

Water dynamics in Confined Geometries by means of Semi-empirical Simulation

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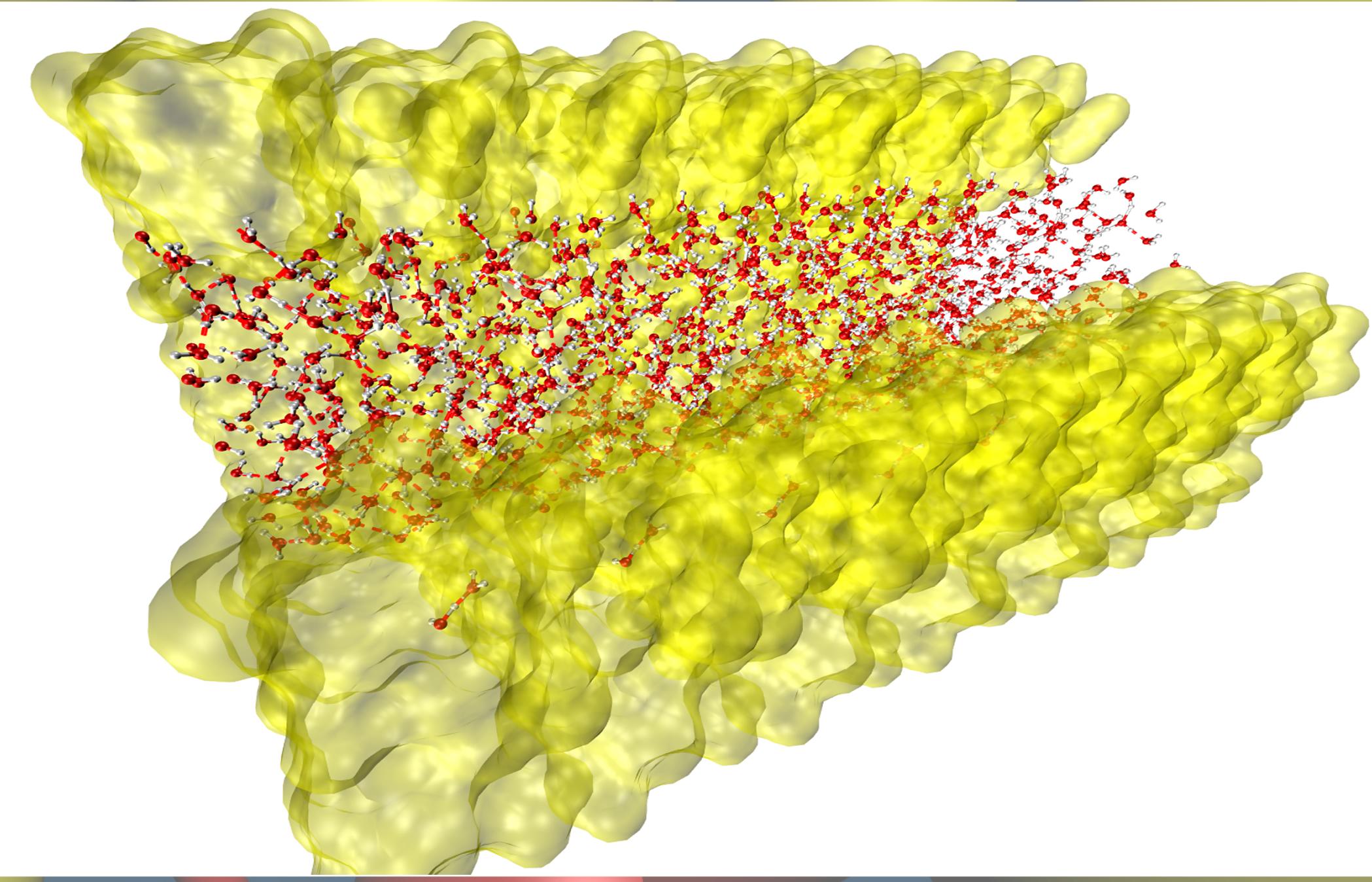
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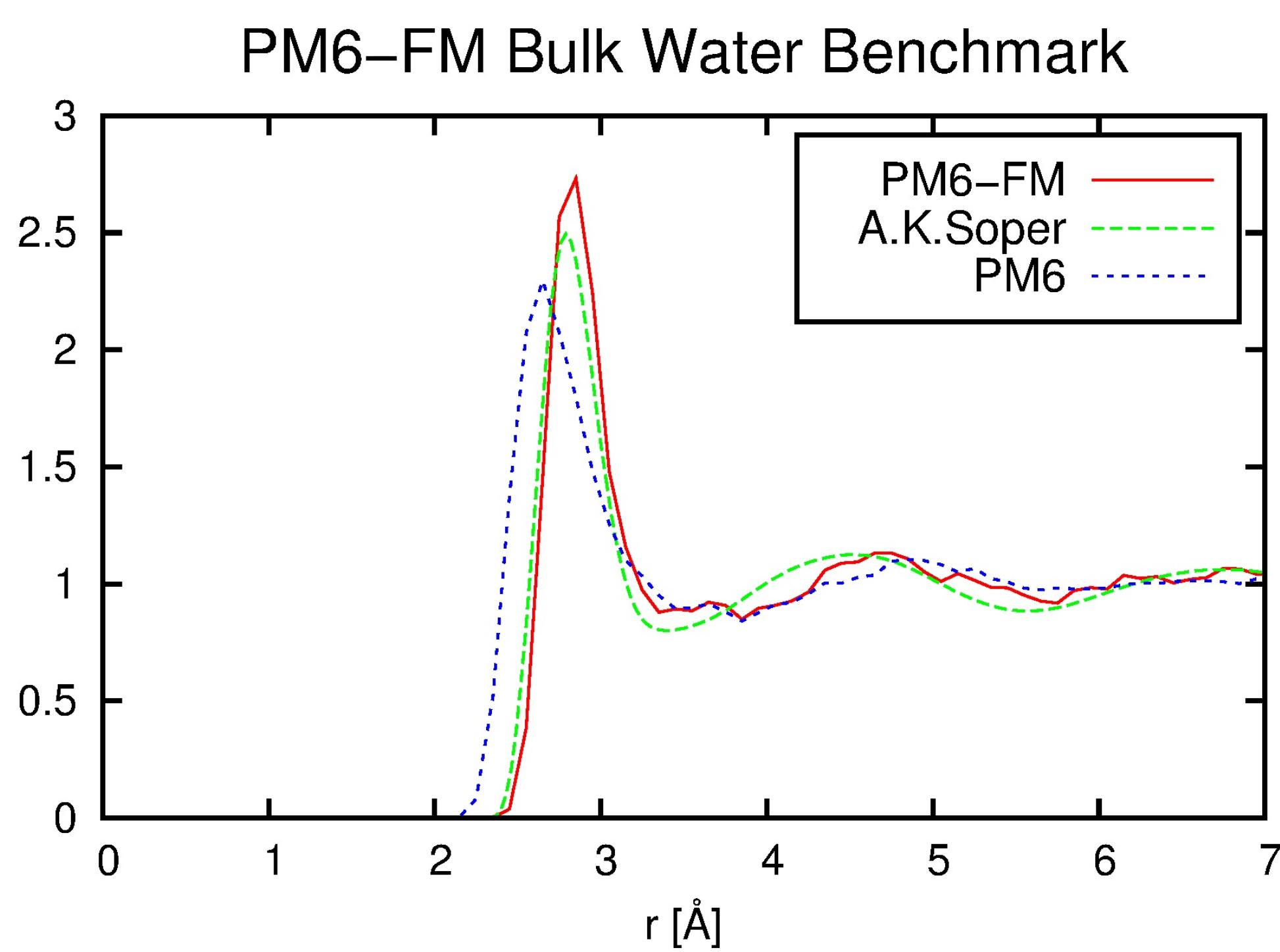
Background

Water dynamics in confined geometries differ drastically from those in bulk and are important for a wide range of applications, such as mesoporous pores, nanotubes or biological cells. MCM-41 has high density and small pore radii, generating a big inner surface to study interesting effects. Using Semi-empirical MD to simulate large systems with high accuracy. PM6-FM is a reparameterization of PM6 that is reported to be more accurate for water. [1]

- › Modulation of a water filled MCM-41 silica pore [2]
- › Analysis of water dynamics with newly implemented PM6-FM method



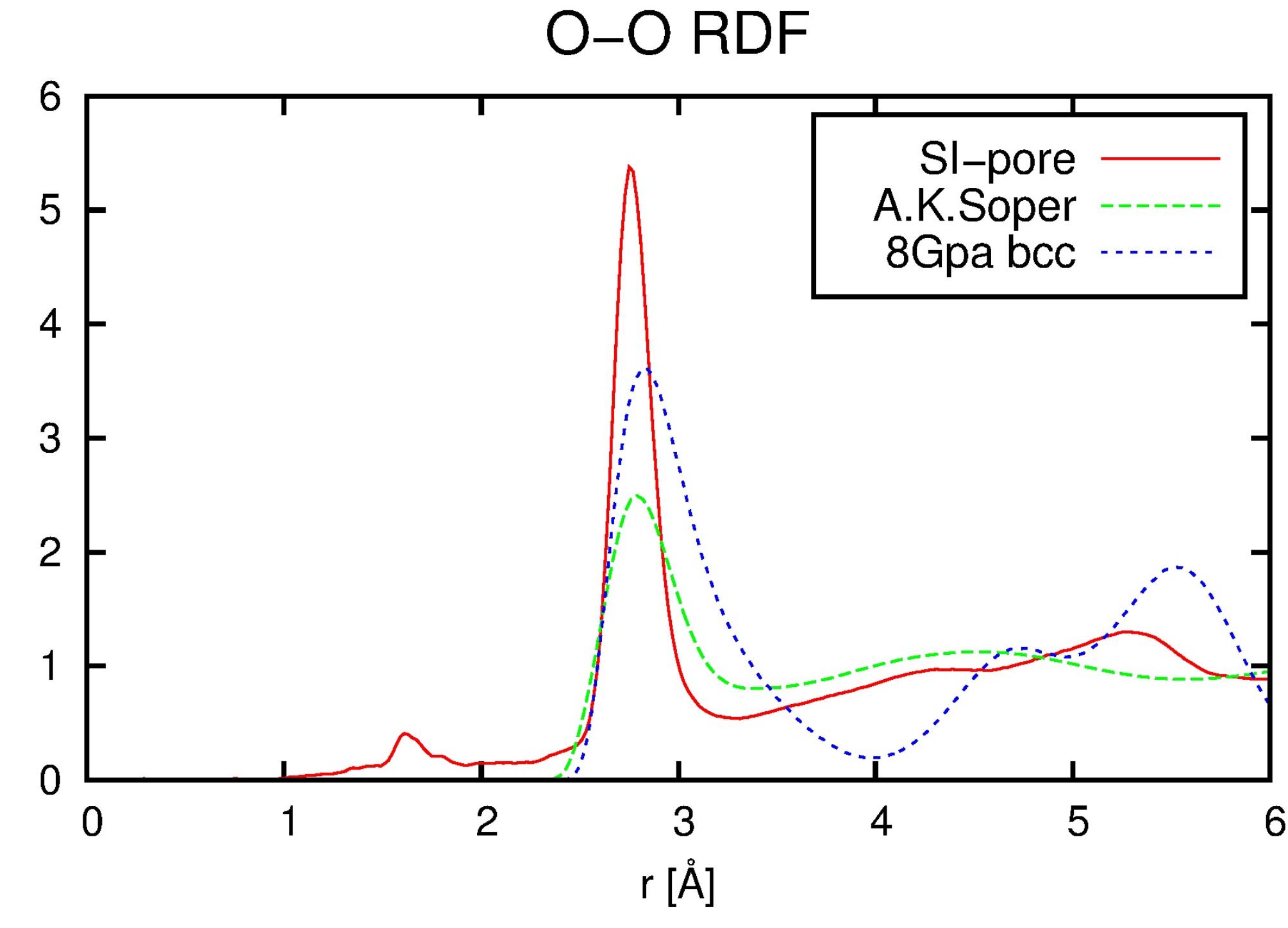
PM6-FM Implementation



Oxygen-hydrogen Radial Pair Distribution Function of bulk water calculated with PM6 (blue), PM6-FM (red) and from experimental data (green).

- › PM6-FM is considerably more accurate for water and our system

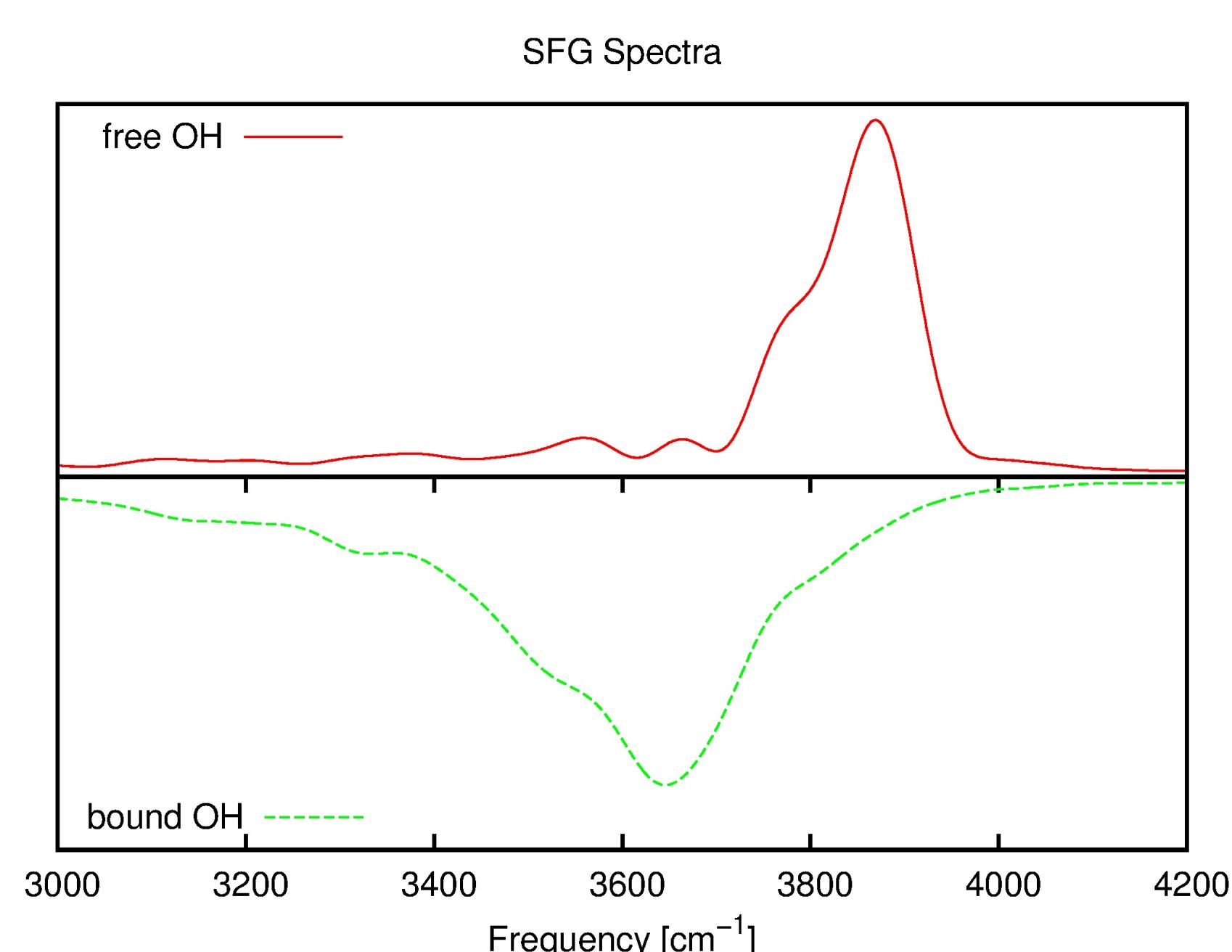
Density and RDF



Oxygen-Oxygen Radial Distribution Function for water in our simulation (red), bulk water (green) and results for bcc plastic water at 8 GP (blue)

- › Water in the pore is highly ordered
- › May indicate existence of supercooled-like water in the pore

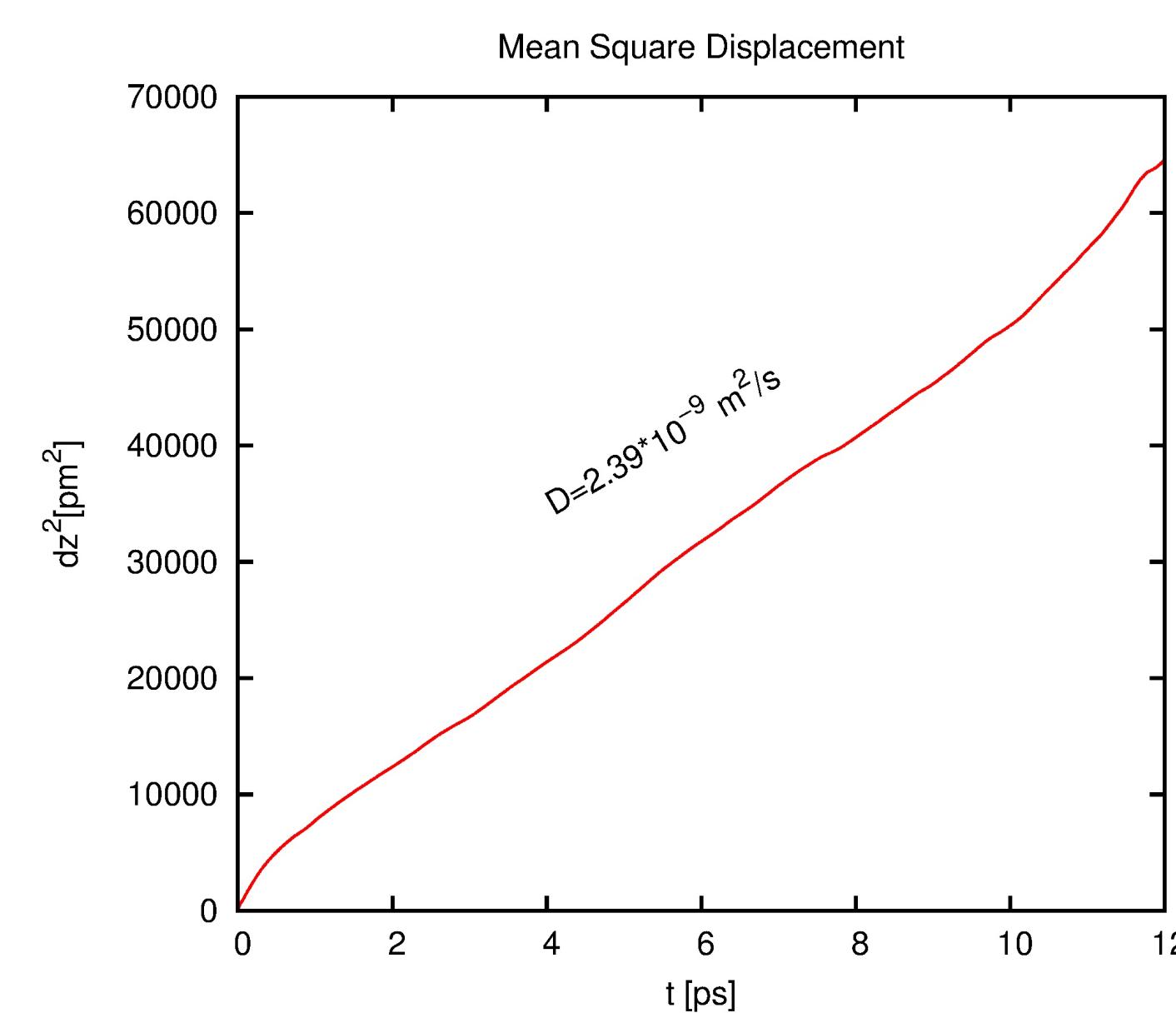
SFG



Sum Frequency Generation spectra calculated for water in the pore, using a surface specific velocity-velocity correlation function for pore surfaces. This method is faster than using polarizability based methods [2]. Imaginary (top) and total (bottom) responses are shown.

- › OH groups pointing to the surface are mostly free or loosely bounded
 - surface may not be distinctly hydrophilic

Diffusion



Calculating the one dimensional mean square displacement in the pore direction. The average value is calculated as $2.3665 \cdot 10^{-9}$ m²/s. Compared to $1.2716 \cdot 10^{-9}$ m²/s for bulk water, using PM6-FM in both cases.

- › Acceleration of water diffusion in the pore

References

- [1] C. Allolio, F. Klameth, M. Vogel and D. Sebastiani, Ab Initio H₂O in Realistic Hydrophilic Confinement, *Chem. Phys. Chem.* 2014, 15, 3955-3962
- [2] N. K. Kaliannan, A. H. Aristizabal, H. Wiebel, F. Zysk, T. Ohto, Y. Nagata and T. D. Kühne, Impact of intermolecular vibrational coupling effects on the sum-frequency spectra of the water/air interface. [submitted for publication]
- [3] M. Wellborn, J. Chen, L-P. Wang, T. V. Voorhis, Why Many Semiempirical Molecular Orbital Theories Fail for Liquid Water and How to fix Them, *J. Comp. Chem.* 2015, 36, 934-939