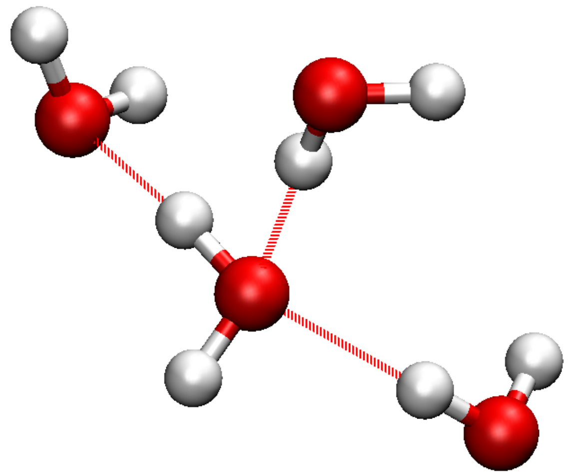
Thermodynamic integration from classical to quantum mechanics

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

↑ ↑

Classically *identical*

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

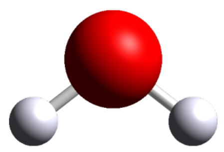
$ZPE_{H2O} > ZPE_{D2O}$

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, $D_{qm} / D_{cl} \sim 1.5$

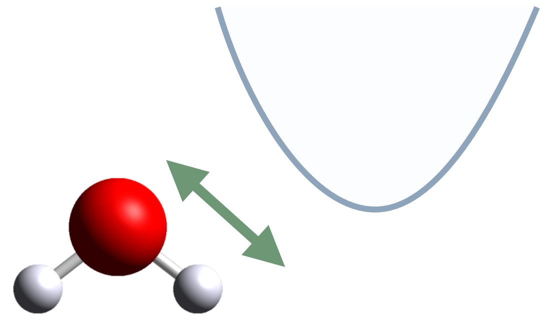
Empirical water models



Rigid models

Intramolecular ZPE ignored

SPC/E TIP4P



Harmonic models

Non-physical vibration

SPC/F SPC/RW

Parameterization again experimental data

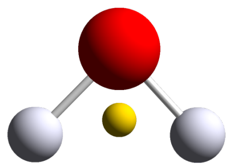
"double-counts" quantum effects

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

q-TIP4P/F water model*

4-site flexible *anharmonic* water model

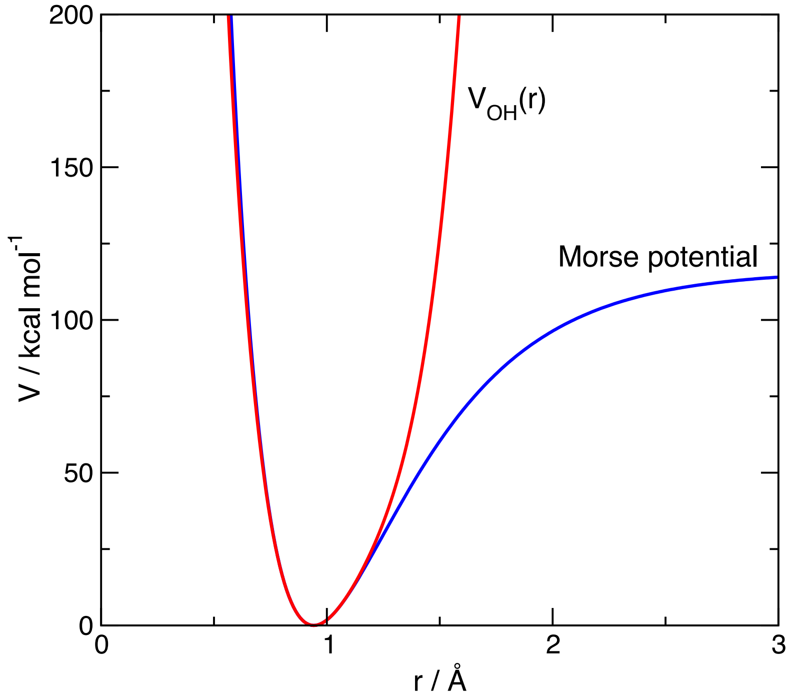
$$V = V_{inter} + V_{intra}$$



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

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

Parameters from Vega's TIP4P/2005 (rigid)



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

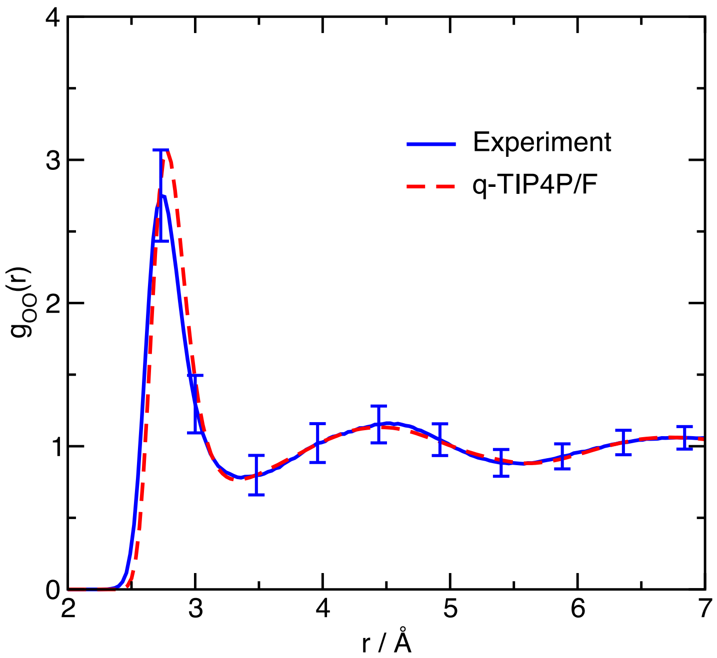
$$V_{\mathrm{OH}}(r) = D_r \left[\alpha_r^2 (r - r_{eq})^2 - \alpha_r^3 (r - r_{eq})^3 + \frac{7}{12} \alpha_r^4 (r - r_{eq})^4 \right]$$

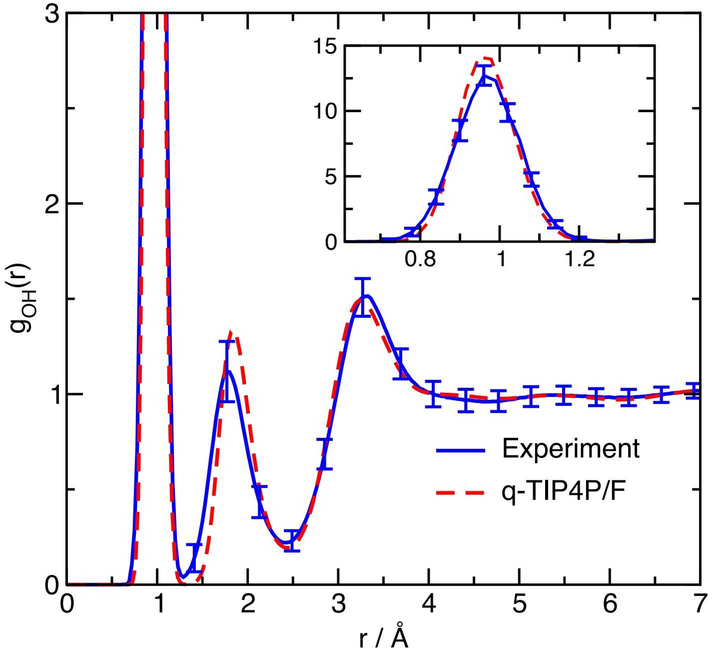
Parameterize using ***quantum*** simulations of:

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

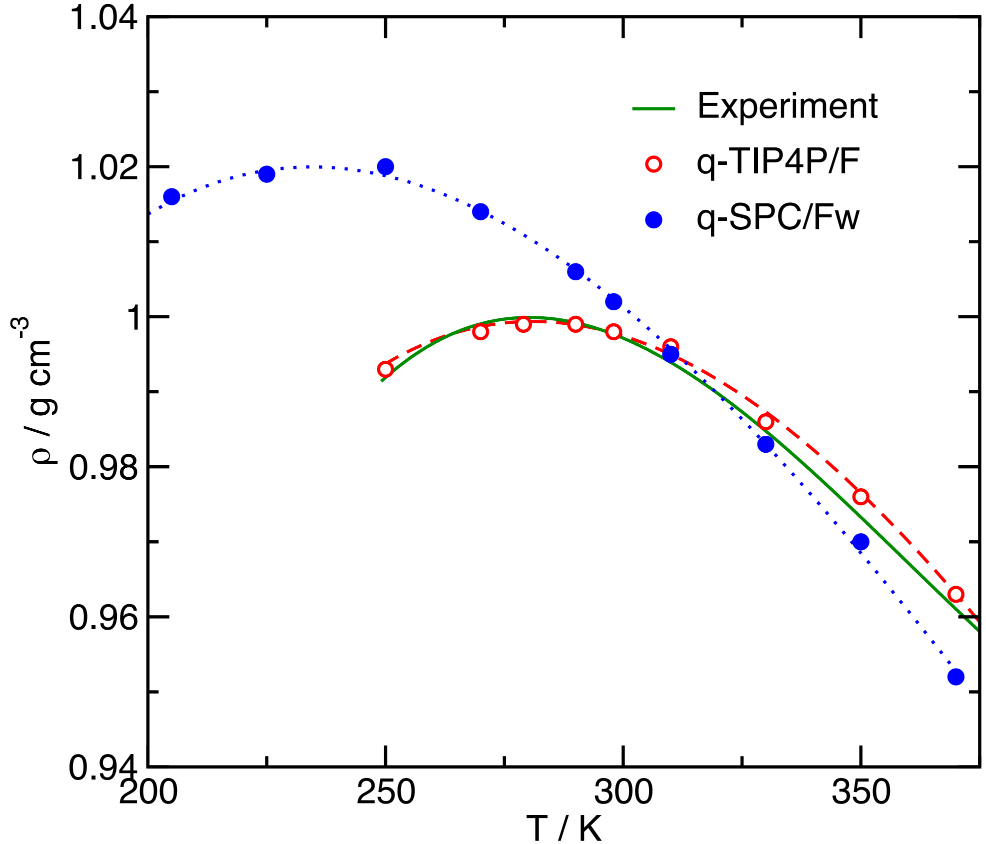
*__S. Habershon__, T. E. Markland and D. E. Manolopoulos, *J. Chem. Phys.*, **131**, 024501 (2009)

q-TIP4P/F water: statics

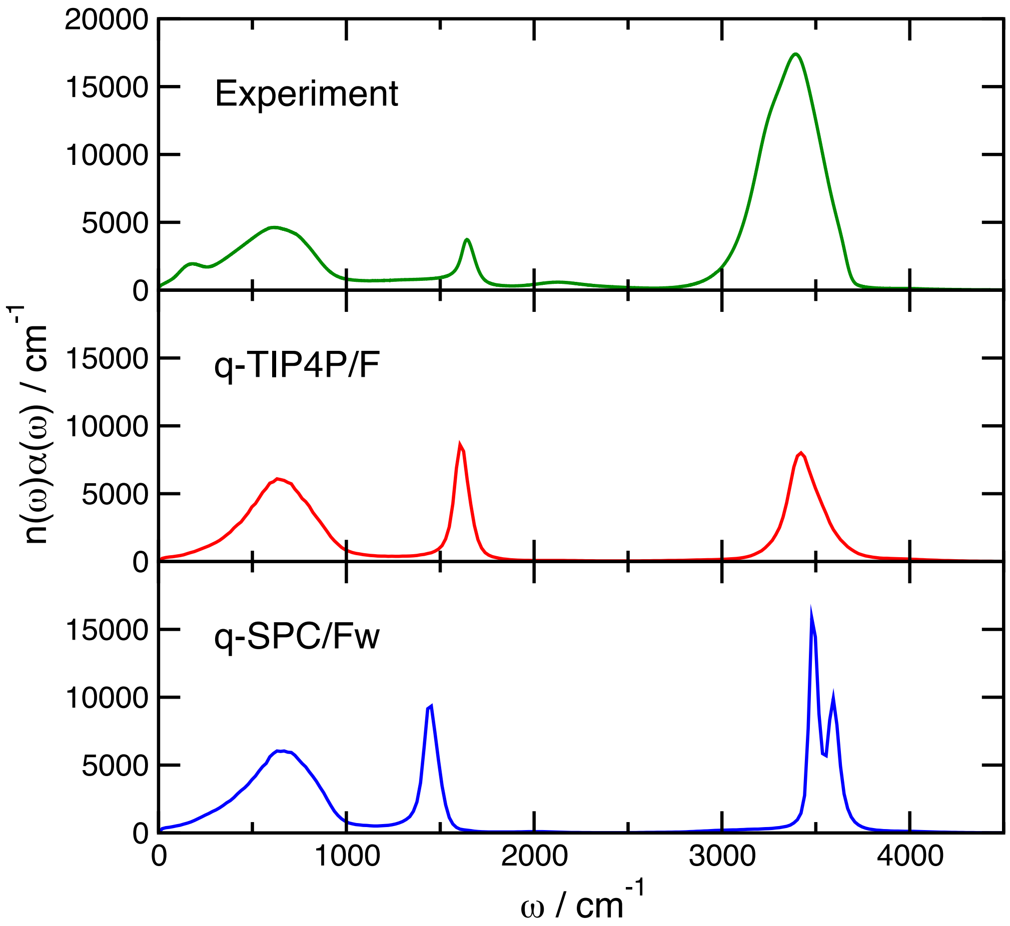




PIMD densities at 1 bar pressure



q-TIP4P/F water: 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

Quantum results from
ring-polymer molecular dynamics (RPMD)

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

An interesting observation...

Model	Quantum method	Classical diffusion	Quantum diffusion	D_{qm} / D_{cl}
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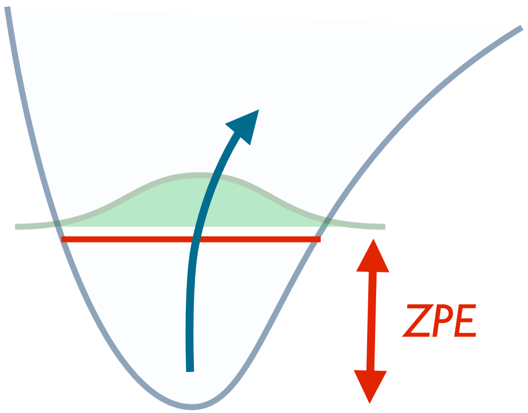
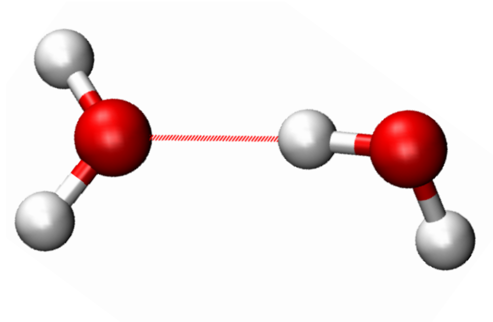
q-TIP4P/F	RPMD	0.192	0.221	**1.15**

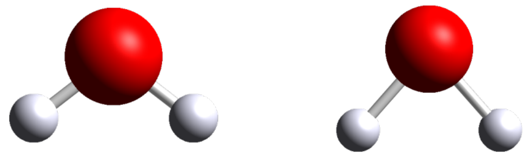
Why is the quantum effect so small in q-TIP4P/F?

Competing quantum effects





	Classical	Quantum
r_{OH} / Å	0.963	0.978
θ / °	104.8	104.7



	Classical	Quantum
μ / D	2.311	2.348

Intermolecular interactions

ZPE weakens hydrogen-bonding network

Expect quantum dynamics faster than classical dynamics

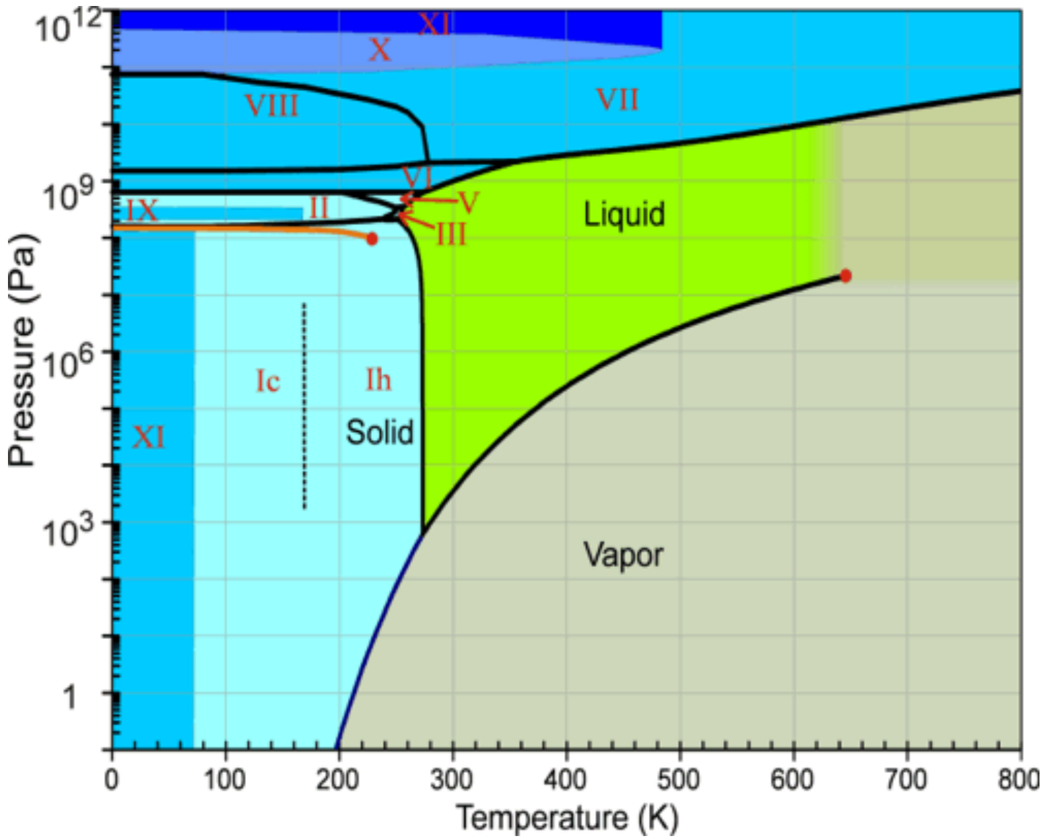
Intramolecular interactions

Geometry changes *increase* dipole moment

Expect quantum dynamics slower than classical dynamics

Competition between quantum effects results in cancellation

Quantum phase diagrams*



$$F_q = F_c + \Delta F_{qc}$$

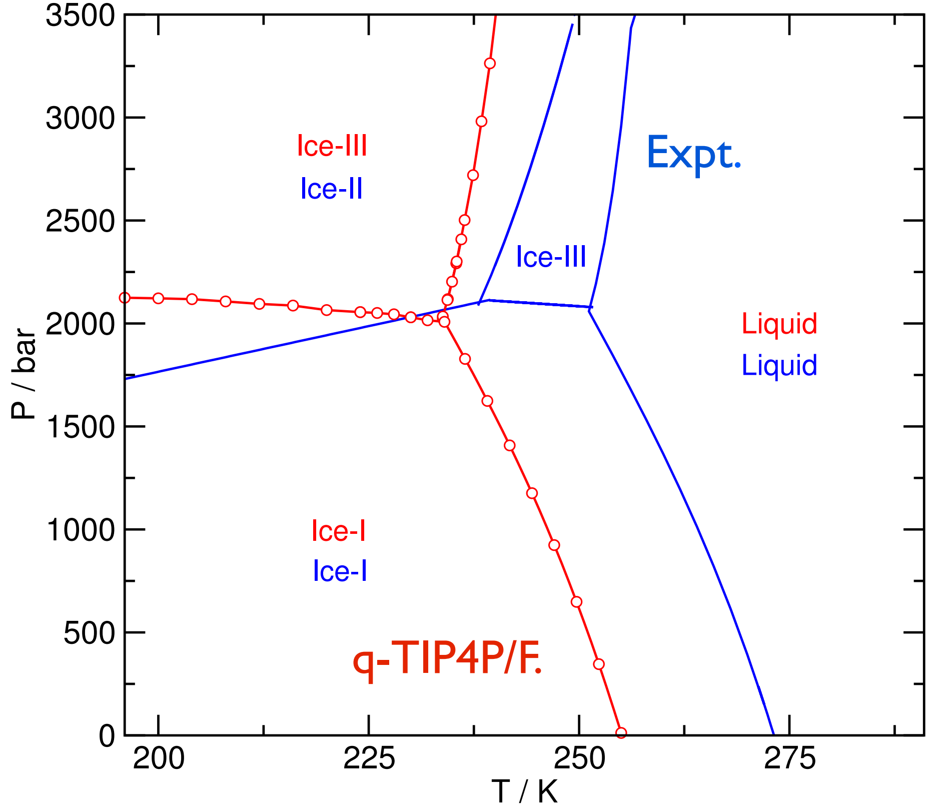
Free energy of quantization

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

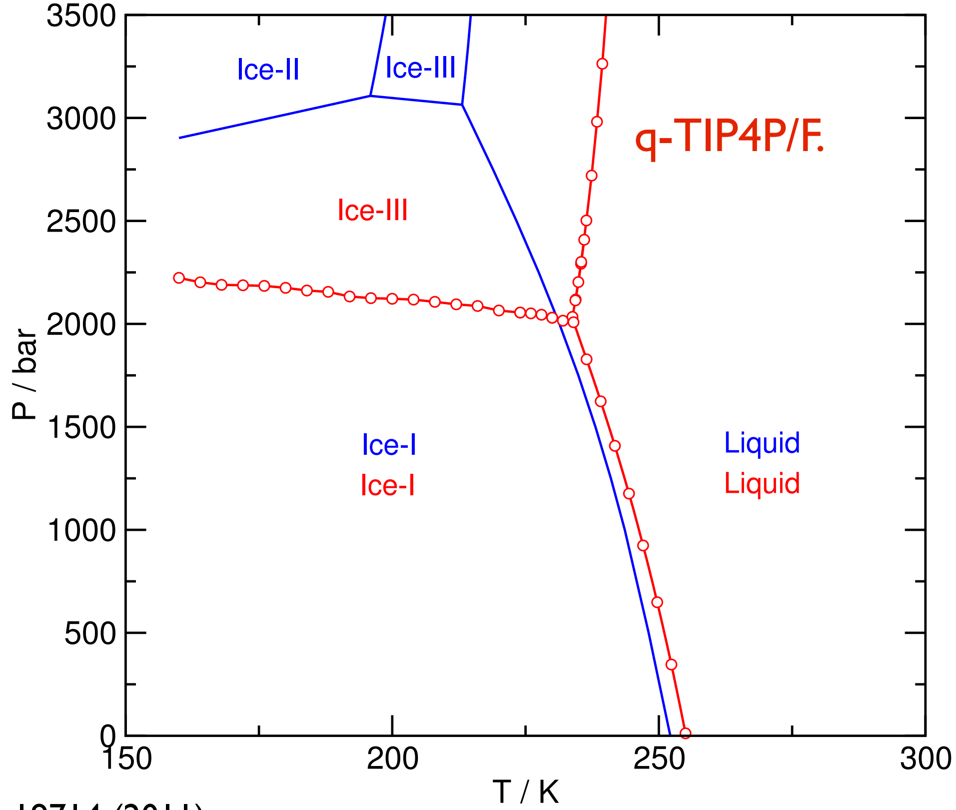
*www.lsbu.ac.uk/water

Classical q-TIP4P/F phase diagram*

Comparison with expt.



Comparison with rigid TIP4P/2005



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

Path integral molecular dynamics

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

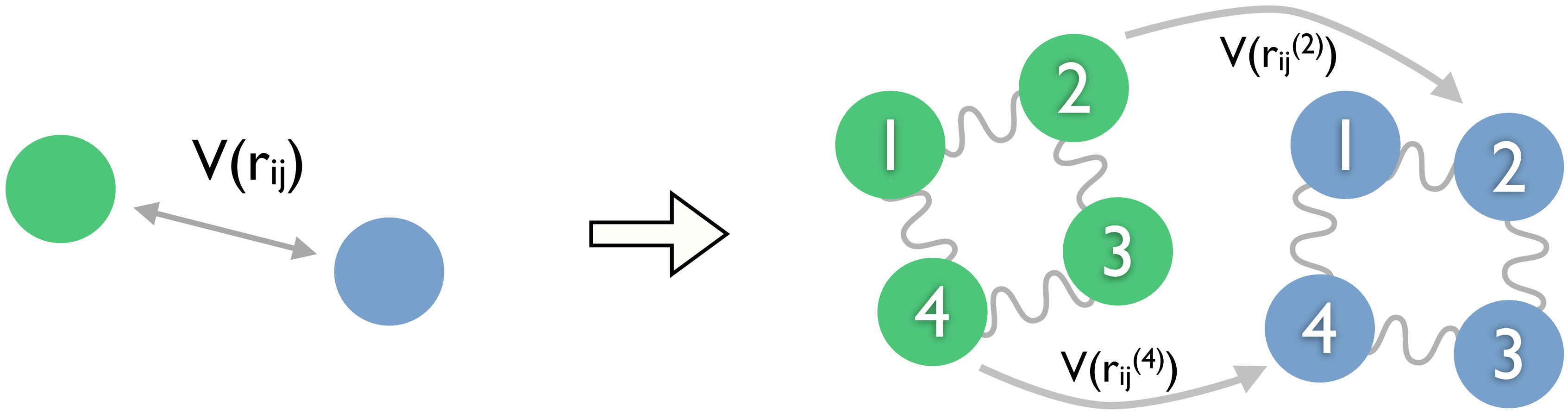
Path integral ⇨

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

3Nn-dimensional integral

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

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



Exact quantum properties from *n* classical simulations

Quantum Free Energies

$$F_q = F_c + \Delta F_{qc}$$ → Free energy of quantization

Introduce a path variable to the Hamiltonian.....

$$H(\mathbf{p}, \mathbf{q}; \lambda)$$

⇩

$$F(\lambda) = -\frac{1}{\beta} \ln \left[Z(\lambda) \right]$$ ⇨

Thermodynamic integration from classical to quantum mechanics

Quantum

$$\Delta F = F(\lambda = 1) - F(\lambda = 0) = \int_0^1 \left(\frac{\partial F}{\partial \lambda} \right) d\lambda$$

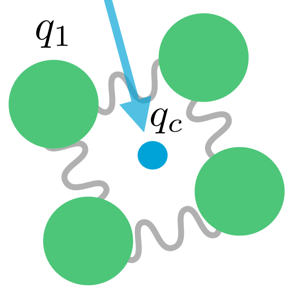
Classical

Integral easy to evaluate by quadrature ⇨

$$\frac{\partial F(\lambda)}{\partial \lambda} = \left\langle \frac{\partial H(\mathbf{p}, \mathbf{q}; \lambda)}{\partial \lambda} \right\rangle_{\lambda}^{NVT,NPT}$$

Morales-Singer (MS) method*

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



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

λ = 1 → *QUANTUM* PI Hamiltonian recovered

λ = 0?

Potential evaluated at centroid only, RP normal modes integrate out to give....

$$Z_n^{\mathrm{MS}}(\lambda=0) = \frac{1}{(2\pi\hbar)}\left(\frac{2\pi m}{\beta}\right)^{1/2}\int dq_c\, e^{-\beta V(q_c)}$$

...which is just the *CLASSICAL* Hamiltonian!

$$\Delta F = F(\lambda=1) - F(\lambda=0) = \int_0^1 \left(\frac{\partial F}{\partial\lambda}\right) d\lambda$$

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

Evaluate in PI simulation with MS Hamiltonian

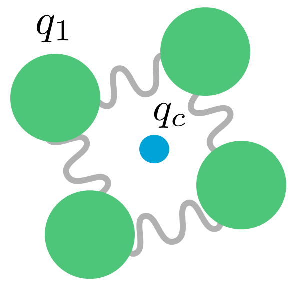
*J. J. Morales and K. Singer, *Mol. Phys.*, **73**, 873 (1991)

MS method fails for strongly quantum systems

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

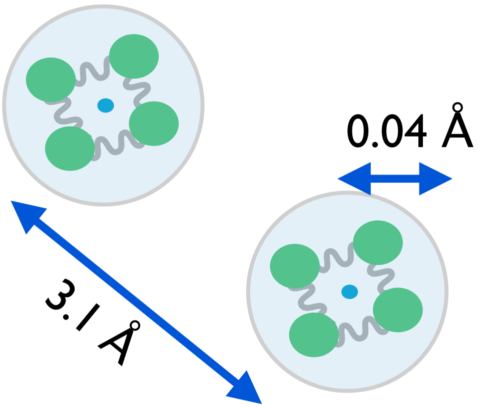
Potential on *beads*

Potential on *centroid*

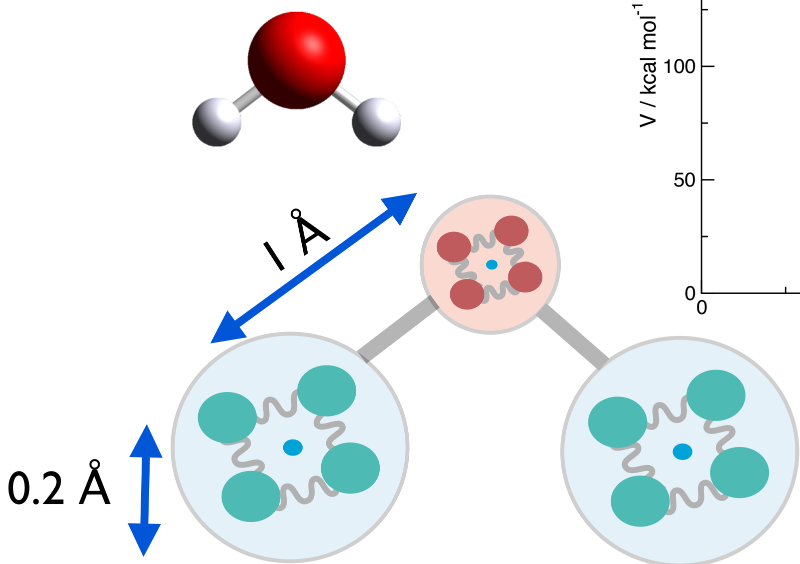


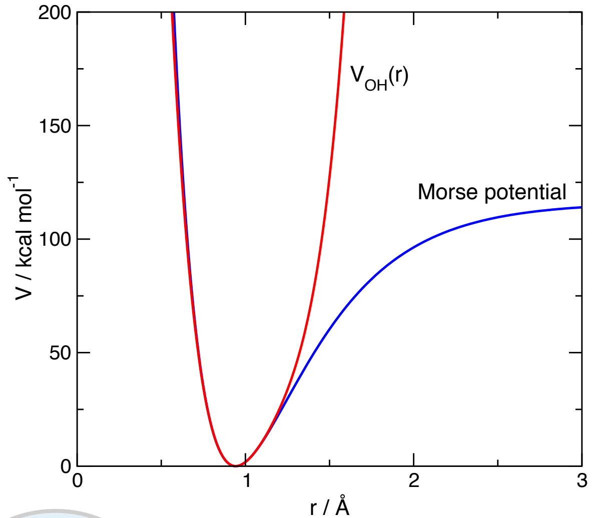
For small λ, bead positions sampled from *free ring-polymer distribution*

Liquid neon, T = 25 K



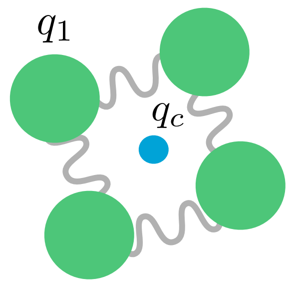
Liquid water, T = 298 K





Scaled coordinate (SC) method

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



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

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

λ = 1 ⟶ *QUANTUM* PI Hamiltonian and partition function recovered

λ = 0 ⟶ *CLASSICAL* Hamiltonian and partition function as before

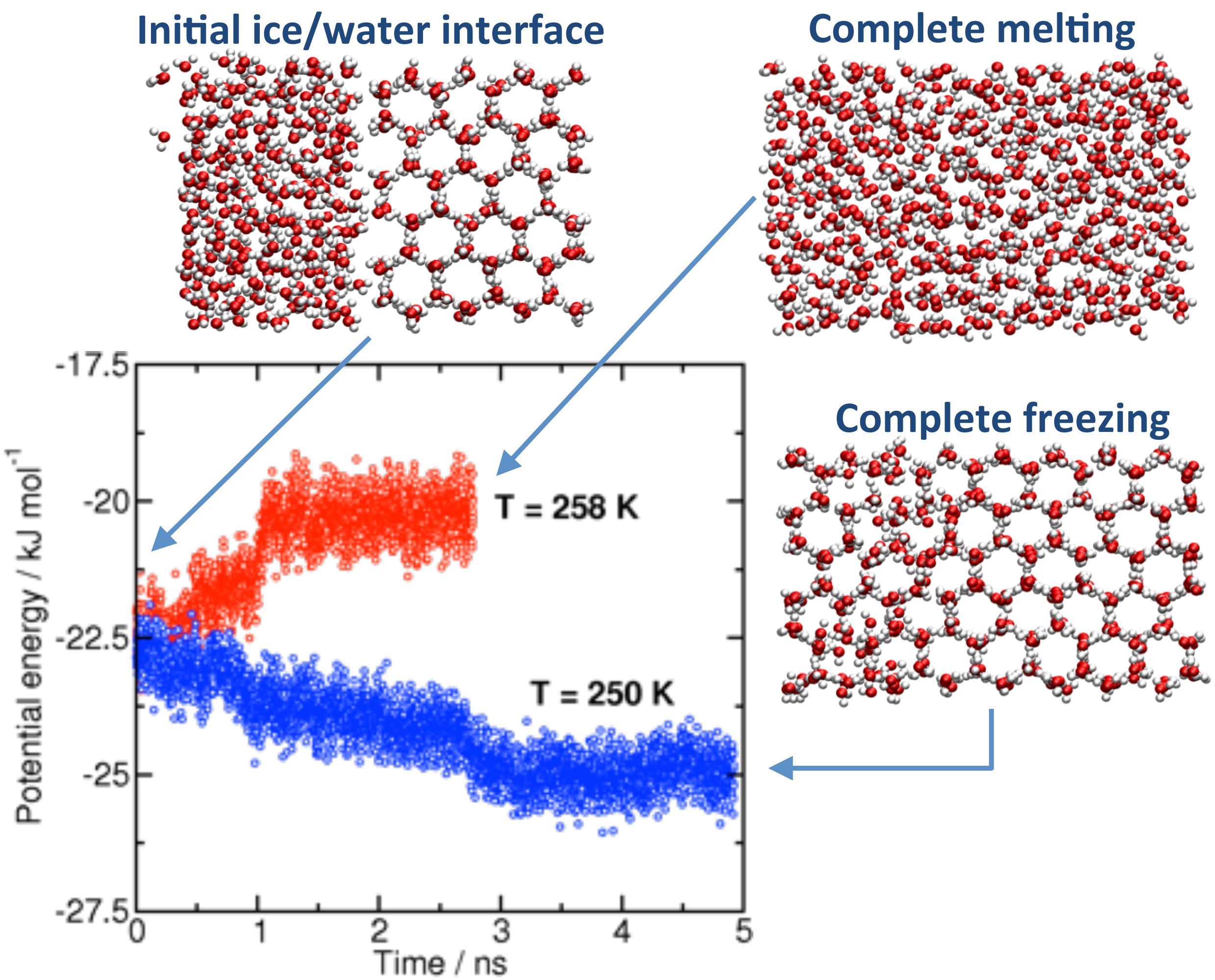
$$\Delta F = F(\lambda = 1) - F(\lambda = 0) = \int_0^1 \left(\frac{\partial F}{\partial \lambda}\right) d\lambda$$

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

Evaluated in *NPT* simulations

Stable estimator for **all** values of λ
No problems with strong delocalization like MS

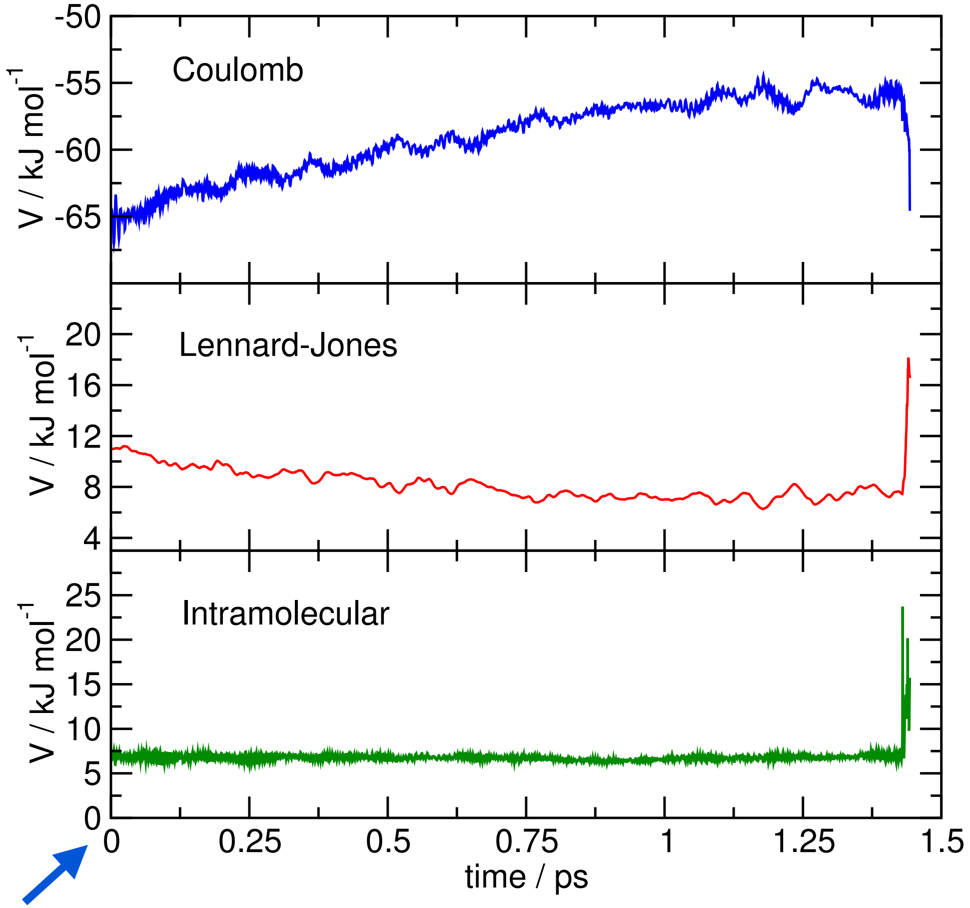
Application: q-TIP4P/F water melting point

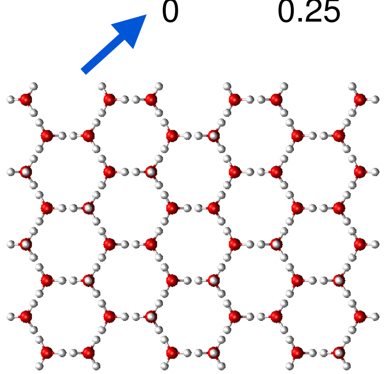


	q-TIP4P/F (classical)	q-TIP4P/F (quantum)	q-SPC/FW (quantum)	TIP3P (classical)
Melting point / K	**259**	**251**	**195**	**146**

Instability in the MS method

q-TIP4P/F water simulation at T = 298 K, p = 1 bar, MS method with $\lambda = 0.01$





Energies shown for melting of initial ice system at 298 K

Large RP radius of hydrogen (0.2 Å)

⇩

H can closely approach O atoms

⇩

Strong attractive Coulomb interactions

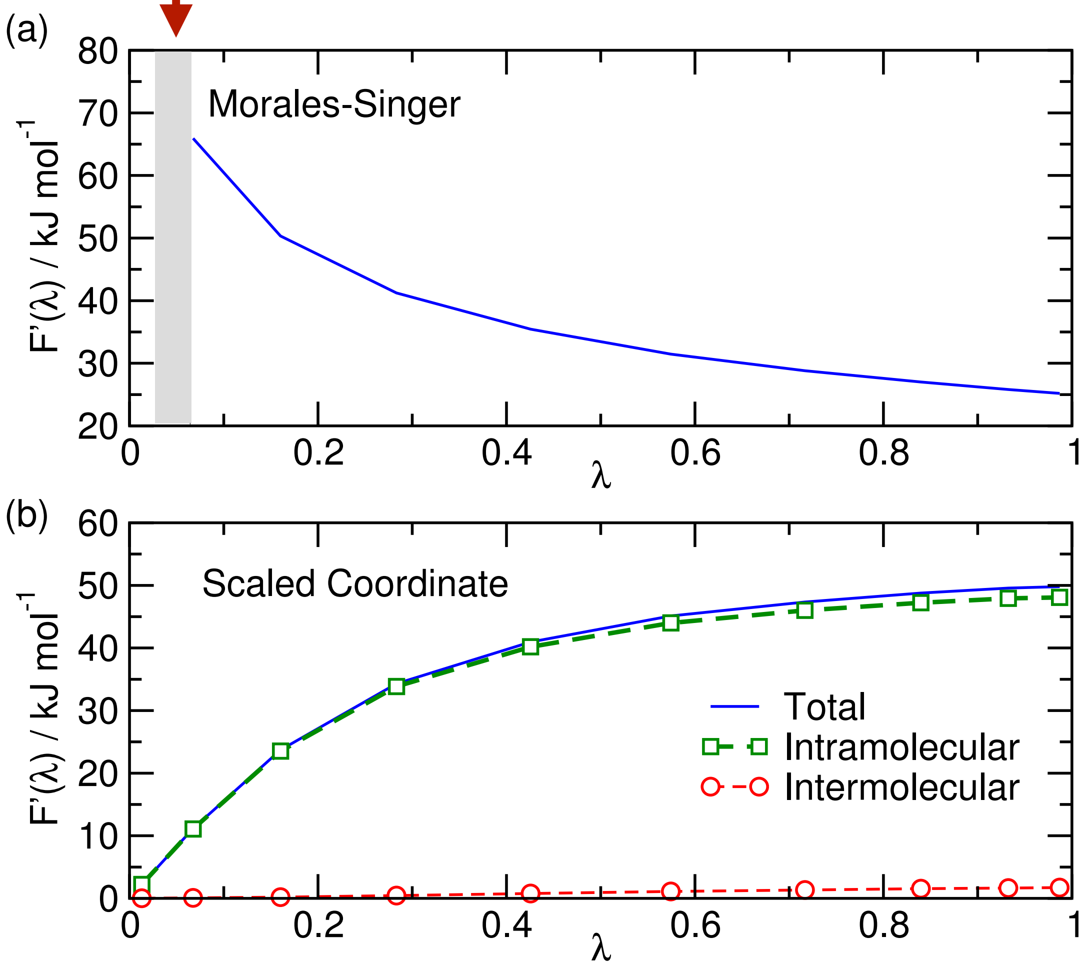
⇩

O-O interactions hit LJ wall...
difficult to integrate equations-of-motion

MS vs. SC methods

q-TIP4P/F water simulation at T = 250 K, p = 1 bar

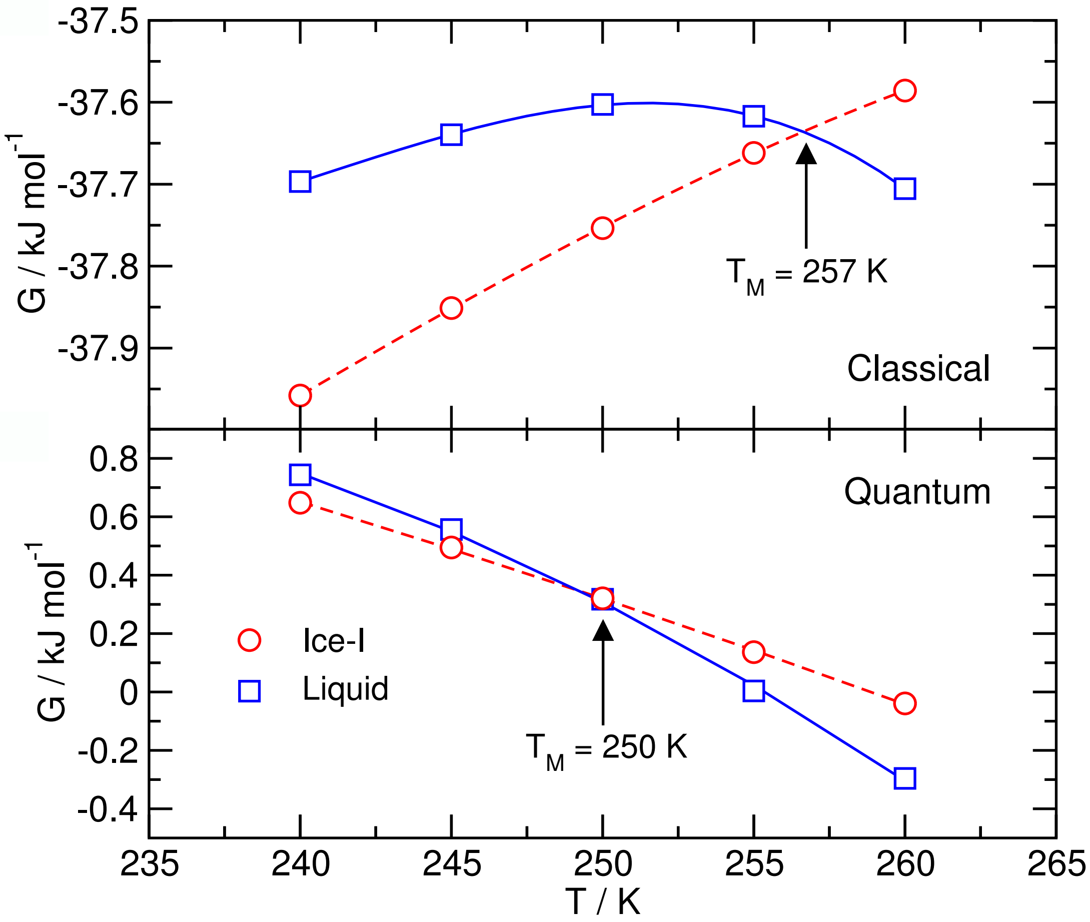
Impossible to calculate integrands for small λ



Major contribution from intramolecular modes

Classical → Quantum

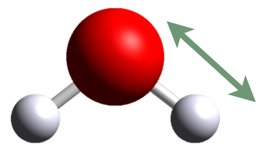
Quantum melting point of q-TIP4P/F



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

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

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



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

From direct coexistence simulation, quantum T_M = 251 K

*__S. Habershon__ and D. E. Manolopoulos, *J. Chem. Phys.*, **135**, 224111 (2011)

Summary

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