Nuclear Quantum Effects on Molecular Packing in Light and Heavy Water

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Outline

Structure of water

- Hydrogen bonding
- Density maximum
- Relevance of nuclear quantum delocalisation (NQD)

Simulation

- Nearest-neighbour analysis
- Structural changes under compression.

Conclusion

- Density increase → tetrahedral cavity expansion
Bonding and structure

Upon heating, second nearest-neighbour molecules move into cavities.

Configuration: thanks to Carlos Vega, Dept. Quimica-Fisica, Univ. Complutense, Madrid.
The density maximum


Competition between H-bonding and simple contraction

H-bonding and NQD

NQD affects molecular orientation

Density maximum in heavy water: $T = 11^\circ C$
Simulation

Details:

Path integral MD

- 5 samples of quantum spread
- 216 molecules
- Constant temperature and volume
- Cubic box with periodic boundary conditions
- Langevin thermostat
- Light water: 277 K  Heavy water: 284 K
- TIP5P model (path integral parameterisation)

Densities: ambient and 10% isotropic volume compression

Distances & bond bending
Neighbour analysis

FNN

SNN
Compression
First nearest-neighbours
Compression
Second nearest-neighbours
So what is happening?
Energy considerations

![Graph showing potential energy vs. 0-0 separation for different bending angles](image)

- Bending = 0 deg
- Bending = 20 deg

Potential energy / eV vs. 0-0 separation / Ang
Heavy water compression
First nearest-neighbours
Heavy water compression
Second nearest-neighbours
Conclusion

- Expansion is a consequence of H-bond formation
- NQD introduces orientational disorder
- Weakens hydrogen bonding
- Behaves more like a simple liquid

Counterintuitive behaviour under compression:

- H-bonding not crushed out of existence
- H-bonds can become longer and remain straight
- Tetrahedral cavity expansion
- Increased number of interstitials