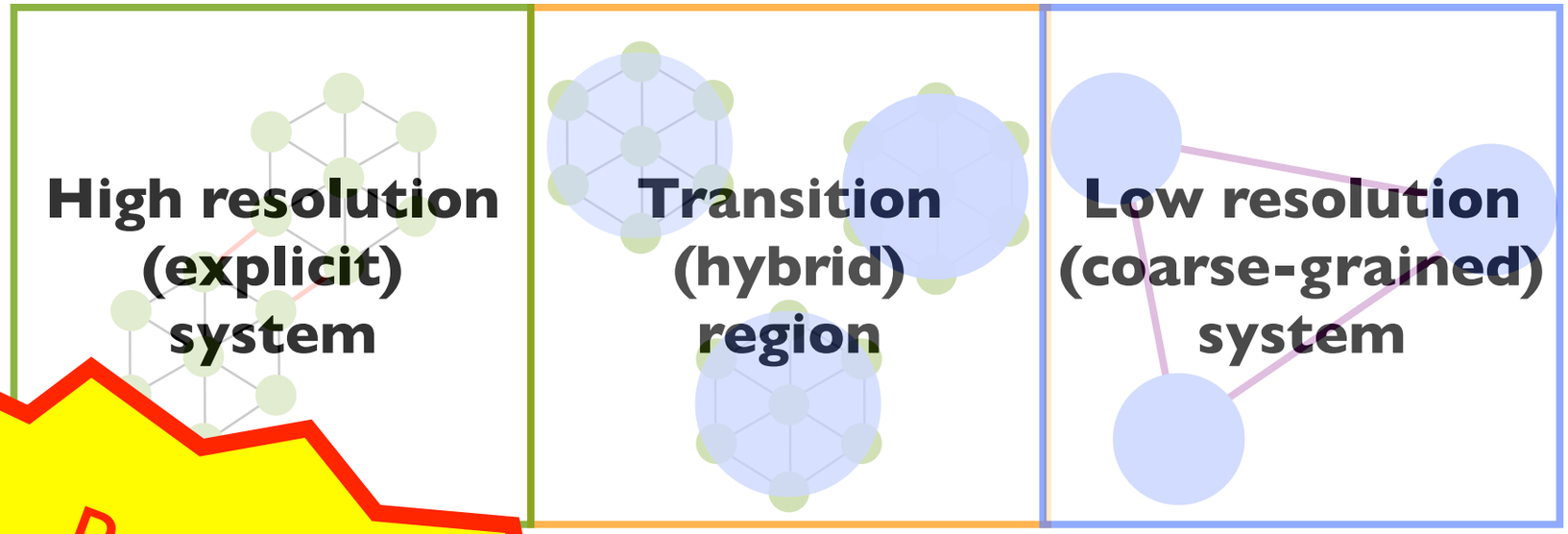

Perfect for classically-mapped quantum systems!

Typical systems investigated with Path Integral approaches

level of "quantumness"

- Superfluid Helium-4
- fluid para-Hydrogen
- room-temperature water

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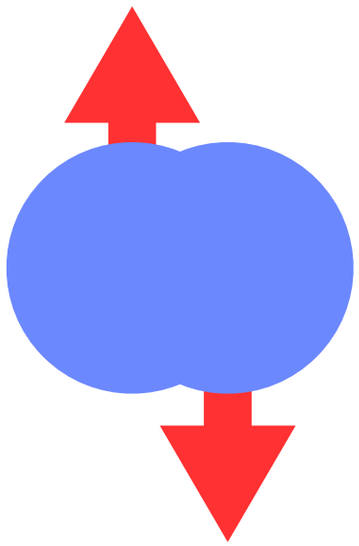
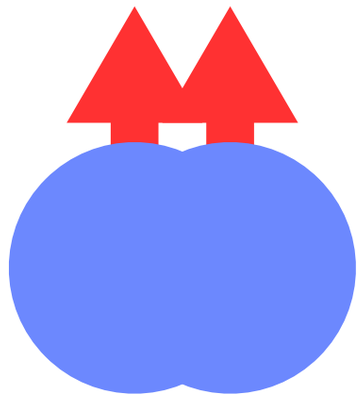
Molecular hydrogen naturally occurs in two species:



para-hydrogen
spin 0 boson
singlet



ortho-hydrogen
spin 1 boson
triplet

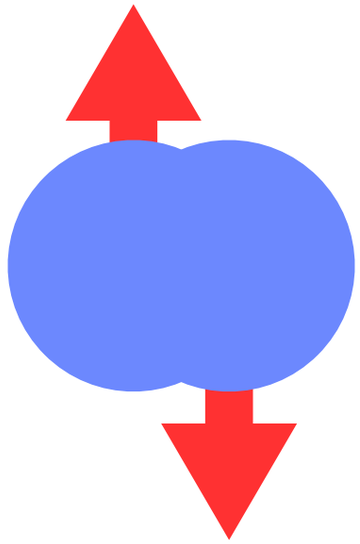
@T = 80K: ortho/para states are equally populated

@T = 19 K: 99.75% para-hydrogen

Intermolecular interaction of para-hydrogen can be modeled by a radial potential

Good description of solid state properties are given by 12-6 Lennard-Jones potential

More accurate estimates are obtained using the Silvera-Goldman potential



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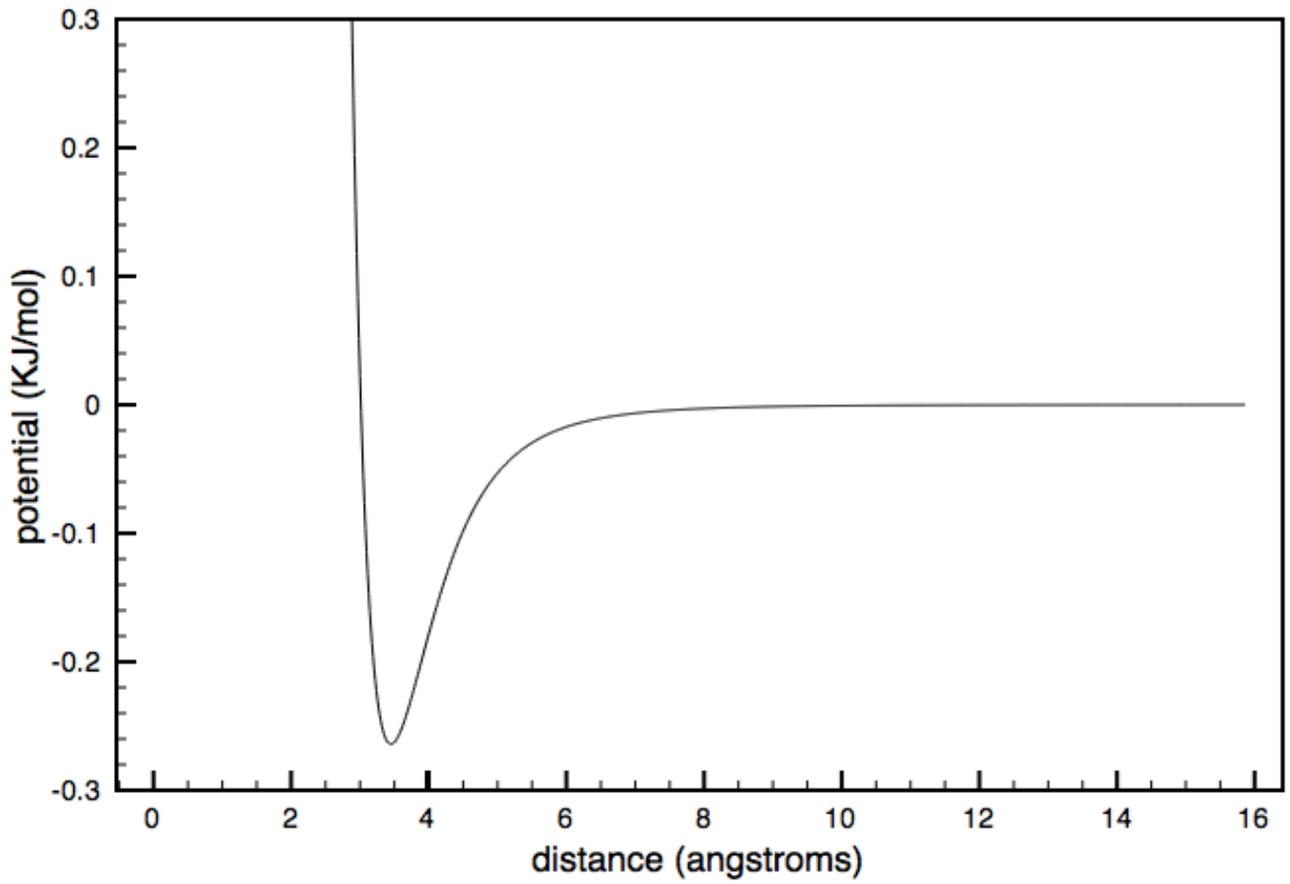
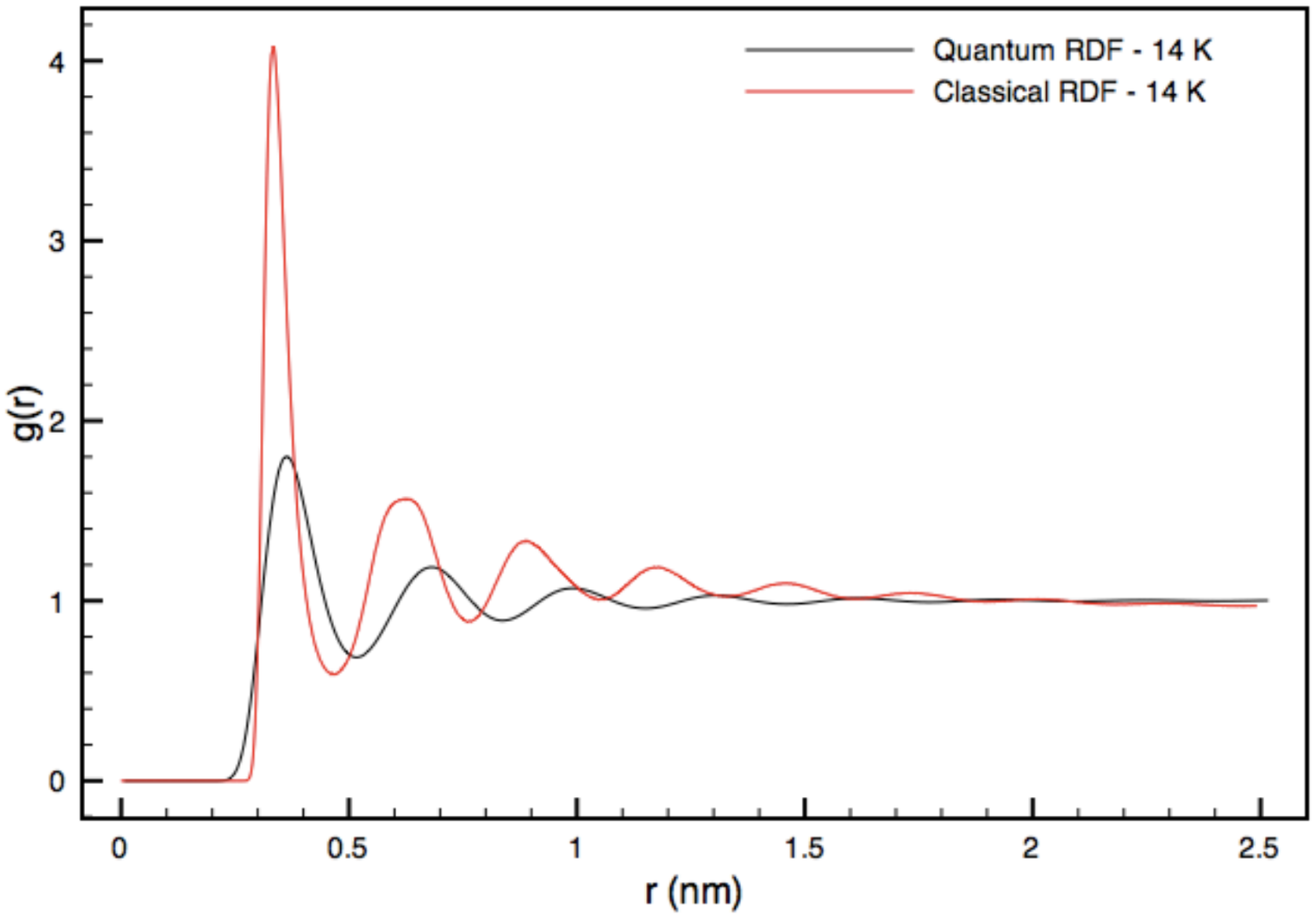


I.F. Silvera *et al.*, J. Chem. Phys. 69 (9), 1978

SG potential was developed for low-T solid phase of parahydrogen

Its straightforward use to simulate the liquid state
leads to an unphysical glassy phase



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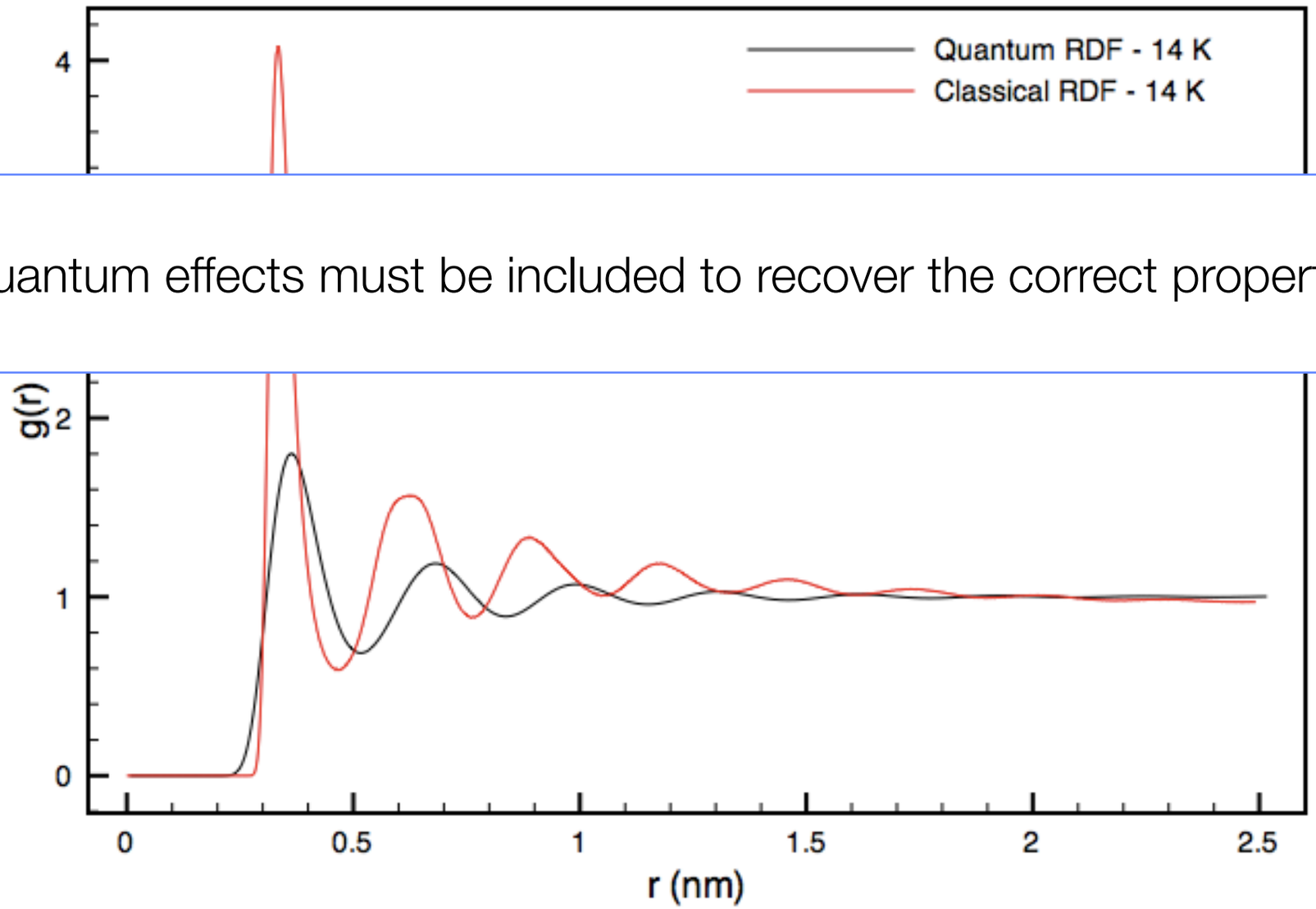
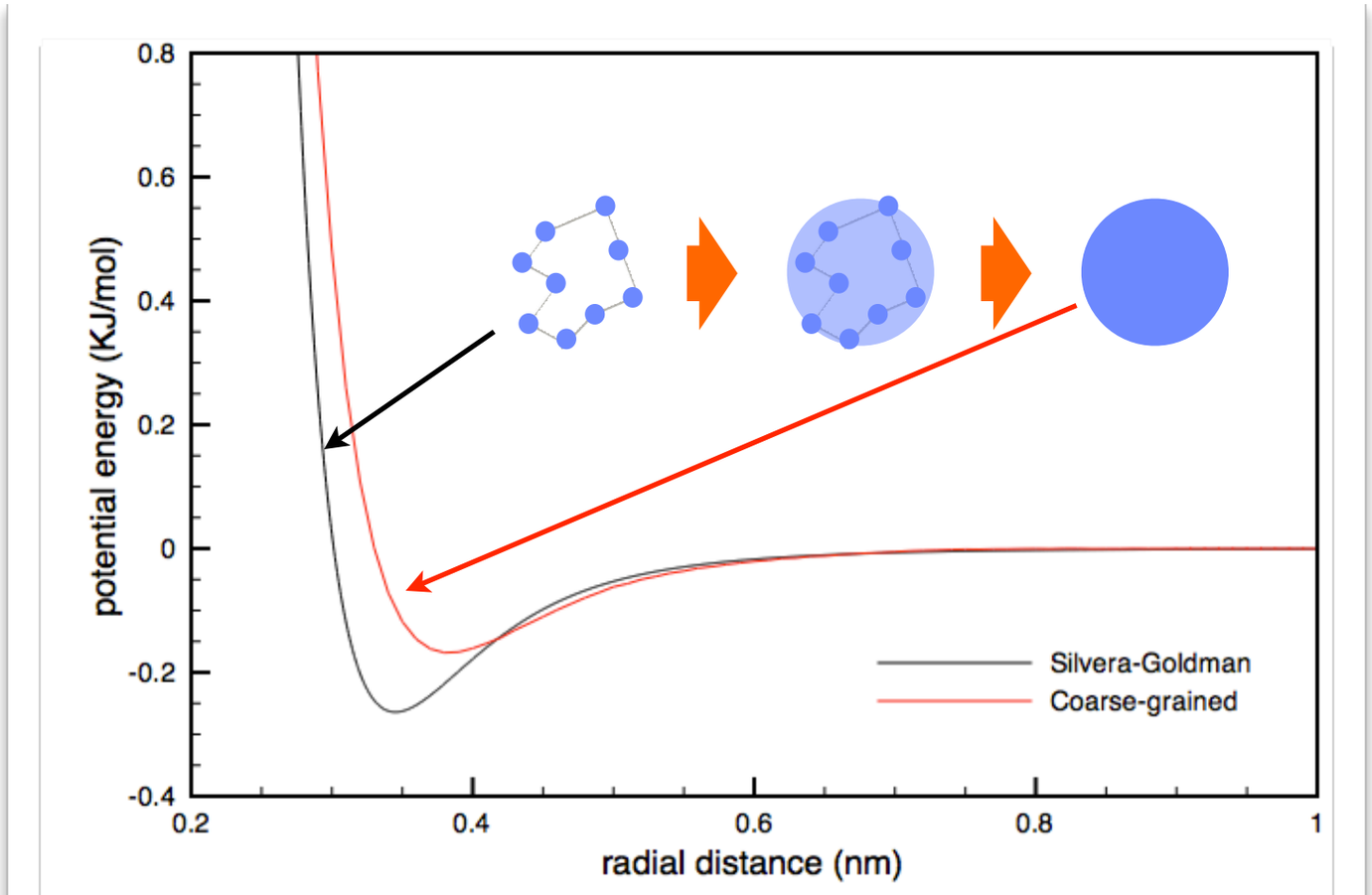


Quantum effects must be included to recover the correct properties

Coarse-grained simulation of para-hydrogen

The polymer rings are mapped onto their center-of-mass (centroid) coordinates

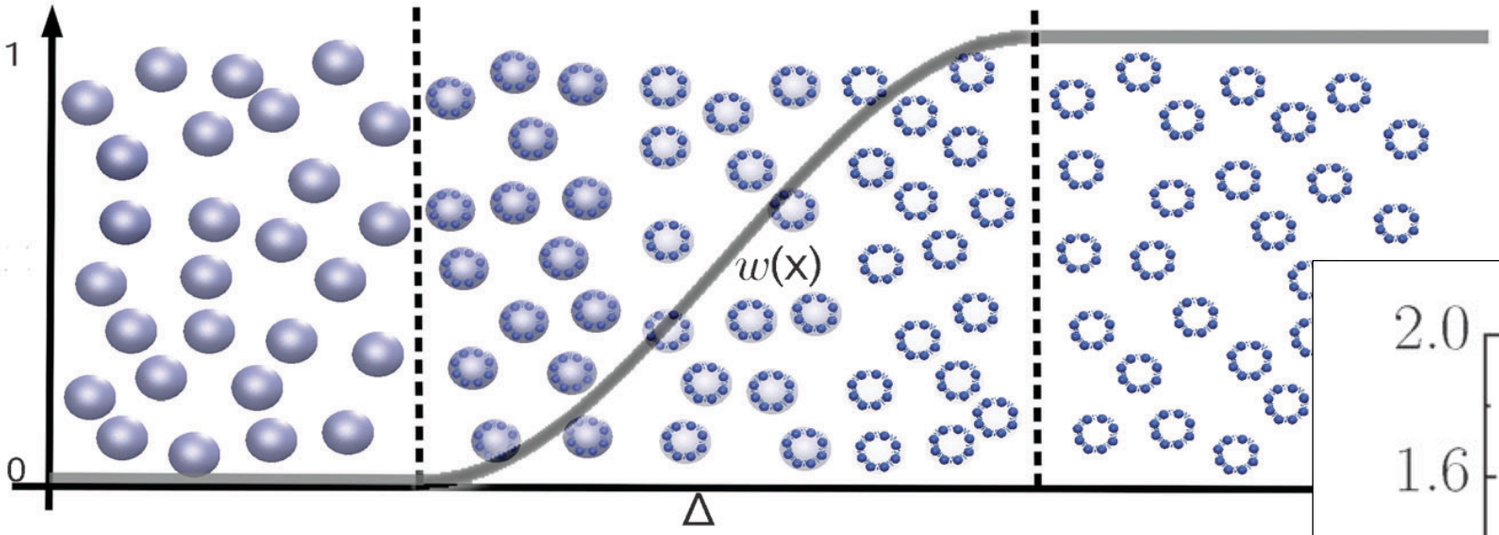
A CG potential is obtained via Iterative Boltzmann Inversion to match the CoM-CoM RDF



Question

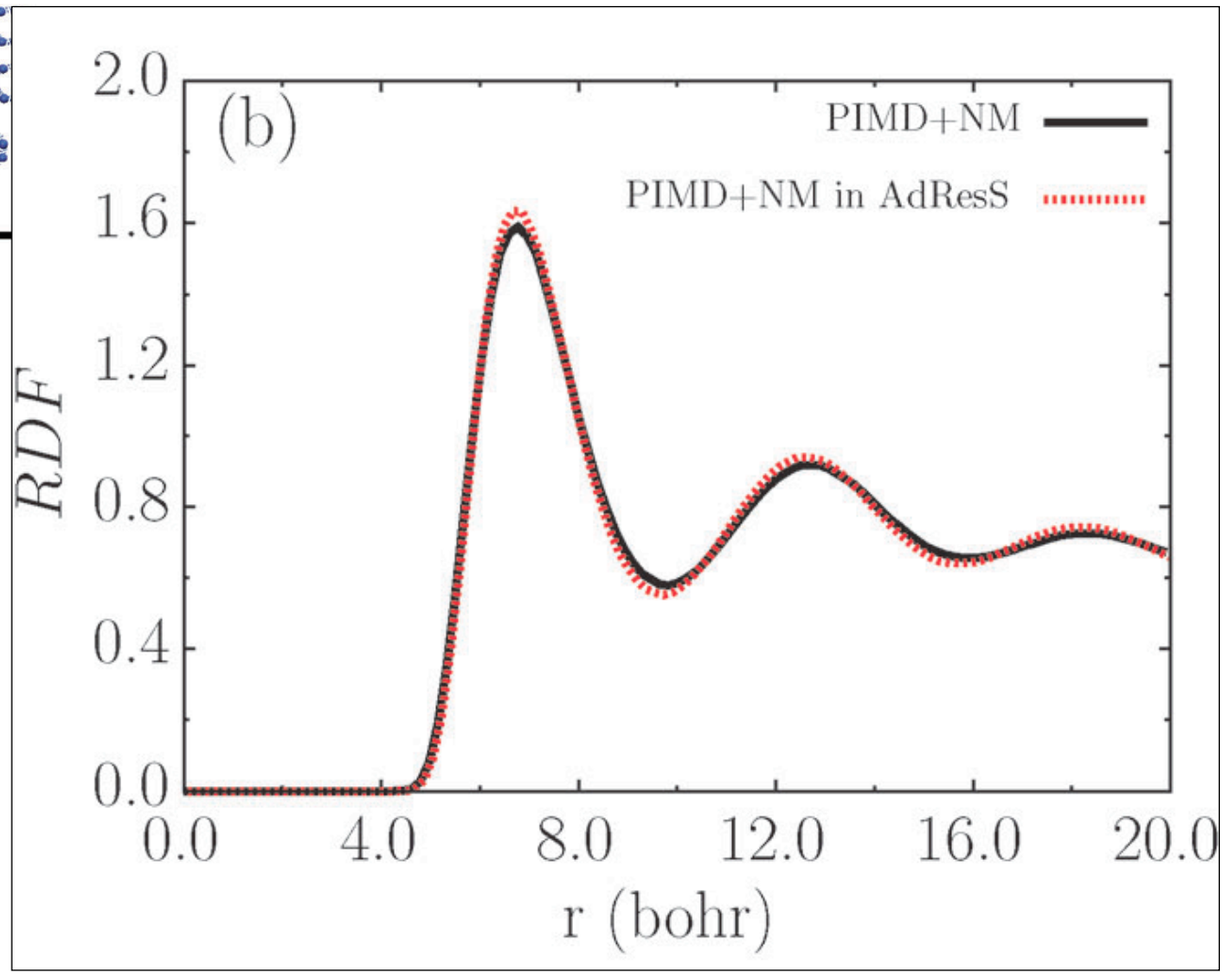
What is the influence of the bulk on the small-scale structural properties?

Previous work [1] investigated the effects of CG bulk on a para-H_2 slab



Set-up of the system

Comparison of the bead-bead RDF's @ T = 14K



[1] A.B.Poma, L.Delle Site, Phys.Chem.Chem.Phys. 13 (2011)
Images from therein

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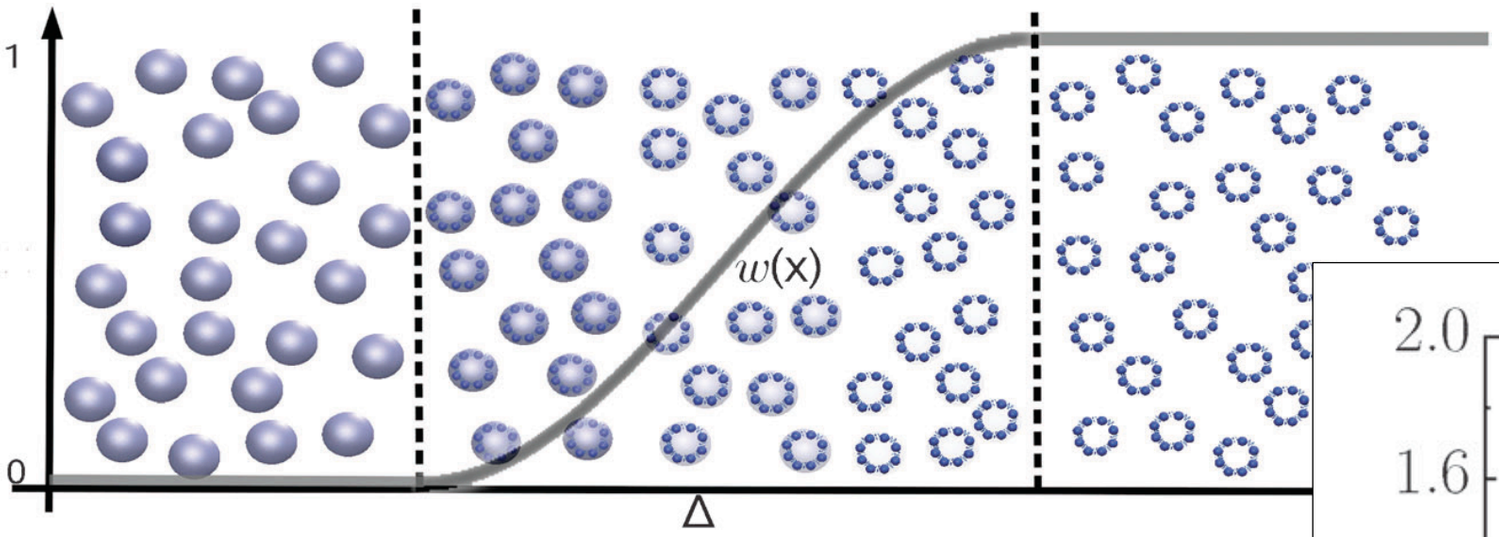
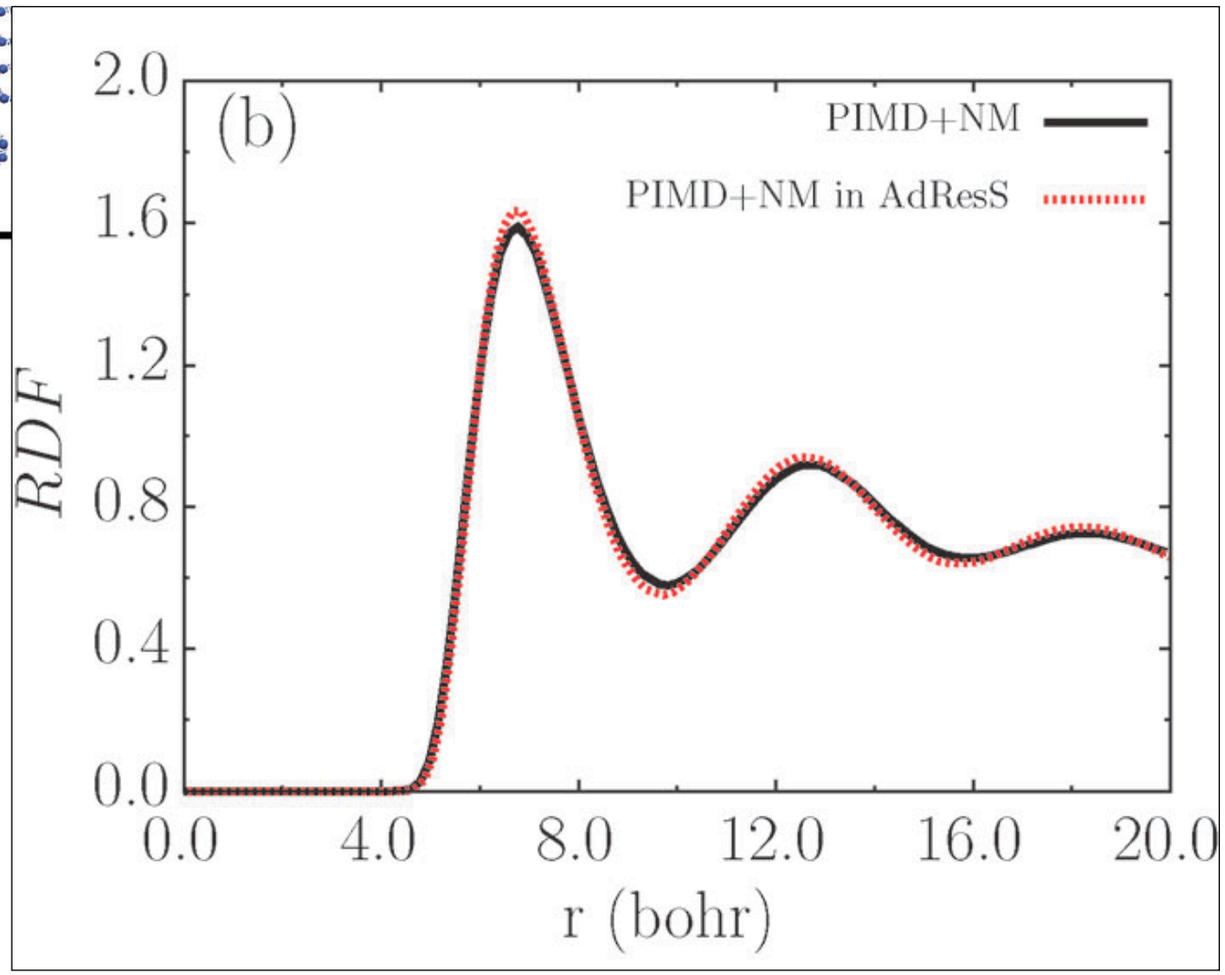


Set-up of the system

What happens if only a bounded subregion is described at the quantum level?

Comparison of the bead-bead RDF's @ T = 14K



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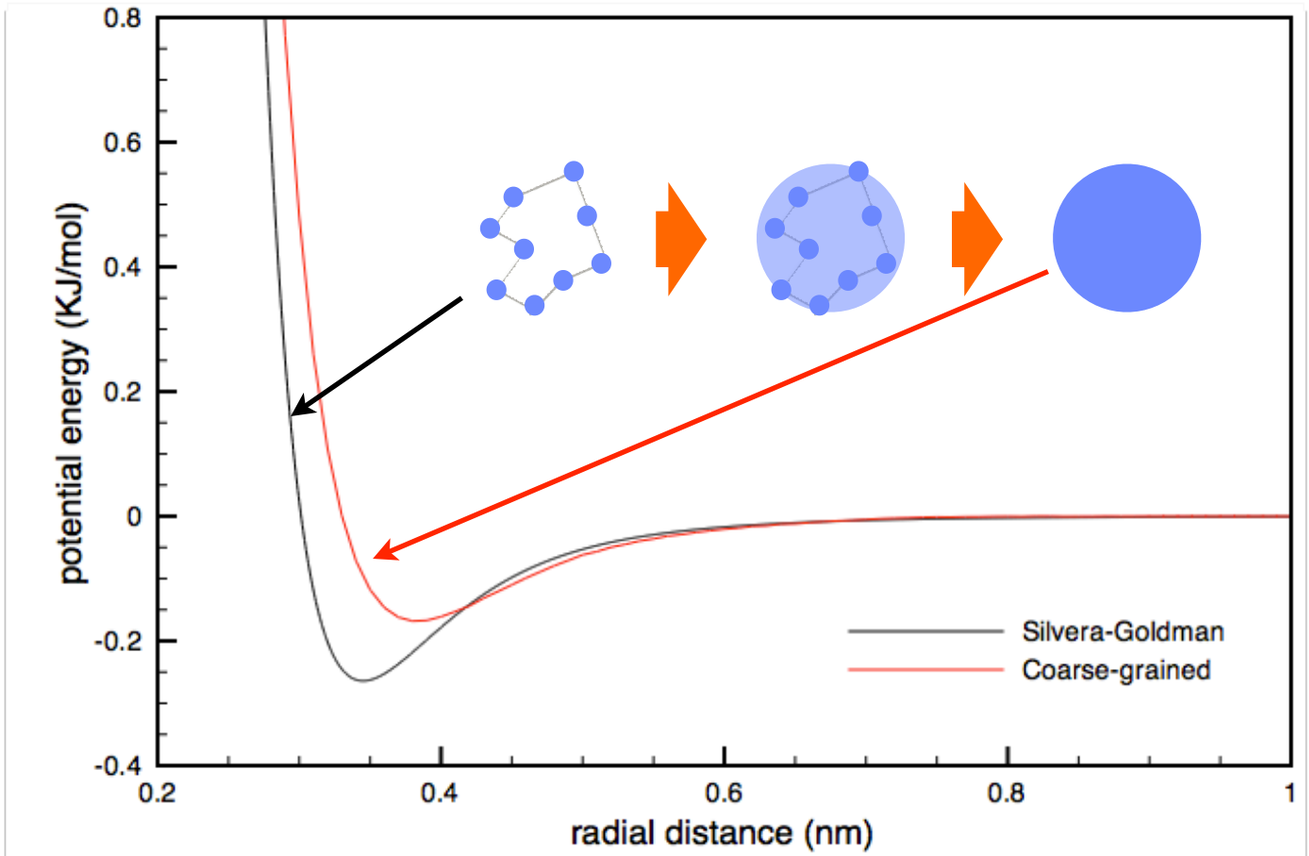
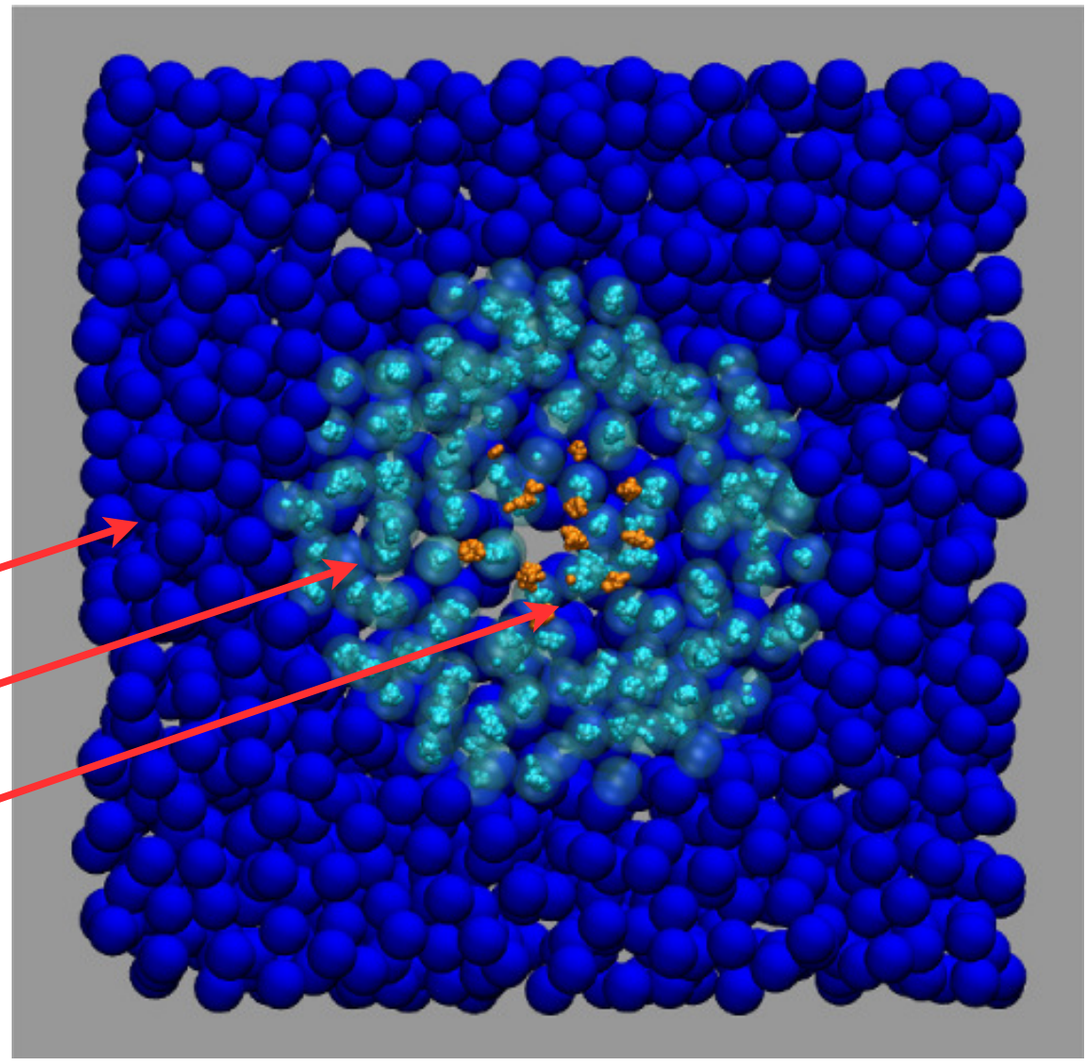
Restrict the complete quantum description of the system to a small region while preserving the thermodynamics



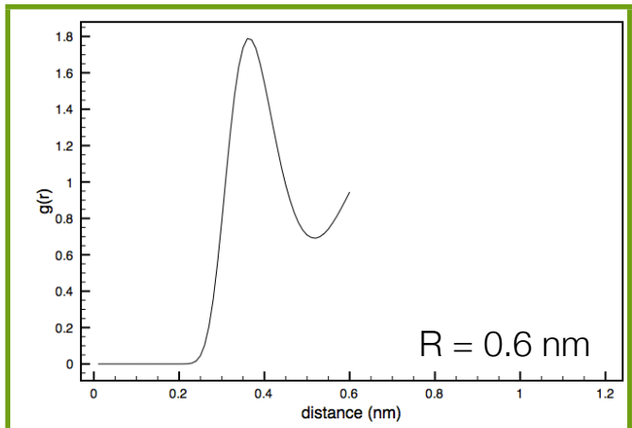
Simulation setup

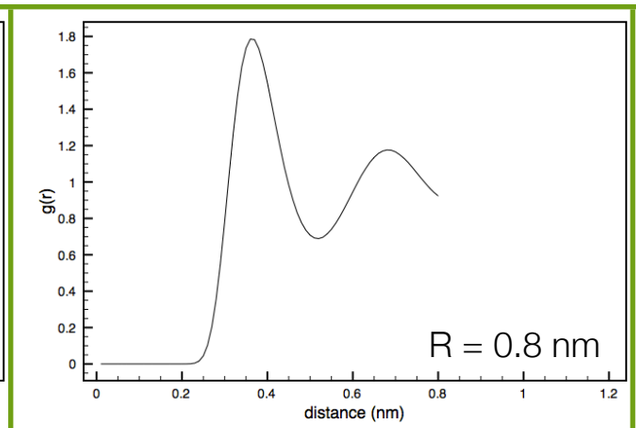
- NVT simulations of 8000 ps, time step 0.5 fs with GROMACS
- 48 beads per polymer ring
- 3000 particles
- experimental reference density
- T = 14 , 20, 25 K
- 4 different explicit region radii (0.6 - 0.8 - 1.0 - 1.2 nm)
- hybrid region size of 1.0 nm

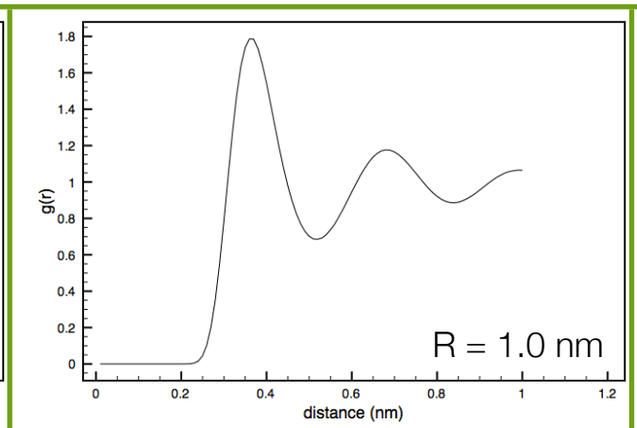


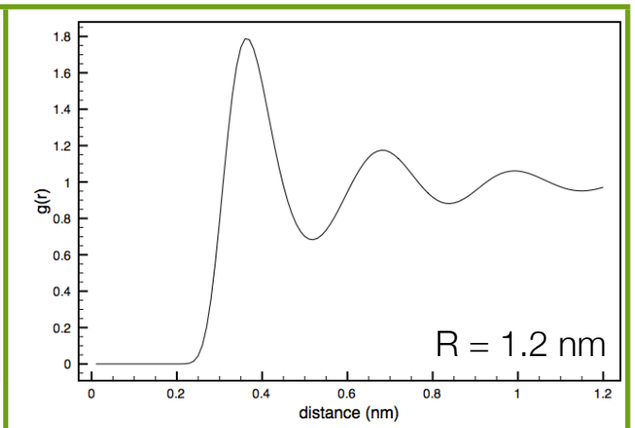
R. Potestio, L. Delle Site, J. Chem. Phys. 136(5), 2012

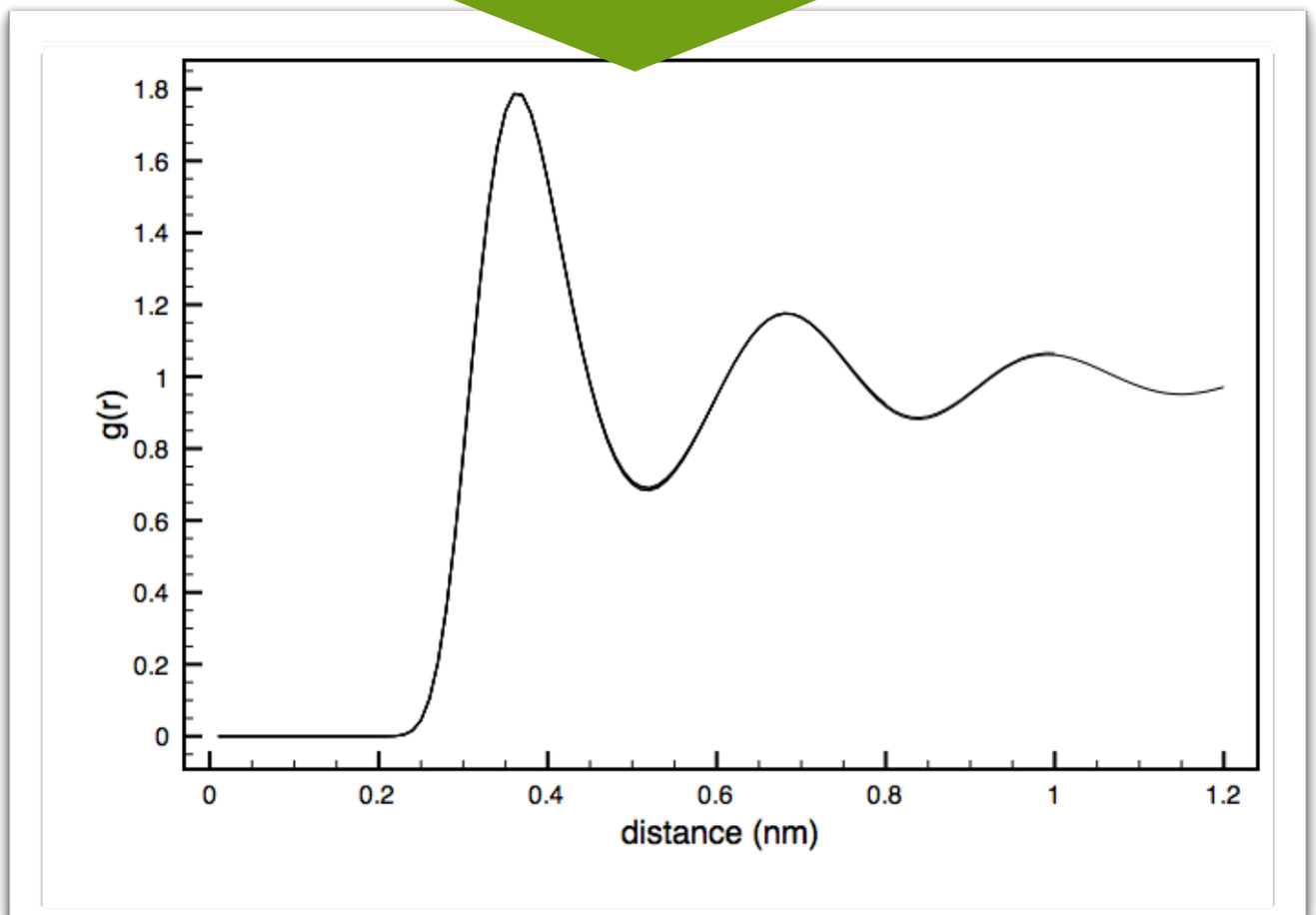
Bead-bead RDF's for T = 14 K

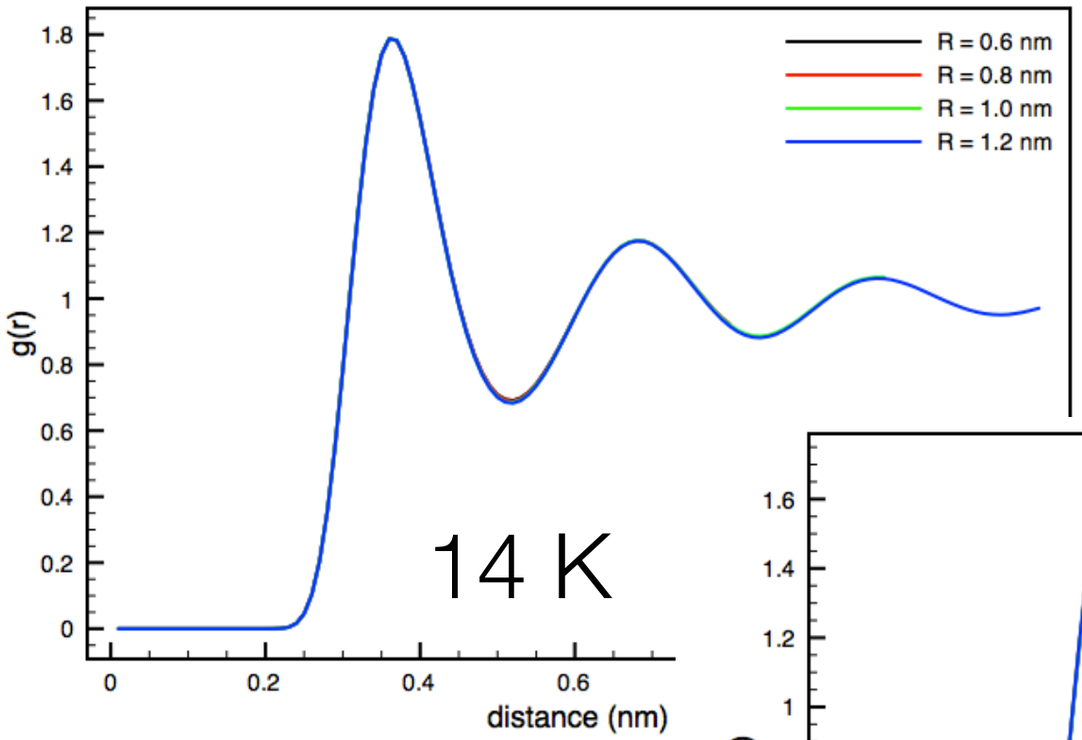




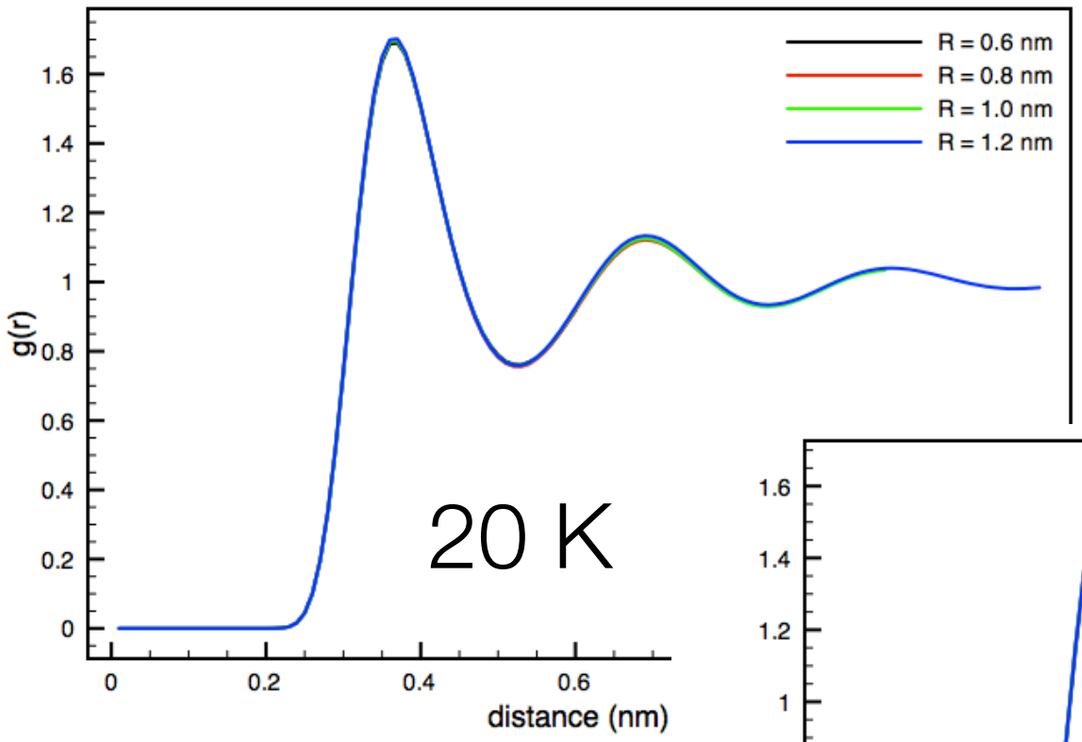


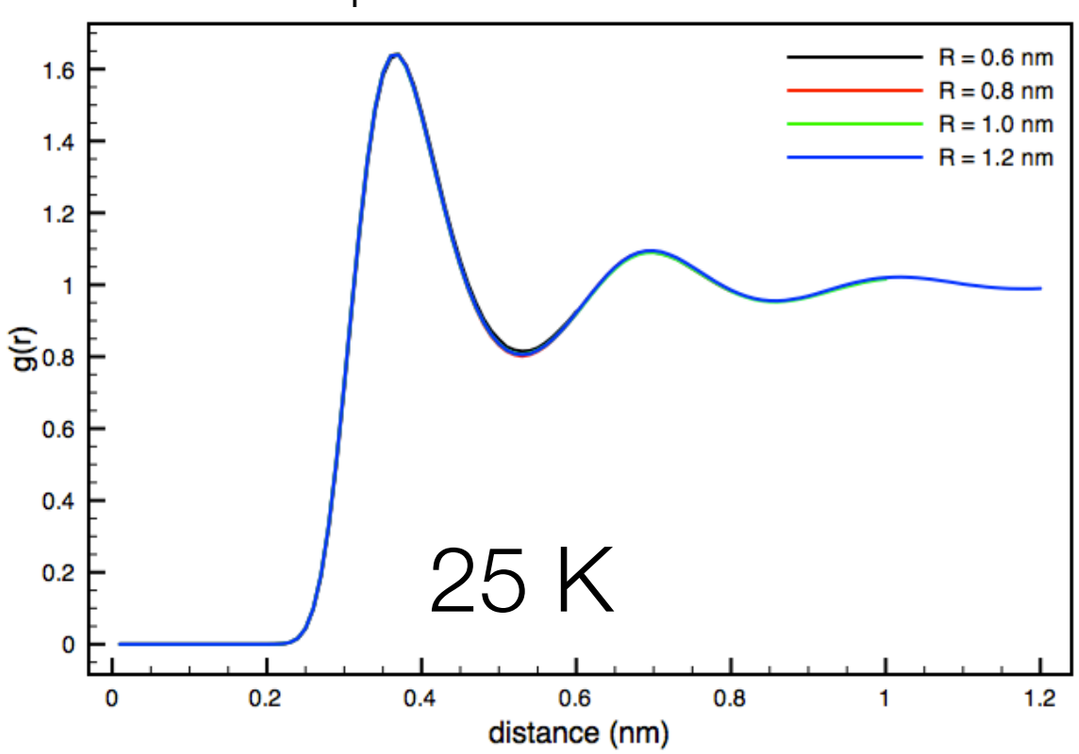






Overview of the results for all temperatures





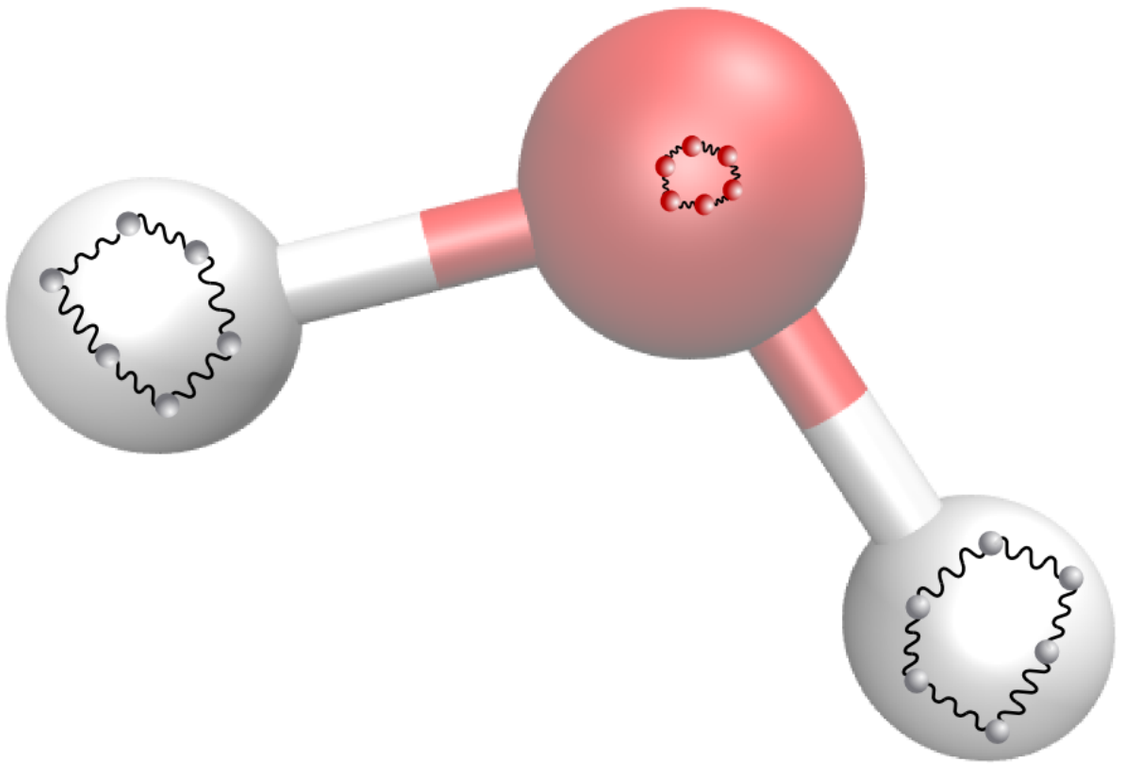
The pairwise structure is unaffected by a CG bulk down to 0.6 nm radius of the spherical explicit region

Typical systems investigated with Path Integral approaches

level of "quantumness"

- Superfluid Helium-4
- fluid para-Hydrogen
- room-temperature water

Path Integral formalism can be used to investigate the effect of proton delocalization in water



Caveat: several force fields effectively include delocalization.

If used together with PI: double-counting of quantum nuclei.

Ongoing work (with S. Fritsch, D. Donadio, K. Kremer)

- “join separately” electron dof’s (DFT) and nuclear delocalization
- characterize the impact of delocalized hydrogens on structure and dynamics
- couple PI water with single-site CG water

Cartoon courtesy of Sebastian Fritsch

Typical systems investigated with Path Integral approaches

level of "quantumness"

T < 1 K **T ~ 14 K** **T ~ 300 K**

- Superfluid Helium-4
- fluid para-Hydrogen
- room-temperature water

Fail: Bose-Einstein condensates and superfluids

Can we think of a multiscale simulation of a superfluid system? Probably not.

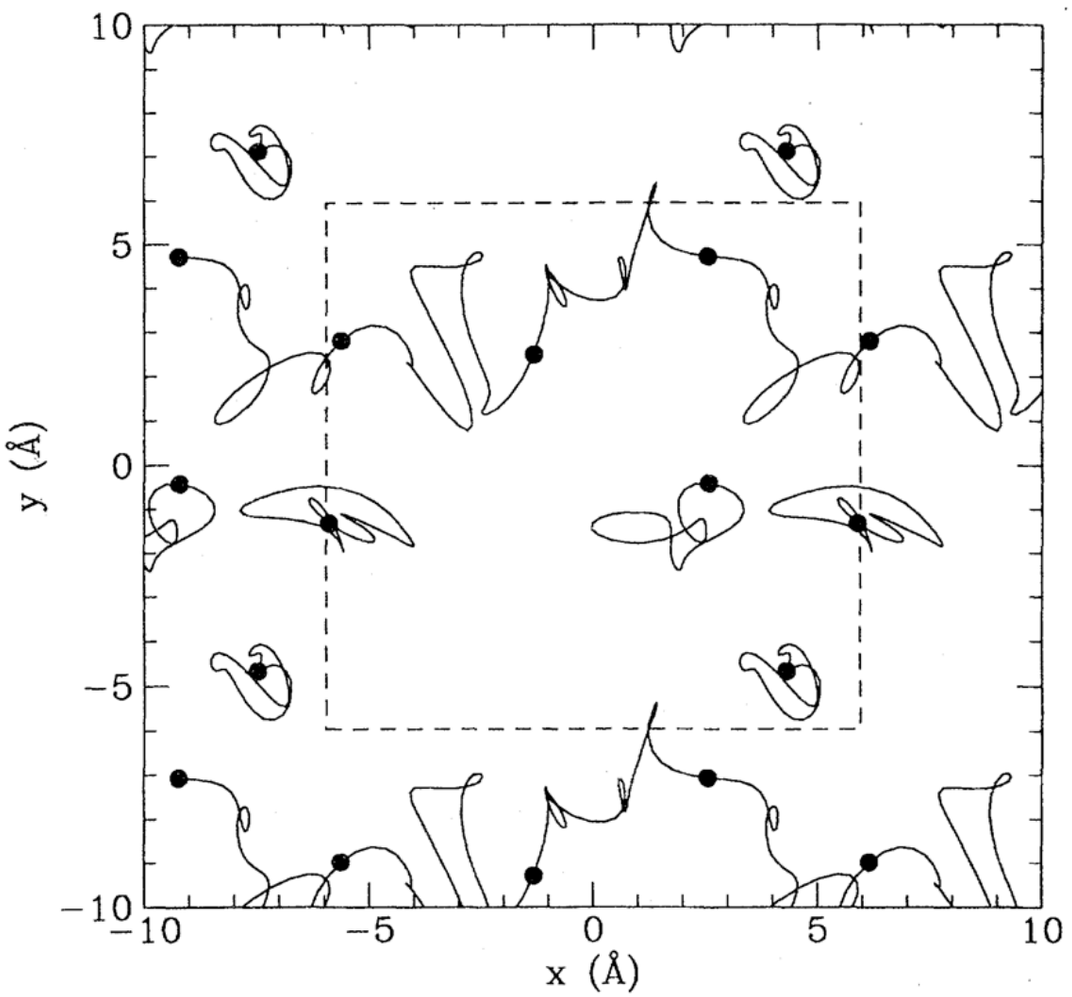


FIG. 10. The extended trace of six ^{4}He atoms at a temperature of 0.75 K and with 53 time slices. The dashed square represents the periodic boundary conditions. Three of the atoms are involved in an exchange which winds around the boundary in the x direction.

The rings open and close: no way to map them on a CG site once for all

Some polymer rings spread throughout the simulation box: impossible to “confine” the quantum dof’s in the explicit region

Path Integrals in the theory of Condensed Helium
D. M. Ceperley, Rev. Mod. Phys 67, 279 (1993)

Bottomlines

- The quantum-to-classical mapping allows us to coarse-grain quantum delocalization effects - *classical force-field as "coarse-grained" quantum interaction*
- Joint use of AdResS and the Path Integrals: quantum/classical hybrid simulations with non-fixed number of quantum molecules (no QM/MM)

Ongoing work

- Quantum and classical descriptions of water can be coupled to accelerate simulations of molecules solvated in "quantum" water with large CG bulks.
- A multiscale implementation of Centroid Molecular Dynamics is presently under development.
- Investigation of effects of delocalized protons on water structure/dynamics.

Thank you for your attention!