2054-1

Structure and Dynamics of Hydrogen-Bonded Systems

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Competing quantum effects in liquid water

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Outline

0. Ring polymer molecular dynamics

Based on the classical isomorphism:[a]

$$\langle r_G \rangle = \Lambda(T)/\sqrt{8\pi}$$

$$\Lambda(T) = h/\sqrt{2\pi m k T}$$
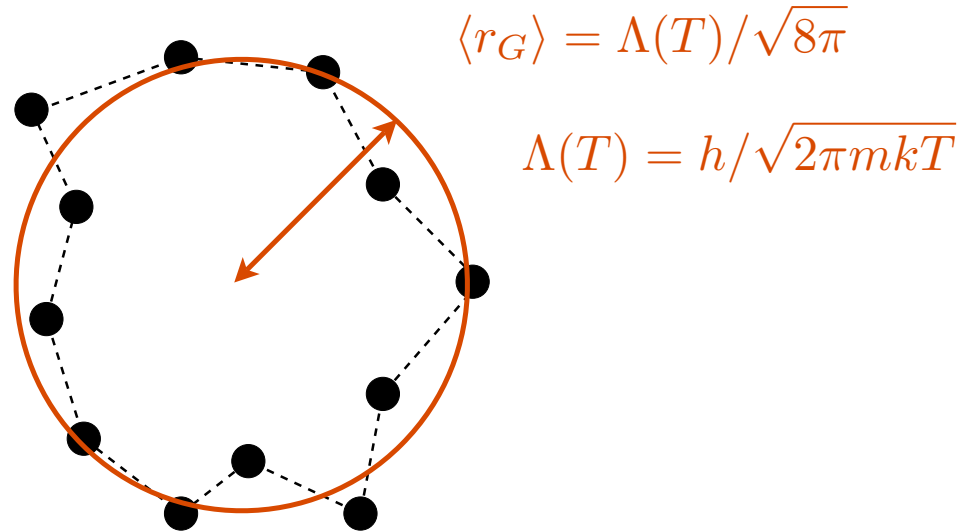
$$Z = \mathrm{tr}\left[e^{-\beta H}\right]$$

$$Z = \frac{1}{(2\pi\hbar)^n} \int d\mathbf{p} \int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})}$$

where

$$H_n(\mathbf{p},\mathbf{q}) = \sum_{j=1}^{n} \left[\frac{p_j^2}{2m} + \frac{1}{2} m \omega_n^2 (q_j - q_{j-1})^2 + V(q_j) \right] \quad \text{with } \beta_n = \beta/n \text{ and } \omega_n = 1/\beta_n\hbar.$$

[a] D. Chandler and P. G. Wolynes, JCP 74, 4078 (1981).

Proof (for those who have not seen this before):

$$Z = \text{tr}\left[e^{-\beta H}\right] = \text{tr}\left[\left(e^{-\beta_n H}\right)^n\right] \text{ where } \beta_n = \beta/n.$$

So

$$Z = \int dq_1 \cdots \int dq_n \; \langle q_1 | \, e^{-\beta_n H} \, | q_2 \rangle \cdots \langle q_n | \, e^{-\beta_n H} \, | q_1 \rangle,$$

where

$$\langle q_{j-1} | \, e^{-\beta_n H} \, | q_j \rangle \simeq \langle q_{j-1} | \, e^{-\beta_n T} e^{-\beta_n V} \, | q_j \rangle$$

$$= \frac{1}{2\pi\hbar} \int dp \, e^{-\beta_n p^2/2m - ip(q_j - q_{j-1})/\hbar - \beta_n V(q_j)}$$

$$= \frac{1}{2\pi\hbar} \left(\frac{2\pi m}{\beta_n}\right)^{1/2} e^{-\beta_n\left[m\omega_n^2 (q_j - q_{j-1})^2/2 + V(q_j)\right]}$$

$$\equiv \frac{1}{2\pi\hbar} \int dp_j \, e^{-\beta_n\left[p_j^2/2m + m\omega_n^2 (q_j - q_{j-1})^2/2 + V(q_j)\right]}, \text{ with } \omega_n = 1/\beta_n\hbar.^a$$

[a] M. Parrinello and A. Rahman, JCP 80, 860 (1984).

Path Integral Molecular Dynamics:

PIMD uses the ring polymer trajectories

$$\dot{\mathbf{q}} = +\frac{\partial H_n(\mathbf{p}, \mathbf{q})}{\partial \mathbf{p}} \qquad \dot{\mathbf{p}} = -\frac{\partial H_n(\mathbf{p}, \mathbf{q})}{\partial \mathbf{q}}$$

as a sampling tool to calculate *exact* values of static equilibrium properties such as

$$\langle A \rangle = \frac{1}{Z} \text{tr} \left[e^{-\beta H} A \right].$$

Ring Polymer Molecular Dynamics:

RPMD uses the same trajectories to calculate *approximate* Kubo-transformed correlation functions of the form

$$\tilde{c}_{AB}(t) = \frac{1}{\beta Z} \int_0^\beta d\lambda \, \text{tr} \left[e^{-(\beta - \lambda)H} A(0) e^{-\lambda H} B(t) \right].$$

Ring Polymer Molecular Dynamics

The RPMD approximation to

$$\tilde{c}_{AB}(t) = \frac{1}{\beta Z} \int_0^\beta d\lambda \, \mathrm{tr}\left[e^{-(\beta-\lambda)H} A(0) e^{-\lambda H} B(t) \right]$$

is simply

$$\tilde{c}_{AB}(t) \simeq \frac{1}{(2\pi\hbar)^n Z} \int d\mathbf{p}_0 \int d\mathbf{q}_0 \, e^{-\beta_n H_n(\mathbf{p}_0, \mathbf{q}_0)} A_n(\mathbf{q}_0) B_n(\mathbf{q}_t),$$

where

$$A_n(\mathbf{q}) = \frac{1}{n} \sum_{j=1}^n A(q_j) \text{ and } B_n(\mathbf{q}) = \frac{1}{n} \sum_{j=1}^n B(q_j).$$

Classical molecular dynamics in an extended phase space!

Properties of RPMD:

1. Exact in the limit as $t \to 0.^{b}$

2. Exact in the classical (high temperature) limit.[a]

3. Exact in the harmonic limit (for linear A and/or B).[a]

4. Correct time-reversal, time-translation, and detailed balance symmetries.[a]

[a] I. R. Craig and D. E. Manolopoulos, JCP 121, 3368 (2004).
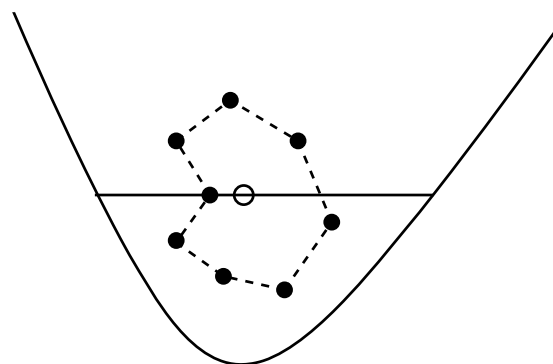[b] B. J. Braams and D. E. Manolopoulos, JCP 125, 124105 (2006).

In short, RPMD includes both:

tunneling   zero point energy

and
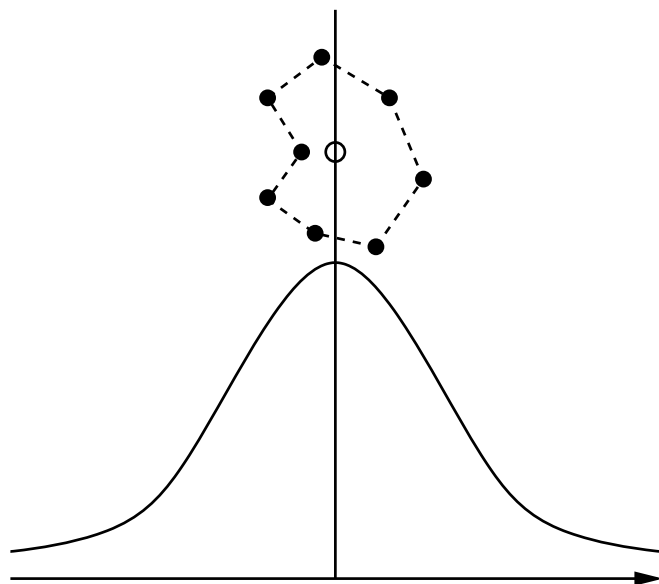
(exact QM rate coefficient   (exact QM $Z = e^{-\beta E_0}$
for a parabolic barrier)   in the low T limit)

But it neglects QM interference effects in the real-time dynamics (no $e^{-iHt/\hbar}$).

Applications of RPMD:

1. Quantum diffusion in liquid para-hydrogen (2005).

2. Quantum diffusion in liquid water (2005).

3. Neutron scattering from liquid para-hydrogen (2006).

4. Proton transfer in a polar solvent (2008).

5. Diffusion of H isotopes in water and ice (2008).

6. Dynamics of the solvated electron (2008).

7. Gas phase chemical reaction rates (2009).

8. Diffusion of H isotopes in transition metals (2009).

9. Competing quantum effects in liquid water (2009).

Quantum diffusion in liquid p-H$_2$:

25K

RPMD

$D_{\text{expt}} = 1.6$ Å^2/ps

Classical

D (Å^2/ps)

N$^{-1/3}$

T

F

G

L

S

ρ
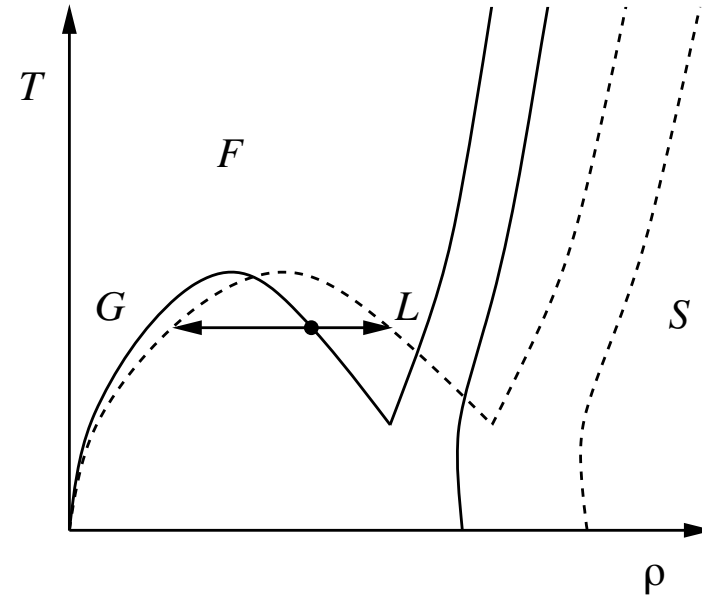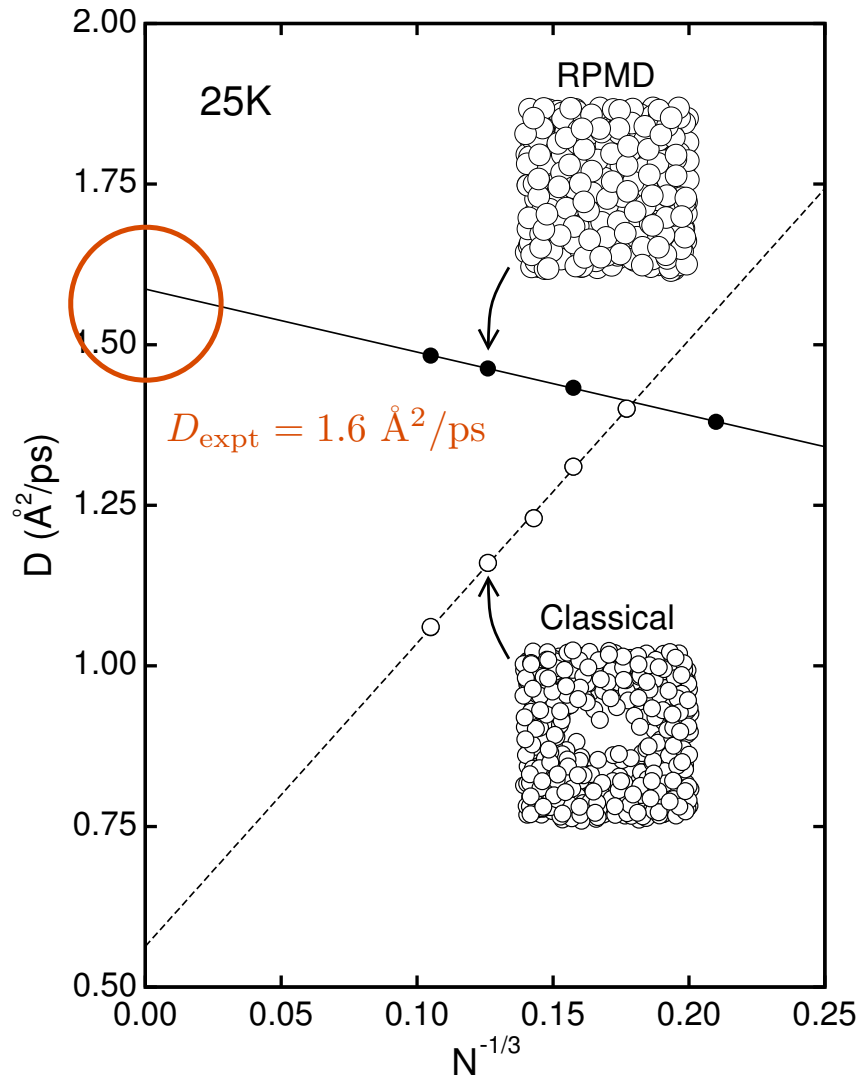
$$D = \frac{1}{3} \int_0^\infty \tilde{c}_{\mathbf{v}\cdot\mathbf{v}}(t)\, dt$$

$$D(L) = D(\infty) - \xi \frac{k_{\mathrm{B}} T}{6\pi\eta L} \, ^*$$

* B. Dünweg and K. Kremer, JCP 99, 6983 (1993).

I. Introduction

Classical AIMD simulations find water to be glassy at room temperature.

For example, Kühne *et al.*[*] have recently obtained D = 0.078 Å^2 ps^{-1} using the PBE functional, and similar results have been obtained with other XC functionals. The experimental diffusion coefficient is three times larger (0.230 Å^2 ps^{-1}).

[*] T. D. Kühne, M. Krack and M. Parrinello, JCTC 5, 235 (2009).

Three possible reasons:

1. DFT is not good enough.

2. System size effects are important.

3. Quantum effects are too large to ignore.

Previous quantum studies (typical examples):

Potential	N	Method	D_{cl}	D_{qm}	D_{qm}/D_{cl}
TIP4P[a]	256	CMD	0.36	0.55	1.53
SPC/E[b]	216	RPMD	0.24	0.34	1.42
SPC/F[c]	125	CMD	0.30	0.42	1.40
SPC/F[d]	216	RPMD	0.28	0.40	1.43

[a] L. Hernandez de la Pena and P. G. Kusalik, JCP 121, 5992 (2004).
[b] T. F. Miller and D. E. Manolopoulos, JCP 123, 154504 (2005).
[c] J. Lobaugh and G. A. Voth, JCP 106, 2400 (1996).
[d] T. E. Markland and D. E. Manolopoulos, JCP 129, 024105 (2008).

All previous quantum studies have found $D_{qm}/D_{cl} \geq 1.4$, regardless of the potential or quantum simulation method employed.

However, nearly all of these studies have used potentials parameterized on the basis of classical simulations, which give the wrong result when quantum effects are included (double counting).

E.g. - Results for the SPC/E model:
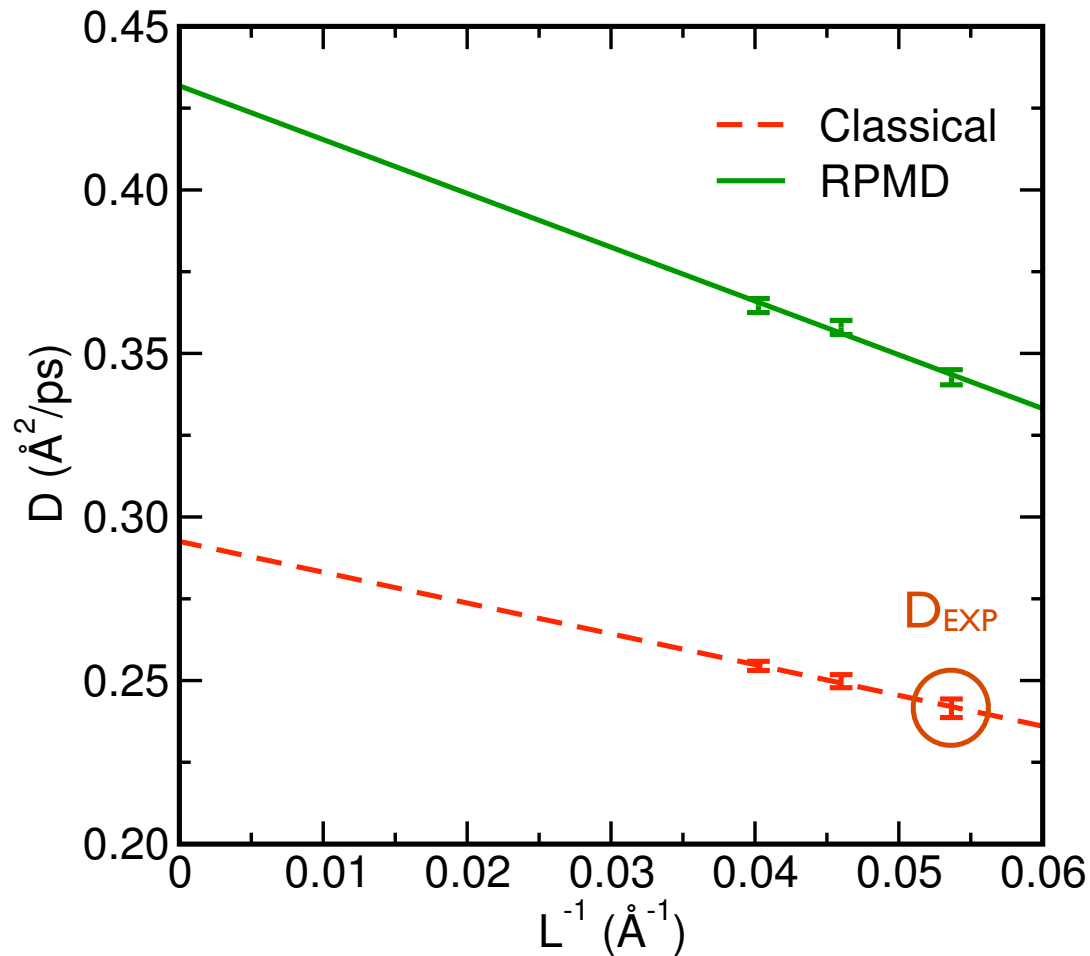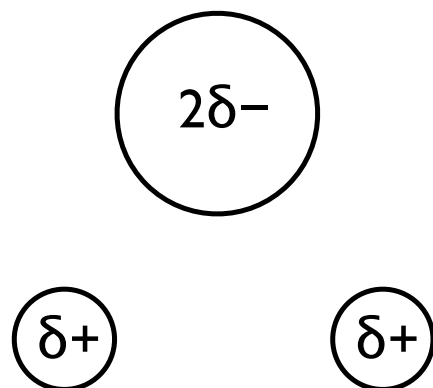

$$D(L) = D(\infty) - \xi\, k_B T / 6\pi\eta L$$

T. F. Miller and D. E. Manolopoulos, JCP 123, 154504 (2005).
B. Dünweg and K. Kremer, JCP 99, 6983 (1993).

2. Two quantum water models

q-SPC/Fw [a]

q-TIP4P/F [b,c]

$2\delta-$

$\delta+$ $\delta+$

$\delta+$ $2\delta-$ $\delta+$

$V_{OH}(r)$ = harmonic
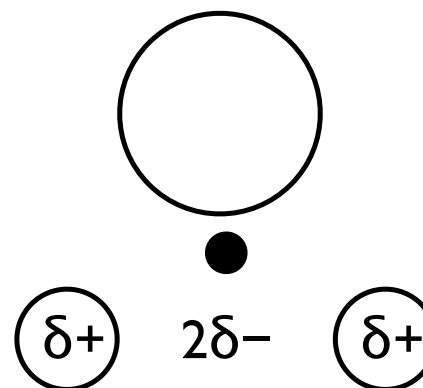
$V_{OH}(r)$ = quartic

[a] F. Paesani, W. Zhang, D. A. Case, T. E. Cheatham and G. A. Voth, , JCP 125, 184507 (2006).
[b] S. Habershon, T. E. Markland and D. E. Manolopoulos, JCP (2009).
[c] J. L. F. Abascal and C. Vega, JCP 123, 234505 (2005).
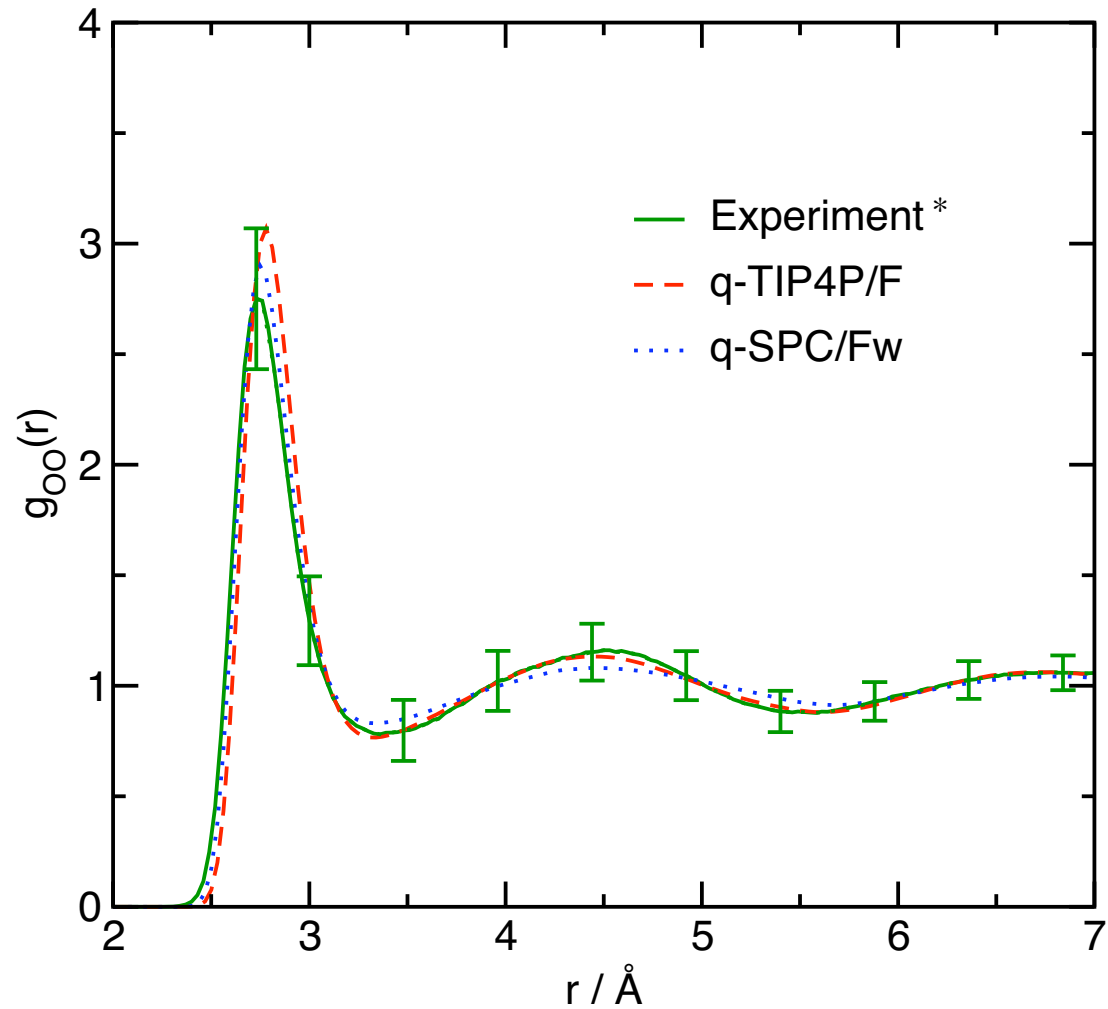
# PIMD radial distribution functions at 298 K and 0.997 g cm^{-3}

* A. K. Soper, CP 258, 121 (2000).

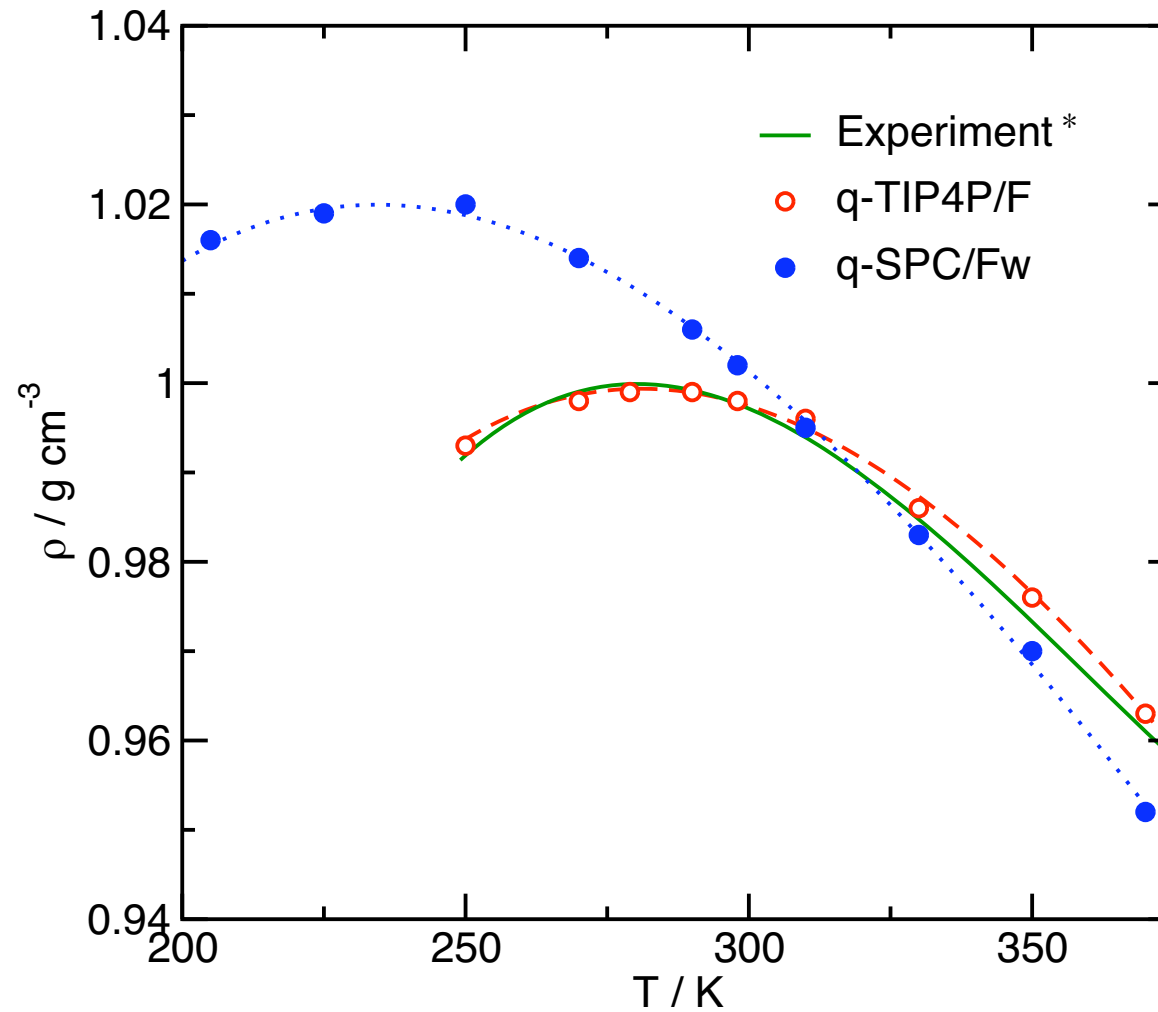PIMD radial distribution functions at 298 K and 0.997 g cm^{-3}

Legend:
- Experiment* (green solid)
- q-TIP4P/F (red dashed)
- q-SPC/Fw (blue dotted)

Axes: $g_{OH}(r)$ vs r / Å

* A. K. Soper, CP 258, 121 (2000).

PIMD radial distribution functions at 298 K and 0.997 g cm^{-3}

Legend:
- Experiment [*]
- q-TIP4P/F
- q-SPC/Fw

Axis labels: $g_{HH}(r)$ versus r / Å
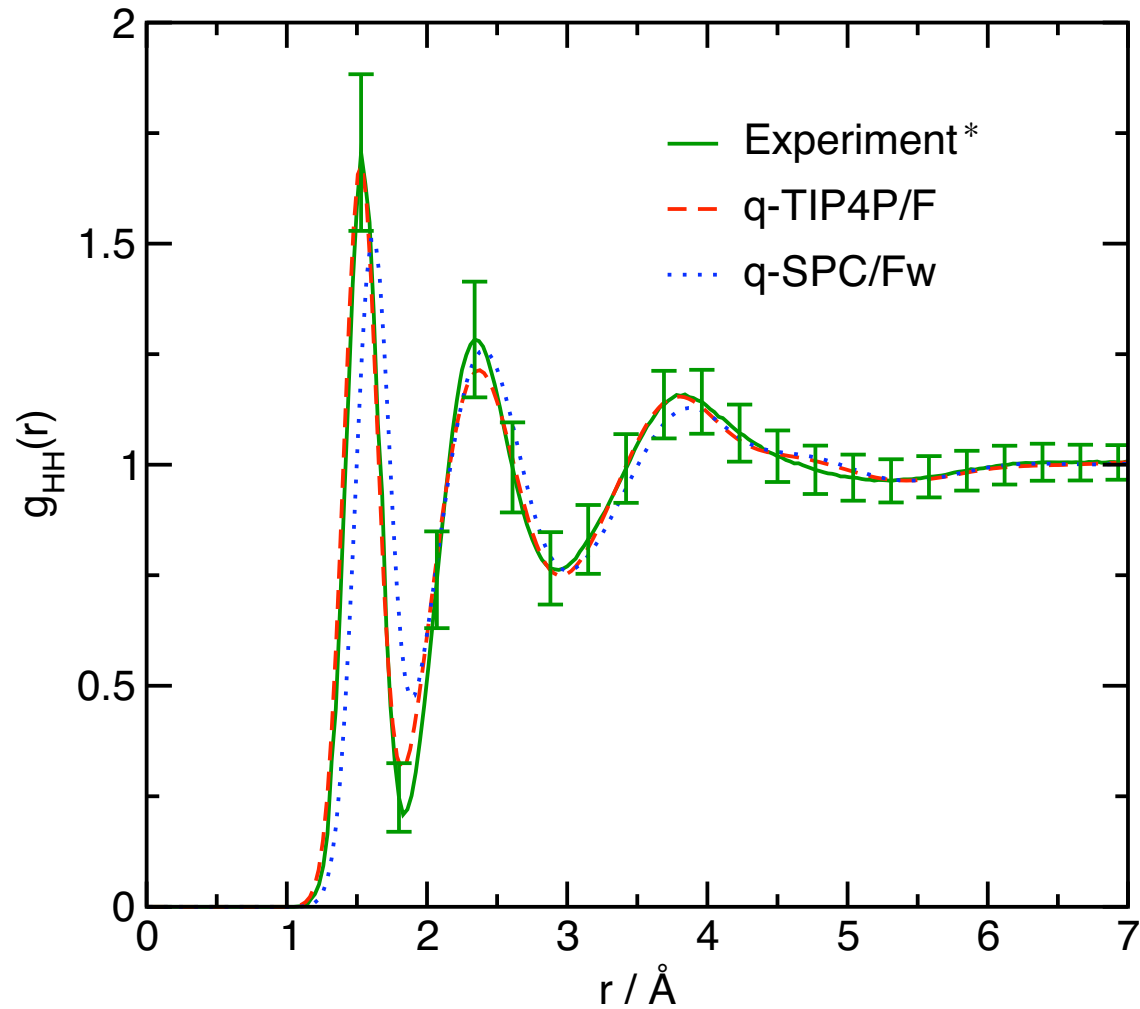
[*] A. K. Soper, CP 258, 121 (2000).

PIMD density curves at 1 atm:

*A. Saul and W. Wagner, JPC Ref Data 18, 1537 (1989).

Other static equilibrium properties:

| Property[a]	q-SPC/Fw	q-TIP4P/F	Expt
$\langle \mu \rangle$ / D	2.465(1)	2.348(1)	
ε_r	90(3)	60(3)	78.4
$\langle Q_T \rangle$ / DÅ	2.009(1)	2.403(1)	
T_m / K	195(5)	251(1)	273

[a] Q_T is the molecular tetrahedral quadrupole moment $Q_T = [Q_{xx} - Q_{yy}]/2$, where the *x* axis is between the hydrogen atoms and the *y* axis is normal to the molecular plane.
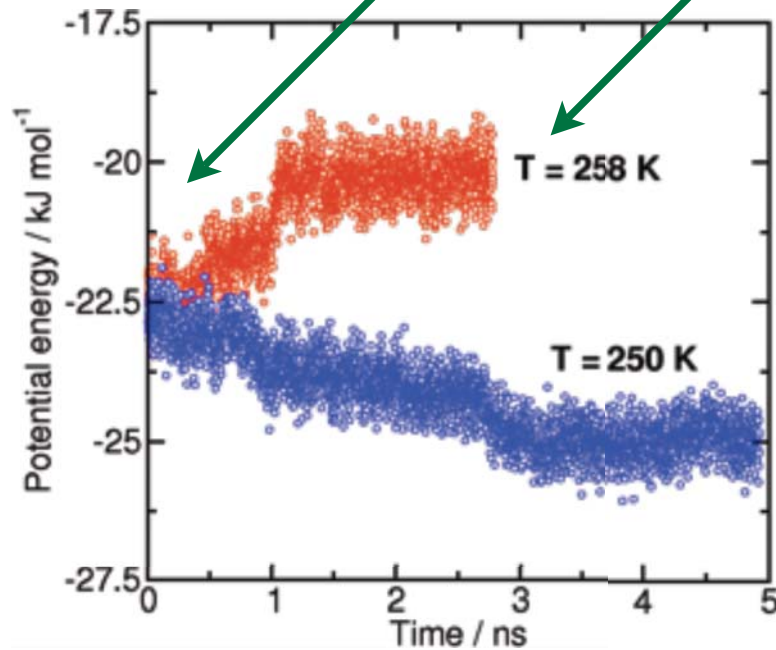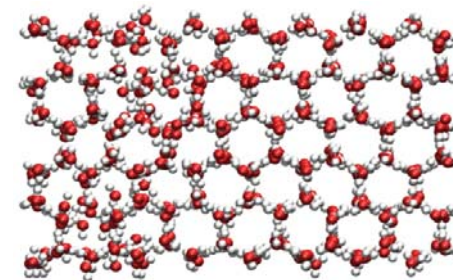
Melting point simulations: [a,b]

Initial configuration
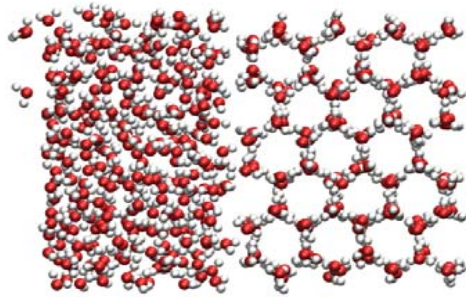
Completely melted

Completely frozen

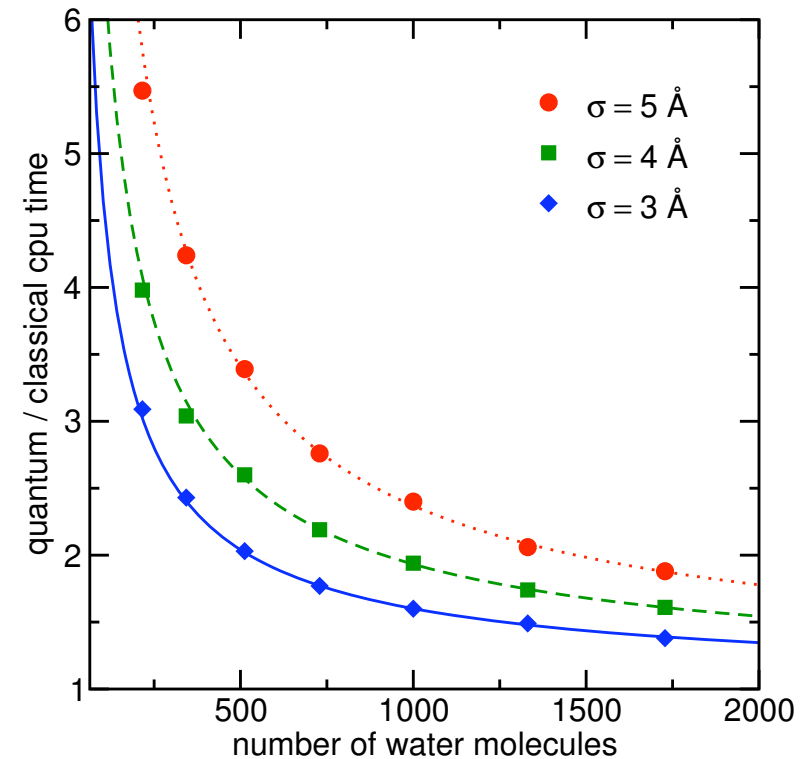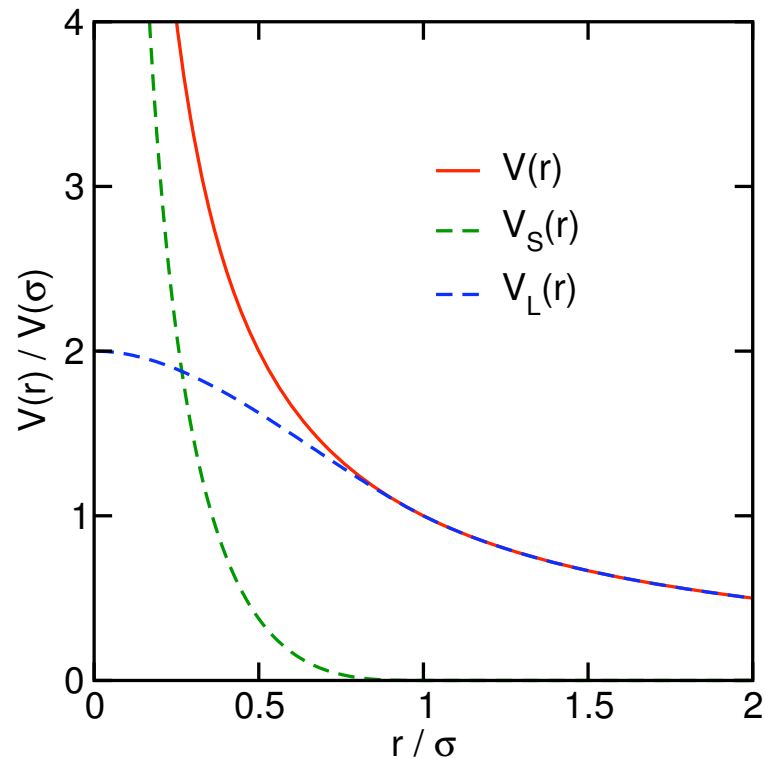Potential energy / kJ mol^{-1} vs Time / ns

T = 258 K

T = 250 K
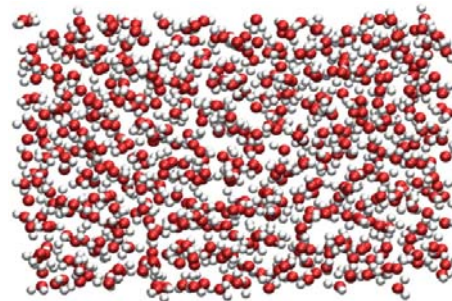
[a] T. Bryk and A. D. J. Haymet, JCP 117, 10258 (2002),
[b] R. G. Fernandez and C. Vega, JCP 124, 144506 (2006).

Ring polymer contraction: [a,b]

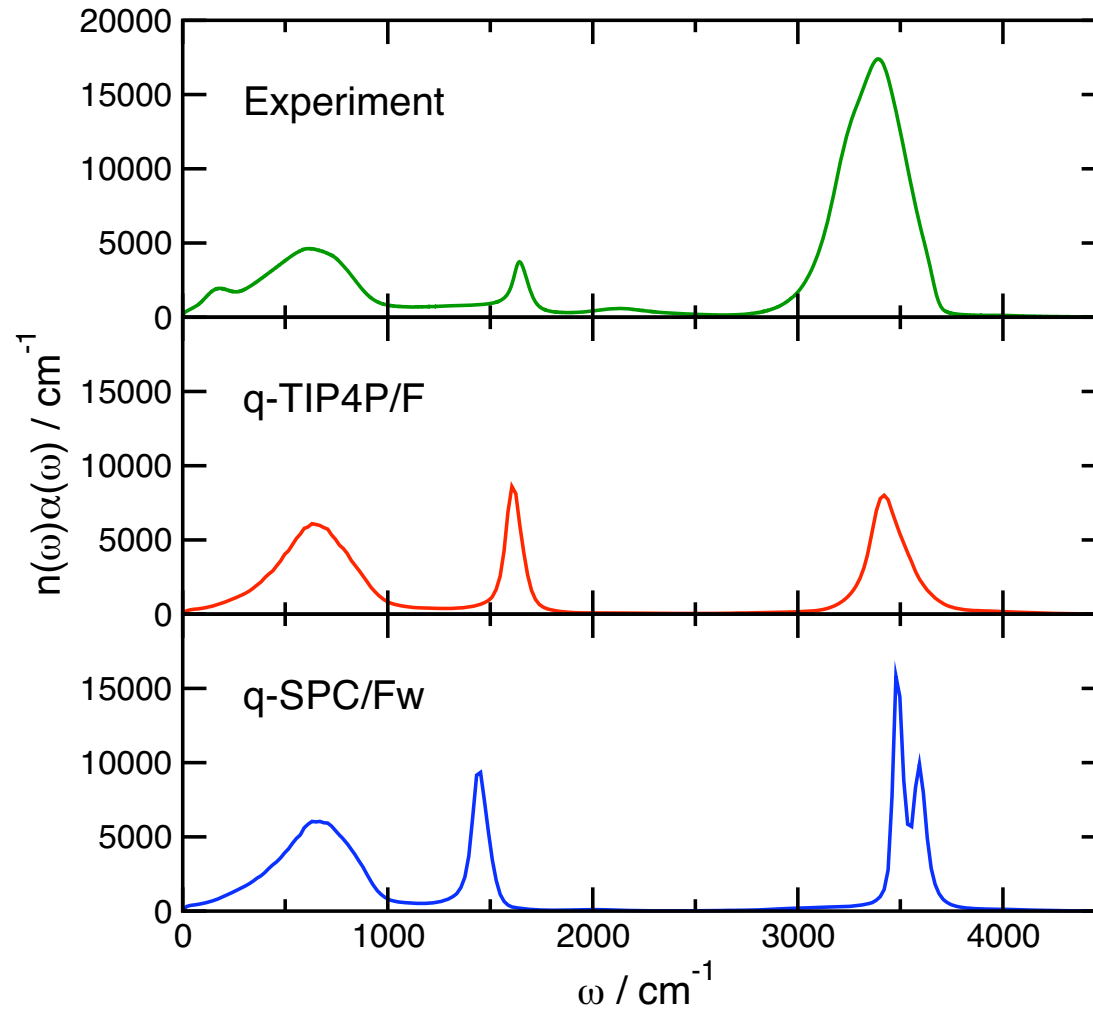$$\sum_{k=1}^{n} V(r_{ij}^{(k)}) \simeq \sum_{k=1}^{n} V_S(r_{ij}^{k}) + nV_L(r_{ij}^{(c)}), \qquad \mathbf{r}_i^{(c)} = \frac{1}{n}\sum_{k=1}^{n}\mathbf{r}_i^{(k)}.$$

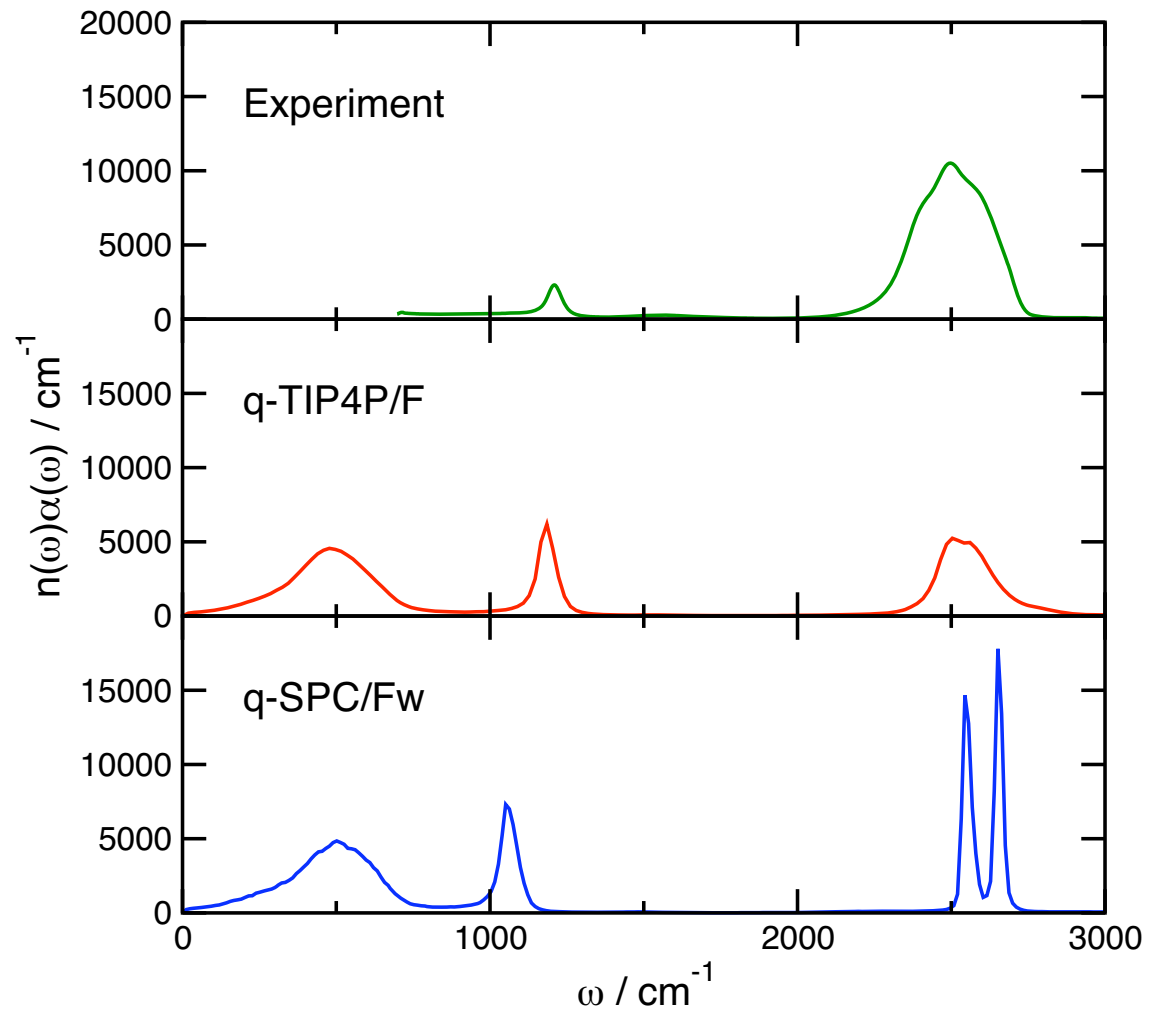[a] T. E. Markland and D. E. Manolopoulos, JCP 129, 074501 (2008),
[b] T. E. Markland and D. E. Manolopoulos, CPL 464, 256 (2008).

CMD dipole absorption spectra at 298 K (H_2O):

[*] J. E. Bertie and Z. Lan, Appl. Spectrosc. 50, 1047 (1996).

CMD dipole absorption spectra at 298 K (D$_2$O):

*J. E. Bertie, M. K. Ahmed and H. H. Eysel, JPC 93, 2210 (1989).

Other dynamical properties:

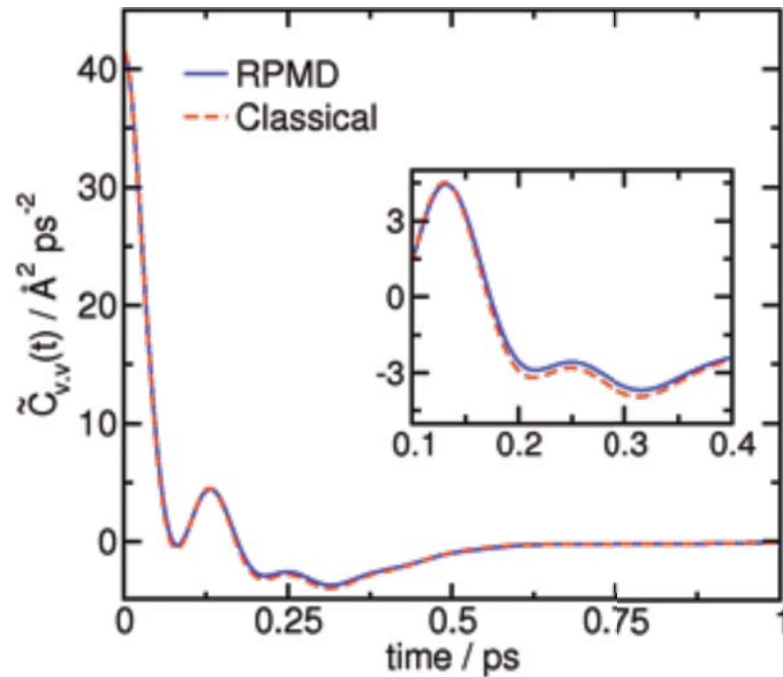| Property	q-SPC/Fw	q-TIP4P/F	Expt
D_{H_2O} / Å^2 ps^{-1}	0.24(1)	0.221(1)	0.230[a,b]
D_{D_2O} / Å^2 ps^{-1}		0.172(1)	0.177[a,b]
D_{H_2O} / D_{D_2O}		1.28	1.30[a,b]
$\tau_2(HH)$ / ps	1.85(5)	2.22(2)	1.6-2.5[c]
$\tau_2(OH)$ / ps	1.70(5)	1.90(2)	1.95[c]
$\tau_2(\mu)$ / ps	1.60(5)	1.52(1)	1.90[c]

[a] W. S. Price, H. Ide and Y. Arata, JPCA 103, 448 (1999).
[b] W. S. Price, H. Ide and Y. Arata, JPCB 104, 5874 (2000).
[c] Various.

3. Competing quantum effects

q-TIP4P/F

$D_{qm} = 0.221(1)$ $D_{cl} = 0.199(2)$

$D_{qm}/D_{cl} = 1.1$

q-TIP4P/F

	τ_{cl} / ps	τ_{qm} / ps	τ_{cl} / τ_{qm}
$\tau_1(HH)$	6.3(1)	5.40(4)	1.17
$\tau_1(OH)$	6.0(1)	5.10(4)	1.18
$\tau_1(\mu)$	5.48(7)	4.64(3)	1.18
$\tau_2(HH)$	2.72(4)	2.22(2)	1.23
$\tau_2(OH)$	2.38(4)	1.90(2)	1.25
$\tau_2(\mu)$	1.92(3)	1.52(1)	1.26

Why such a small quantum effect?

	Classical	PIMD
$\langle r_{OH} \rangle$ / Å	0.963(1)	0.978(1)
$\langle \mu \rangle$ / D	2.311(1)	2.348(1)

A recent *ab initio* PIMD study of liquid water has also found that $\langle\mu\rangle_{qm} > \langle\mu\rangle_{cl}$,[a] and a recent experimental study has found that $\langle r_{OH}\rangle$ in H_2O is larger than $\langle r_{OD}\rangle$ in D_2O.[b]

[a] B. Chen, I. Ivanov, M. L. Klein and M. Parrinello, PRL 91, 215503 (2003).
[b] A. K. Soper and C. J. Benmore, PRL 101, 065502 (2008).

So:

Intramolecular quantum fluctuations (ZPE in the O-H stretch) increase $<\mu>$, strengthen the intermolecular interactions, and slow down the diffusion.

Whereas intermolecular quantum fluctuations (ZPE in the H······O stretch) disrupt the H-bonding network and speed up the diffusion.

The net result is a very small overall quantum effect in the diffusion coefficient ($D_{qm}/D_{cl} \sim 1.1$) and orientational relaxation ($\tau_{cl}/\tau_{qm} \sim 1.2$).

Check:

Confining the q-TIP4P/F water molecules to their equilibrium geometry "turns off" the intramolecular quantum effect and gives

$D_{cl} = 0.308(3)$ Å^2 ps^{-1}

$D_{qm} = 0.440(2)$ Å^2 ps^{-1}

$D_{qm} / D_{cl} = 1.43$

in agreement with the results obtained for rigid body water models and flexible models with harmonic O-H potentials.

4. Conclusions

1. DFT is not good enough.   √

2. System size effects are important.   √

3. Quantum effects are too large to ignore.   ?