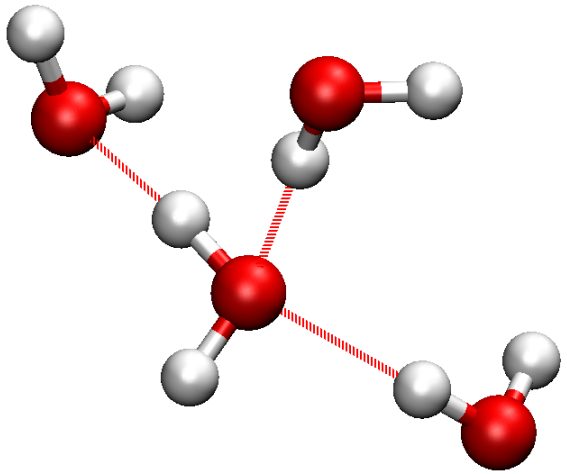
Ring polymer molecular dynamics simulations of aqueous systems

Scott Habershon



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Quantum effects in water

	H_2O	D_2O	
Melting point / °C	0	4	
Molar volume / cm^3	18.069	18.133	

Classically *identical*

Diffusion coefficient (25 °C) / Å ps^{-2}	0.23	0.18	**Ratio: 1.28**

Classical ratio is **1.05**
(Boltzmann RMS speed)

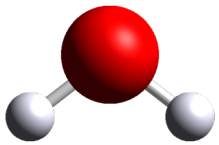
$ZPE_{H2O} > ZPE_{D2O}$

Quantum simulations of water

Model	Quantum method	Classical diffusion	Quantum diffusion	D_{qm} / D_{cl}
SPC/E	RPMD	0.242	0.343	**1.42**
TIP4P	CMD	0.358	0.548	**1.53**
SPC/F	RPMD	0.279	0.400	**1.43**
SPC/F	CMD	0.30	0.42	**1.40**
SPC/RW	LSC-IVR	0.25	0.47	**1.88**

On average, D_{qm} / D_{cl} ~ 1.5

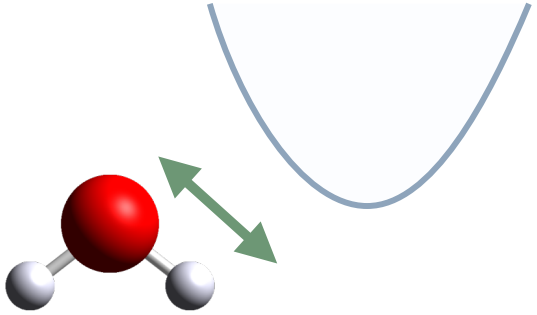
Empirical water models



Rigid models

Intramolecular ZPE ignored

SPC/E TIP4P



Harmonic models

Non-physical vibration

SPC/F SPC/RW

Parameterization again experimental data

"double-counts" quantum effects

Flexible, anharmonic model
parameterized for quantum simulations: q-TIP4P/F

Path integral molecular dynamics

$$\langle A \rangle = \frac{1}{Z} \mathrm{Tr}\left[e^{-\beta \hat{H}} \hat{A} \right]$$

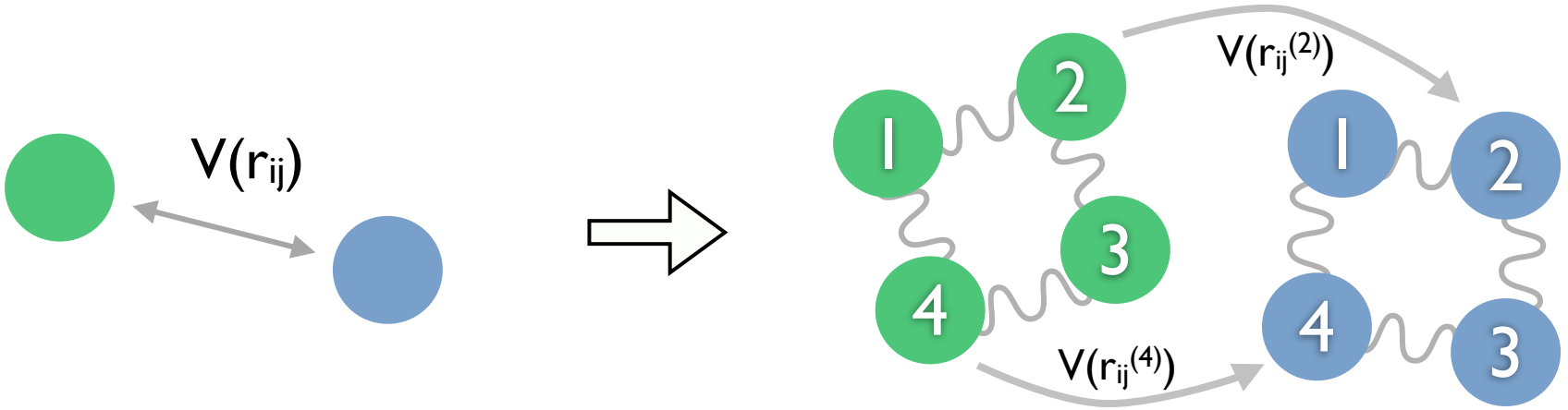
Path integral

$$\langle A \rangle = \frac{1}{2\pi\hbar Z_n} \int d\mathbf{p}^n \, d\mathbf{q}^n \; e^{-\frac{\beta}{n} H_n(\mathbf{p},\mathbf{q})} A_n(\mathbf{q})$$

3Nn-dimensional integral

$$A_n = \frac{1}{n} \sum_{j=1}^{n} A(q_j)$$

$$H_n(\mathbf{p},\mathbf{q}) = \sum_{j=1}^{n} \left[\frac{p_j^2}{2m_j} + V(q_j) + \frac{m_j (n k_B T)^2}{2\hbar^2} (q_j - q_{j-1})^2 \right]$$



Exact quantum properties from *n* classical simulations

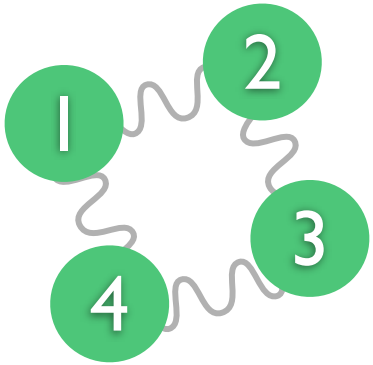
Ring polymer molecular dynamics (RPMD)*

$$\tilde{C}_{AB}(t) = \frac{1}{\beta Z}\int_0^\beta d\lambda\, \mathrm{Tr}\left[e^{-(\beta-\lambda)\hat{H}}\hat{A}e^{-\lambda\hat{H}}e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}\right] \Rightarrow D = \frac{1}{3}\int_0^\infty \tilde{C}_{\mathbf{v}\cdot\mathbf{v}}(t)\,dt$$

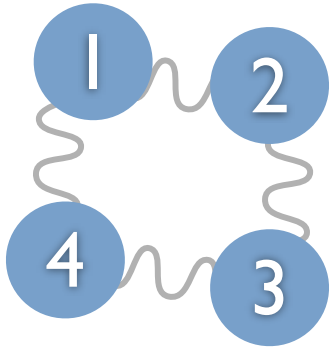
$$\tilde{C}_{AB} \approx \frac{1}{2\pi\hbar Z_n}\int d\mathbf{p}^n\, d\mathbf{q}^n\, e^{-\frac{\beta}{n}H_n(\mathbf{p},\mathbf{q})}A_n(0)B_n(t)$$

$$A_n = \frac{1}{n}\sum_{j=1}^{n} A(q_j)$$

Sample with PI Boltzmann weight



Evolve on $H_n(\mathbf{p},\mathbf{q})$

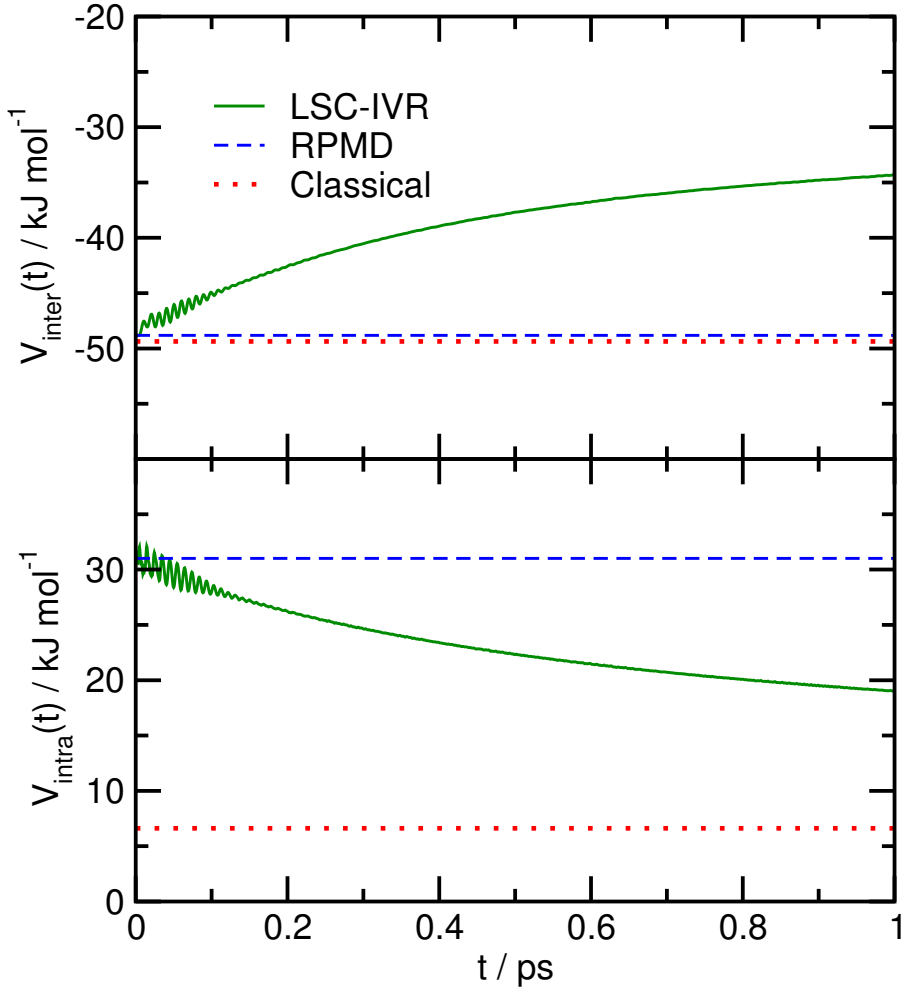


- *Exact* for SHO for linear A and/or B
- *Exact* at t = 0 and high-T limits
- Same symmetries as exact quantum TCF

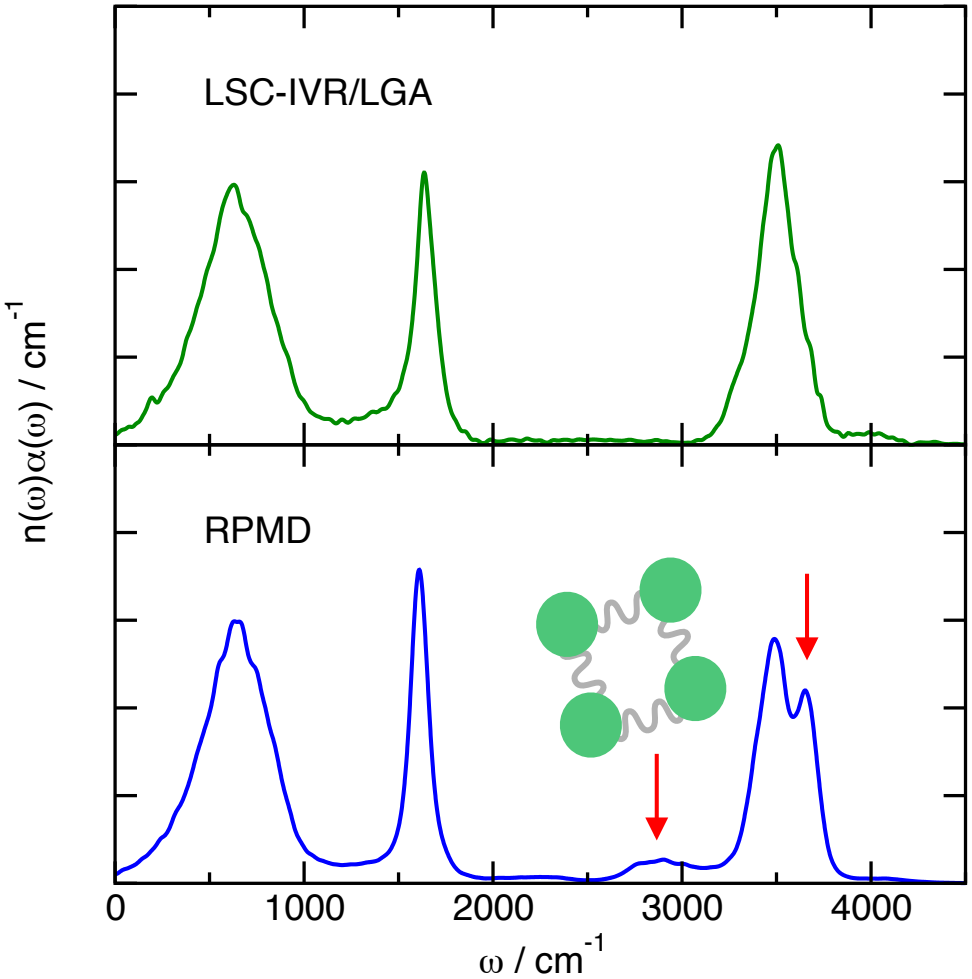
*I. R. Craig and D. E. Manolopoulos, *J. Chem. Phys.*, **121**, 3368 (2004)

Zero-point energy leakage*

Quantum simulations of simple flexible water model



RPMD conserves quantum Boltzmann distribution *at all times*



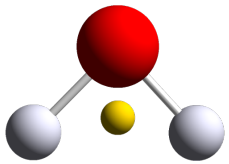
RPMD exhibits spurious Matsubara frequencies in vibrational spectra

*S. Habershon and D. E. Manolopoulos, *J. Chem. Phys.*, **131**, 244518 (2009)

q-TIP4P/F water model*

4-site flexible *anharmonic* water model

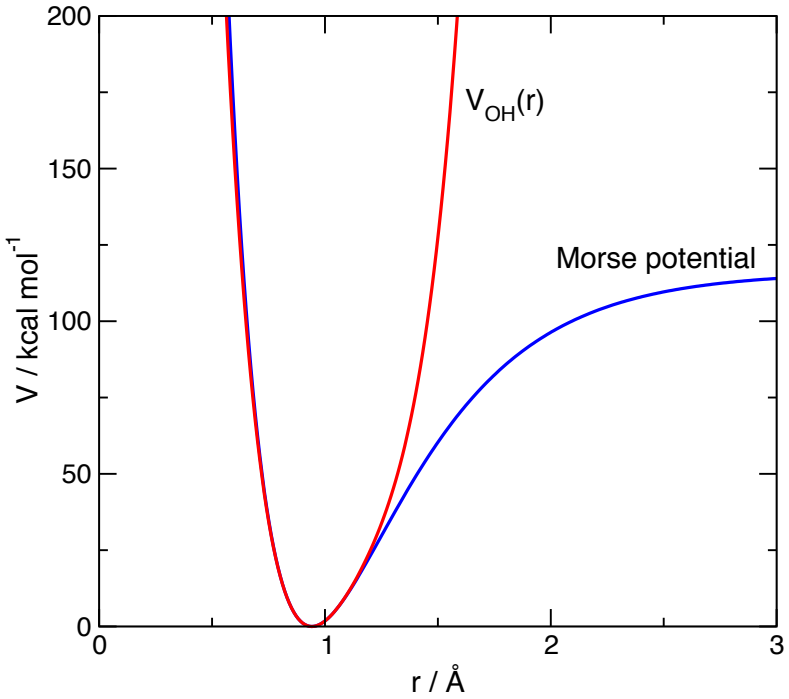
$$V = V_{inter} + V_{intra}$$



$$\mathbf{r}_{\mathrm{M}} = \gamma \mathbf{r}_{\mathrm{O}} + (1-\gamma)[\mathbf{r}_{\mathrm{H1}} + \mathbf{r}_{\mathrm{H2}}]/2$$

$$V_{inter} = \sum_i \sum_{j>i} \left\{ 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] + \sum_{m \in i} \sum_{n \in j} \frac{q_m q_n}{r_{mn}} \right\}$$

Parameters from Vega's TIP4P/2005 (rigid)



$$V_{intra} = \sum_i \left[V_{\mathrm{OH}}(r_{i1}) + V_{\mathrm{OH}}(r_{i2}) + \frac{1}{2} k_\theta (\theta_i - \theta_{eq})^2 \right]$$

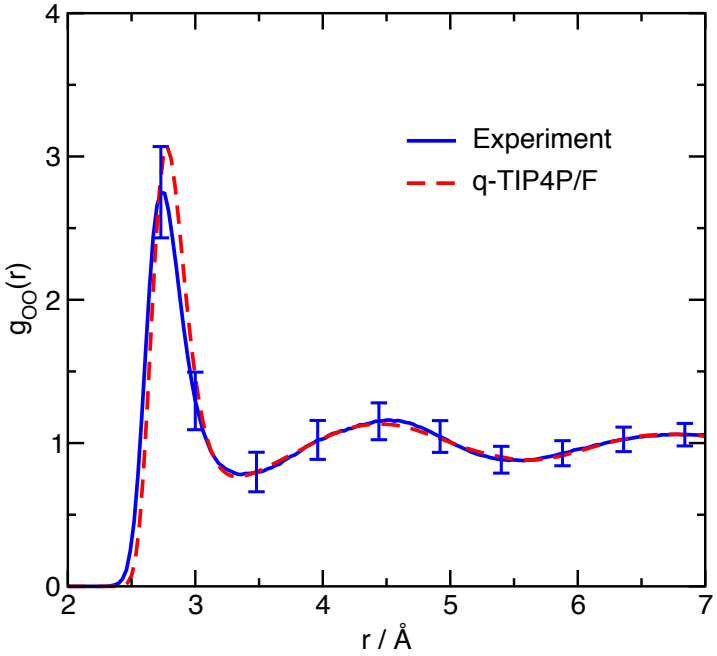
$$V_{\mathrm{OH}}(r) = D_r \left[\alpha_r^2 (r - r_{eq})^2 - \alpha_r^3 (r - r_{eq})^3 + \frac{7}{12} \alpha_r^4 (r - r_{eq})^4 \right]$$

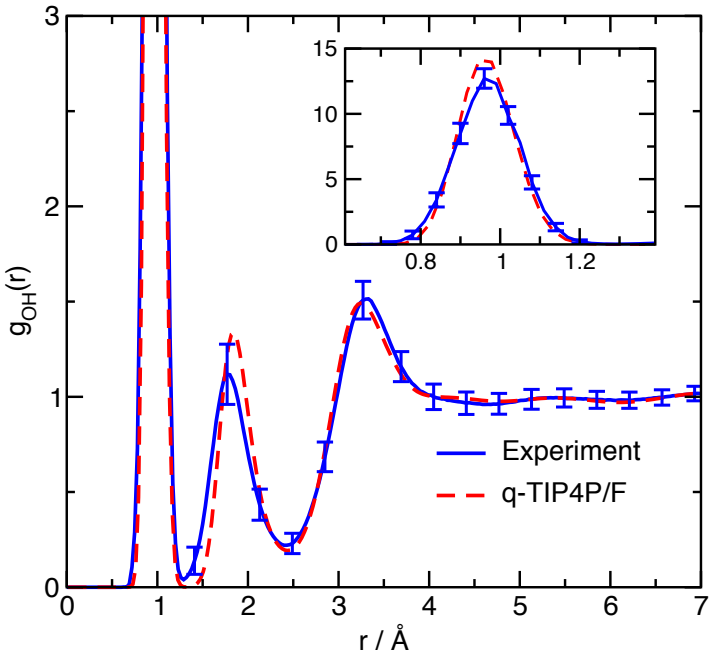
Parameterize using PIMD/RPMD simulations of:

- Experimental RDFs
- Experimental diffusion coefficient
- Experimental liquid vibrational frequencies

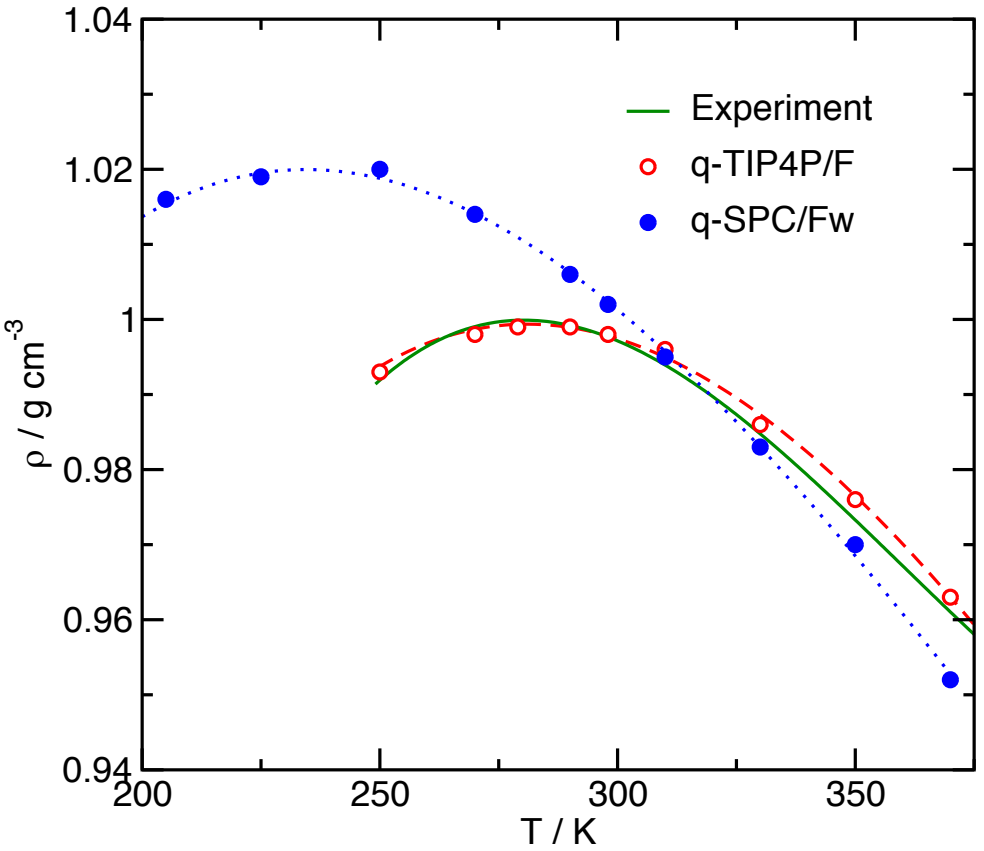
***S. Habershon**, T. E. Markland and D. E. Manolopoulos, *J. Chem. Phys.*, **131**, 024501 (2009)

q-TIP4P/F water: statics

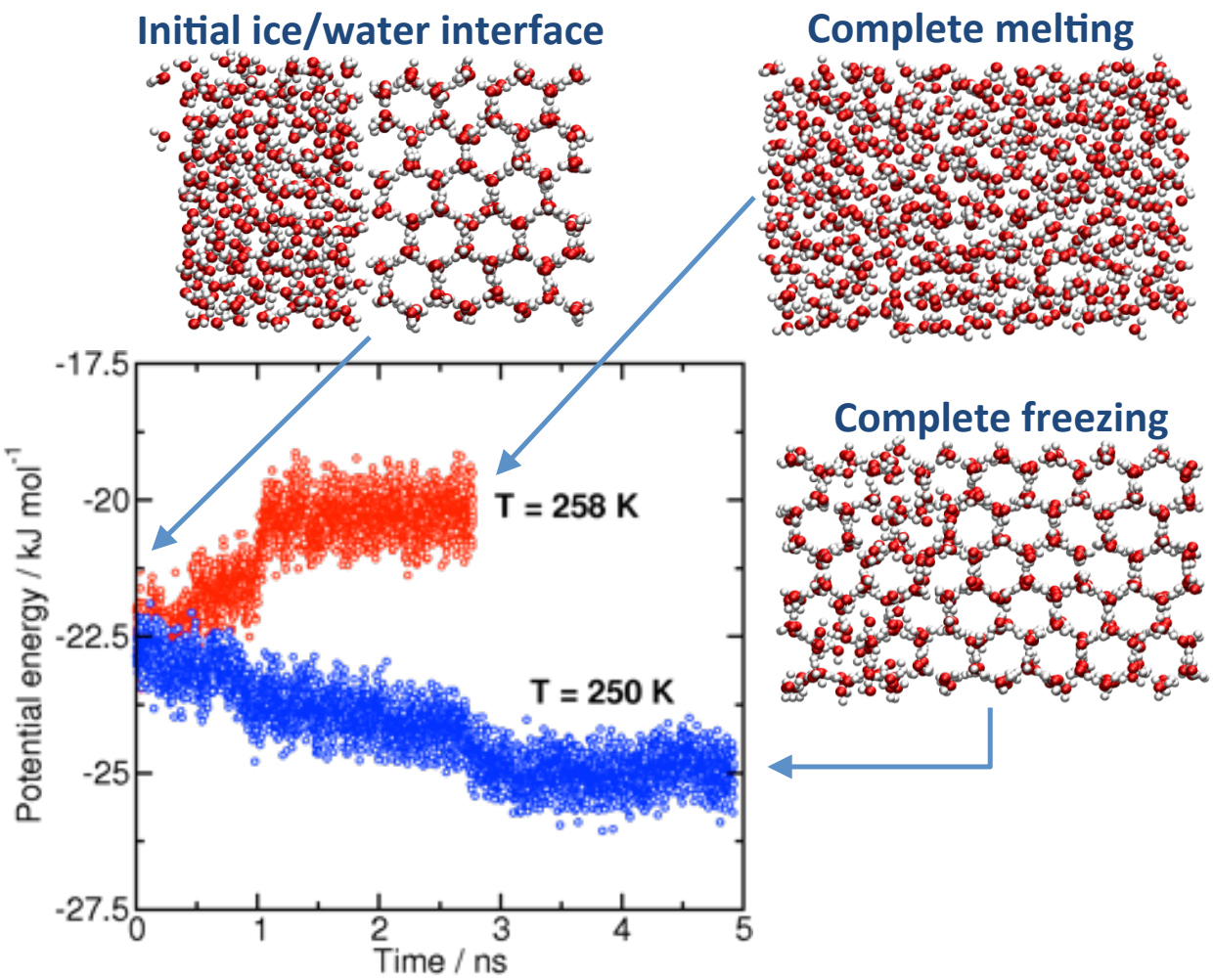




PIMD densities at 1 bar pressure

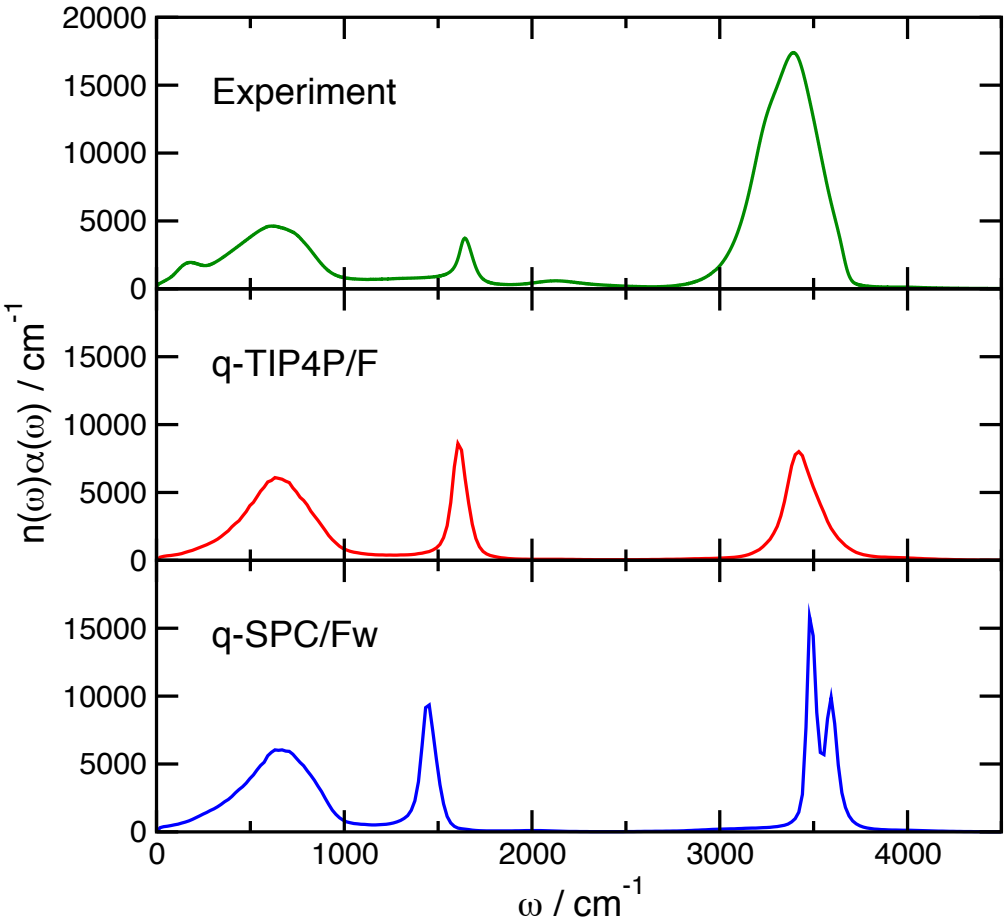


q-TIP4P/F water: melting point



	q-TIP4P/F (classical)	q-TIP4P/F (quantum)	q-SPC/FW (quantum)	TIP3P (classical)
Melting point / K	**259**	**251**	**195**	**146**

q-TIP4P/F water: dynamics



	q-TIP4P/F	Expt.
D_{H2O} / Å ps^{-2}	0.221	0.23
D_{D2O} / Å ps^{-2}	0.172	0.177
D_{H2O} / D_{D2O}	1.28	1.30
τ_2^{HH} / ps	2.22	1.6 - 2.5
τ_2^{OH} / ps	1.90	1.95
τ_2^{μ} / ps	1.52	1.90

An interesting observation...

Model	Quantum method	Classical diffusion	Quantum diffusion	D_{qm} / D_{cl}
SPC/E	RPMD	0.242	0.343	**1.42**
TIP4P	CMD	0.358	0.548	**1.53**
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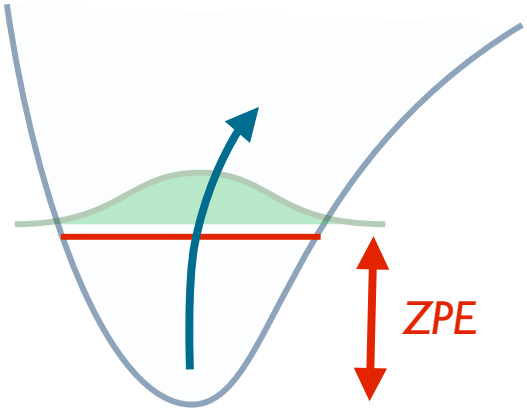
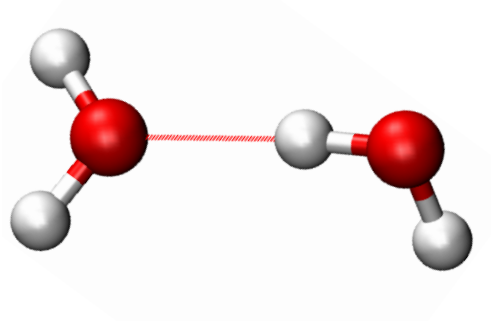
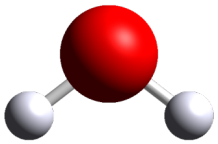
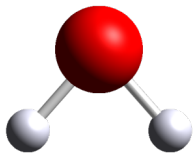
SPC/F	CMD	0.30	0.42	**1.40**
SPC/RW	LSC-IVR	0.25	0.47	**1.88**
q-TIP4P/F	RPMD	0.192	0.221	**1.15**

Why is the quantum effect smaller in q-TIP4P/F?

Competing quantum effects





	Classical	Quantum
r_{OH} / Å	0.963	0.978
θ / °	104.8	104.7
		
μ / D	2.311	2.348

Intermolecular interactions
ZPE weakens hydrogen-bonding network

Expect quantum dynamics faster than classical dynamics

Intramolecular interactions
Geometry changes *increase* dipole moment

Expect quantum dynamics slower than classical dynamics

Competition between quantum effects results in cancellation

Further verification

Turning off flexibility results in a large QM effect again

Rigid q-TIP4P/F simulations

Classical D / Å ps^{-2}	0.308
Quantum D / Å ps^{-2}	0.440
D_{qm} / D_{cl}	**1.43**

Not specific to q-TIP4P/F: *ab initio* simulations demonstrate similar results

PIMD simulations of BLYP water*

Classical μ = 3.04 D

Quantum μ = 3.18 D

Experimental support

X-ray / neutron diffraction studies**

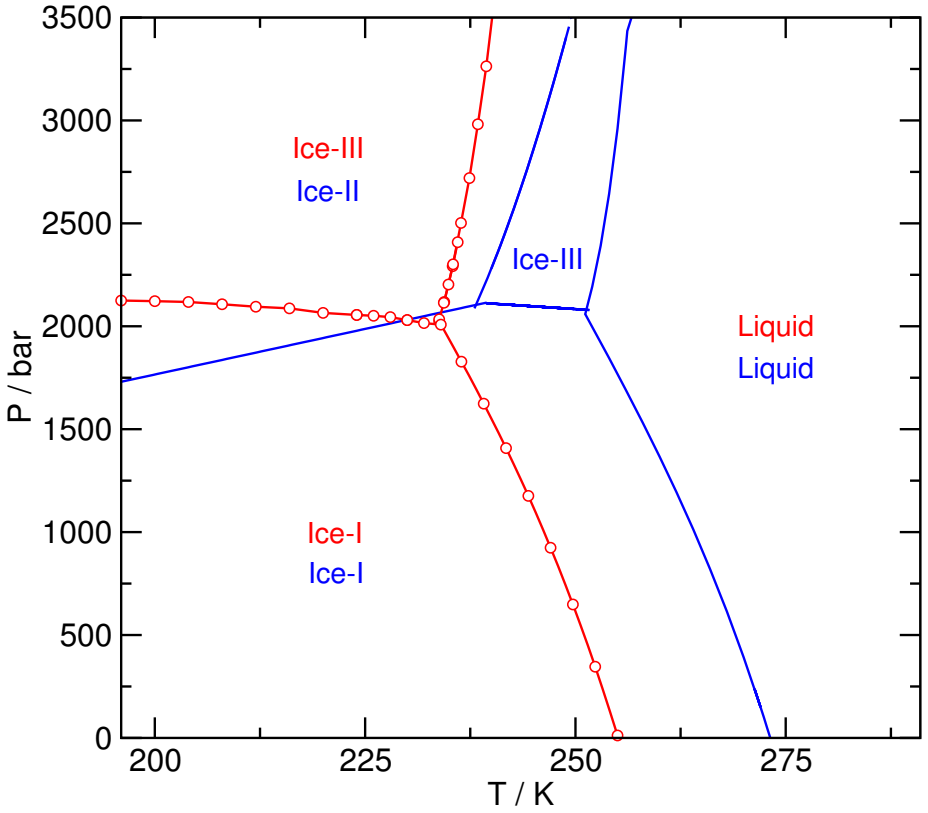
O-H bond length in H_2O ~3% longer than O-D bond length in D_2O

*M. Parrinello *et. al*, *Phys. Rev. Letters*, **91**, 215503 (2003)

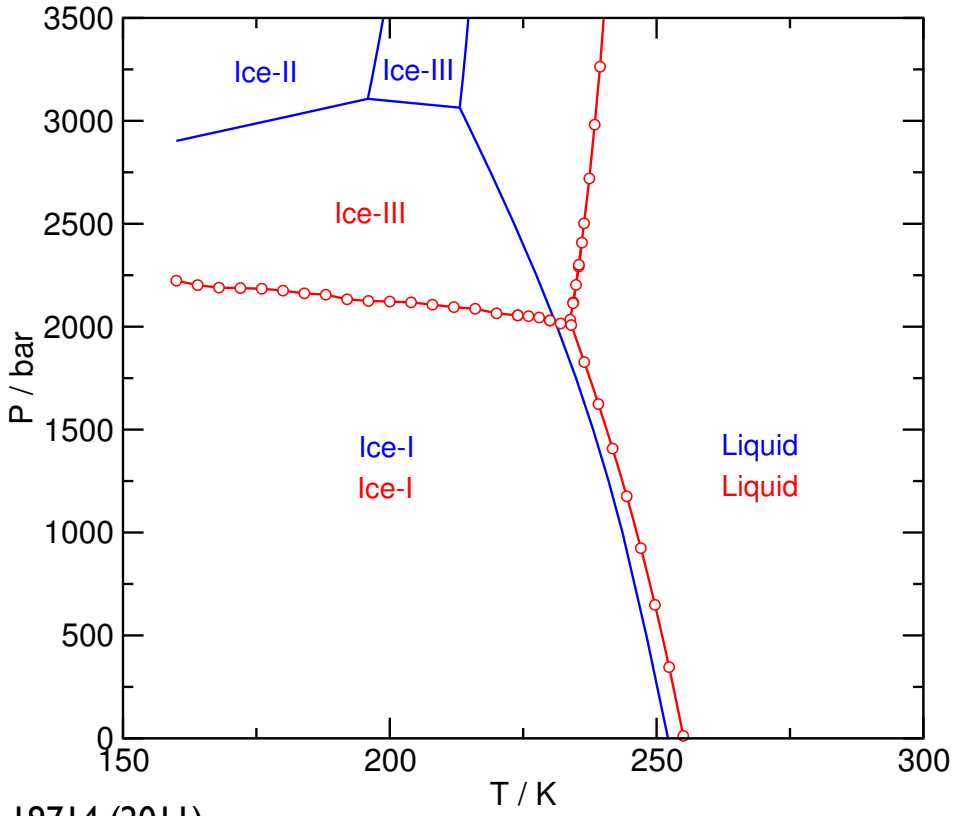
A. K. Soper *et. al*, *Phys. Rev. Letters*, **101, 065502 (2008)

q-TIP4P/F phase diagram (classical)*

Comparison with expt.



Comparison with rigid TIP4P/2005



*S. Habershon and D. E. Manolopoulos, *Phys. Chem. Chem. Phys.*, **13**, 19714 (2011)

Quantum thermodynamic integration

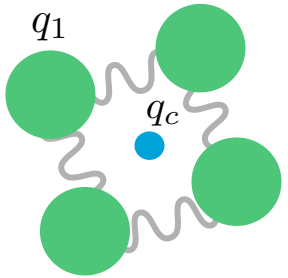
$$F(\lambda) = -\frac{1}{\beta}\ln\left[Z(\lambda)\right] \quad \Longrightarrow \quad \Delta F = F(\lambda=1) - F(\lambda=0) = \int_0^1 \left(\frac{\partial F}{\partial \lambda}\right) d\lambda$$

Quantum

Classical

$$H_n(\mathbf{p},\mathbf{q}) = \sum_{j=1}^{n}\left[\frac{p_j^2}{2m_j} + \mathbf{V(q_j)} + \frac{1}{2}m_j\omega_j^2(q_j - q_{j-1})^2\right]$$

$$H_n(\lambda;\mathbf{p},\mathbf{q}) = \sum_{j=1}^{n}\left[\frac{p_j^2}{2m_j} + \mathbf{V}(\lambda\mathbf{q_j} + (\mathbf{1}-\lambda)\mathbf{q_c}) + \frac{1}{2}m_j\omega_j^2(q_j - q_{j-1})^2\right]$$

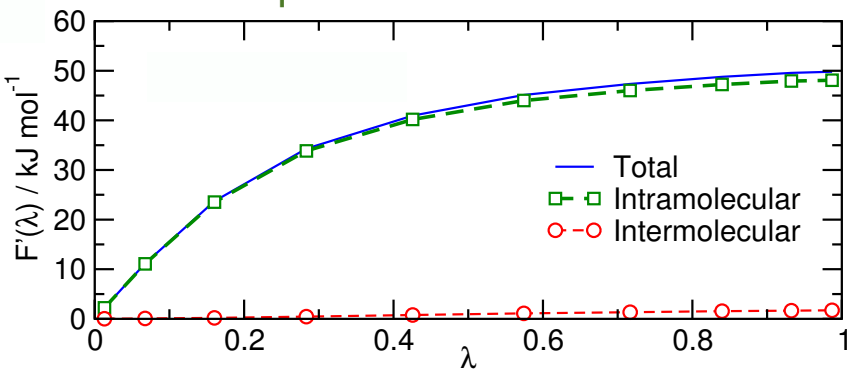


$$u_j^\lambda = \lambda q_j + (1-\lambda)q_c$$

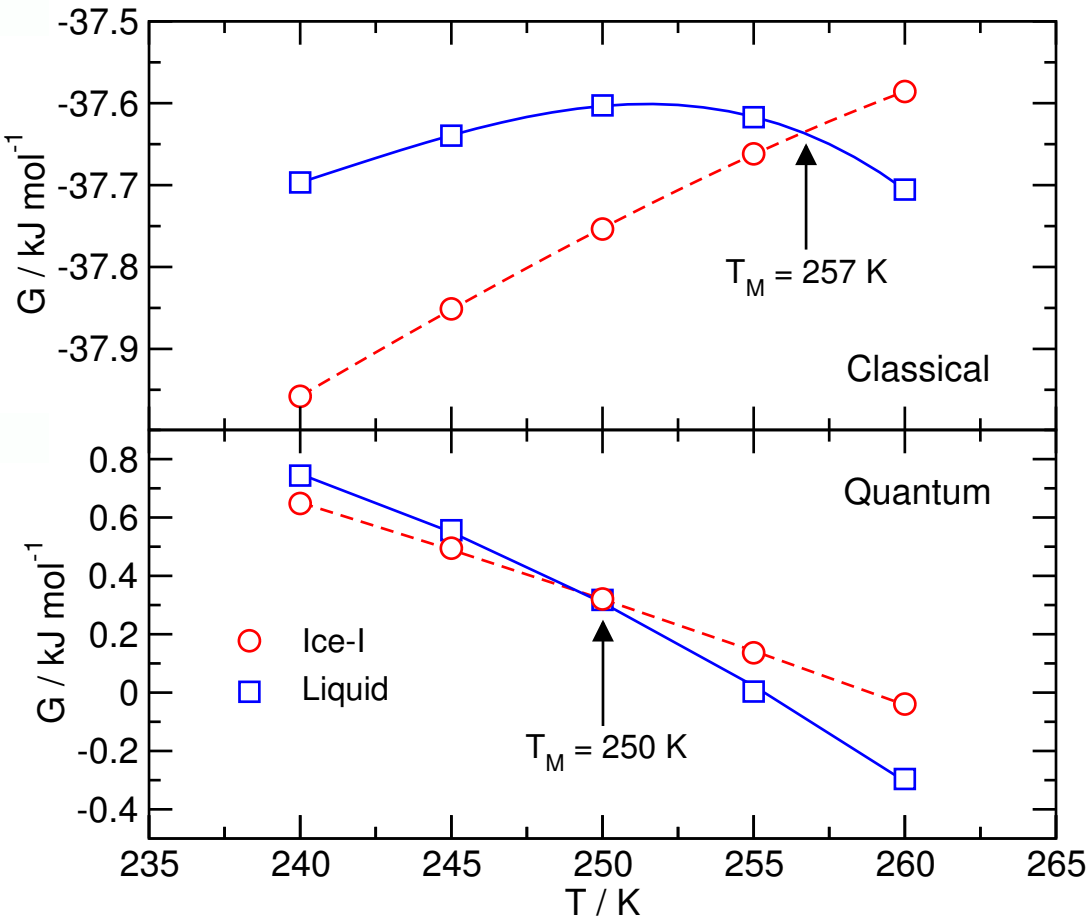
$$\left(\frac{\partial F}{\partial \lambda}\right) = \left\langle \frac{1}{n}\sum_{j=1}^{n}(q_j - q_c)\frac{\partial V(u_j^\lambda)}{\partial u_j^\lambda}\right\rangle_\lambda$$

Evaluated in *NPT* simulations

216 q-TIP4P/F water molecules



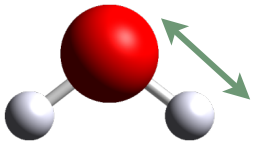
Application: liquid / ice-I boundary*



$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$S_{cl} = k_{\mathrm{B}}\left[1 - \ln(\beta\hbar\omega)\right]$$

$$\hbar\omega > 2.72 k_B T$$



$$\hbar\omega \simeq 18 k_B T$$

*S. Habershon and D. E. Manolopoulos, *J. Chem. Phys.*, **135**, 224111 (2011)

Summary

Competing quantum effects in liquid water,
S. Habershon, T. E. Markland and D. E. Manolopoulos, *J. Chem. Phys.*, **131**, 024501 (2009)

Free energy calculations for a flexible water model,
S. Habershon and D. E. Manolopoulos, *Phys. Chem. Chem. Phys..*, **13**, 19714 (2011)

Thermodynamic integration from classical to quantum mechanics,
S. Habershon and D. E. Manolopoulos, *J. Chem. Phys.*, **135**, 224111 (2011)

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