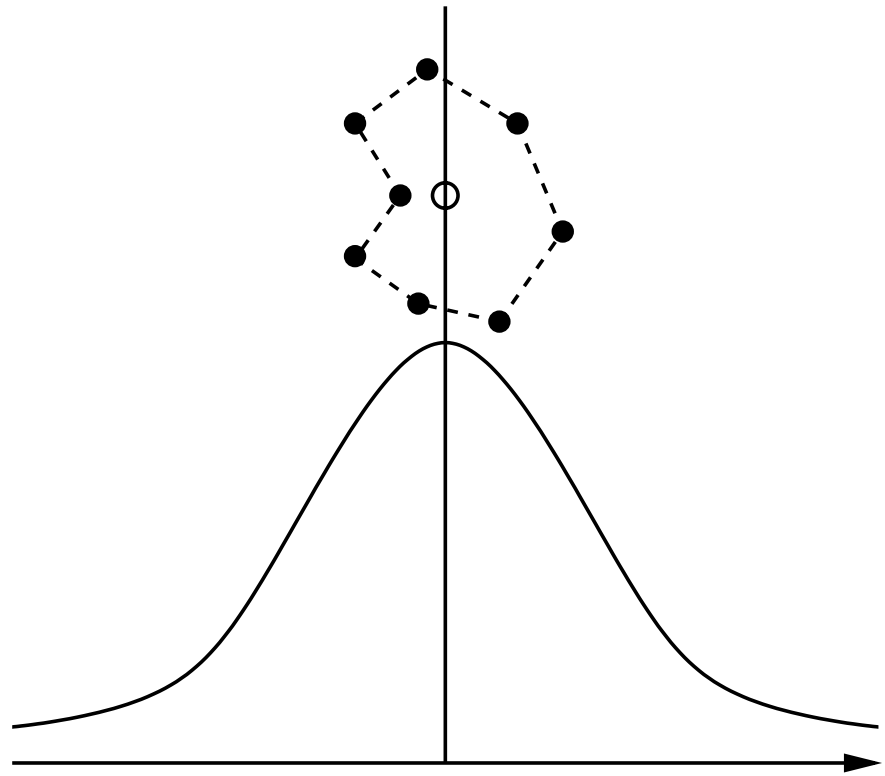
Ring polymer molecular dynamics



David Manolopoulos

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Outline

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Quantum mechanical correlation functions

Many dynamical observables can be related to real-time correlation functions of the form

$$c_{AB}(t) = \frac{1}{Z}\mathrm{tr}\left[e^{-\beta H}A(0)B(t)\right],$$

where

$$Z = \mathrm{tr}\left[e^{-\beta H}\right],$$

and

$$B(t) = e^{+iHt/\hbar}Be^{-iHt/\hbar}.$$

For example, diffusion coefficients are given by

$$D(T) = \frac{1}{3}\int_0^\infty c_{\mathbf{v}\cdot\mathbf{v}}(t)\,dt,$$

chemical reaction rate coefficients by

$$k(T) = \frac{1}{Q_r(T)}\int_0^\infty c_{ff}(t)\,dt,$$

and dipole absorption spectra by

$$n(\omega)\alpha(\omega) = \frac{\pi\omega}{3\hbar c V\epsilon_0}(1 - e^{-\beta\hbar\omega})C_{\mu\cdot\mu}(\omega),$$

where

$$C_{\mu\cdot\mu}(\omega) = \frac{1}{2\pi}\int_{-\infty}^\infty e^{-i\omega t}c_{\mu\cdot\mu}(t)\,dt.$$

The standard real-time correlation function is

$$c_{AB}(t) = \frac{1}{Z}\mathrm{tr}\left[e^{-\beta H}A(0)B(t)\right],$$

whereas the *Kubo-transformed* correlation function is

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

There are several reasons why $\tilde{c}_{AB}(t)$ is the more classical of the two objects – and it is $\tilde{c}_{AB}(t)$ that is approximated in RPMD.

If

$$C_{AB}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} c_{AB}(t)\, dt,$$

and

$$\tilde{C}_{AB}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \tilde{c}_{AB}(t)\, dt,$$

then it is straightforward to show by working in the basis of energy eigenstates that

$$C_{AB}(\omega) = D(\omega)\tilde{C}_{AB}(\omega),$$

where

$$D(\omega) = \frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}}.$$

Proof:

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

$$= \frac{1}{Z\beta}\int_0^\beta d\lambda \sum_{kl} e^{-(\beta-\lambda)E_k} A_{kl} e^{-\lambda E_l} e^{+iE_l t/\hbar} B_{lk} e^{-iE_k t/\hbar}$$

$$= \frac{1}{Z\beta}\int_0^\beta d\lambda \sum_{kl} A_{kl} B_{lk} e^{-\beta E_k} e^{-\lambda(E_l-E_k)} e^{+i(E_l-E_k)t/\hbar}$$

$$\therefore \tilde{C}_{AB}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}\tilde{c}_{AB}(t)\, dt$$

$$= \frac{1}{Z\beta}\int_0^\beta d\lambda \sum_{kl} A_{kl} B_{lk} e^{-\beta E_k} e^{-\lambda(E_l-E_k)} \delta(\omega - [E_l - E_k]/\hbar)$$

$$= \frac{1}{\beta}\int_0^\beta e^{-\lambda\hbar\omega}\, d\lambda \times \frac{1}{Z}\sum_{kl} A_{kl} B_{lk} e^{-\beta E_k} \delta(\omega - [E_l - E_k]/\hbar)$$

$$= \frac{(1-e^{-\beta\hbar\omega})}{\beta\hbar\omega} \times C_{AB}(\omega).$$

It follows from this that dynamical observables can be written equally well in terms of $\tilde{c}_{AB}(t)$.

For example:

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

$$k(T) = \frac{1}{Q_r(T)}\int_0^\infty \tilde{c}_{ff}(t)\,dt,$$

and

$$n(\omega)\alpha(\omega) = \frac{\pi\beta\omega^2}{3cV\epsilon_0}\tilde{C}_{\mu\cdot\mu}(\omega),$$

where

$$\tilde{C}_{\mu\cdot\mu}(\omega) = \frac{1}{2\pi}\int_{-\infty}^\infty e^{-i\omega t}\tilde{c}_{\mu\cdot\mu}(t)\,dt.$$

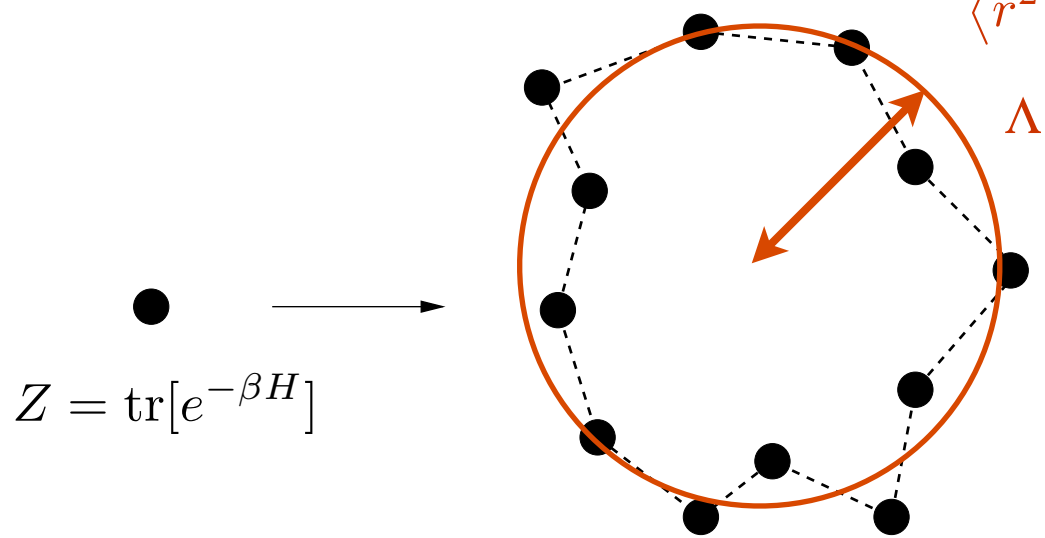
Notice that none of these equations involves $\hbar$!

Ring polymer molecular dynamics

Based on the classical isomorphism:

$$\langle r^2 \rangle^{1/2} = \Lambda(T)/\sqrt{8\pi}$$

$$\Lambda(T) = h/\sqrt{2\pi mkT}$$



$$Z = \mathrm{tr}[e^{-\beta H}]$$

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

where

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

Proof (as in earlier lectures):

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

So

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

with

$$\begin{aligned}
\left\langle q\right| e^{-\beta_n H} \left|q'\right\rangle &\simeq \left\langle q\right| e^{-\beta_n V/2} e^{-\beta_n T} e^{-\beta_n V/2} \left|q'\right\rangle \\
&= \frac{1}{2\pi\hbar} \int dp\, e^{-\beta_n p^2/2m + ip(q-q')/\hbar - \beta_n [V(q)/2 + V(q')/2]} \\
&= \frac{1}{2\pi\hbar} \left(\frac{2\pi m}{\beta_n}\right)^{1/2} e^{-\beta_n [m\omega_n^2 (q-q')^2 + V(q)/2 + V(q')/2]} \\
&\equiv \frac{1}{2\pi\hbar} \int dp\; e^{-\beta_n \left[p^2/2m + m\omega_n^2 (q-q')^2/2 + V(q)/2 + V(q')/2\right]},
\end{aligned}$$

gives Z with an error of $O(n^{-2})$.

Path integral molecular dynamics:

PIMD uses the ring polymer trajectories

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

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

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

Ring polymer molecular dynamics:

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

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

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

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

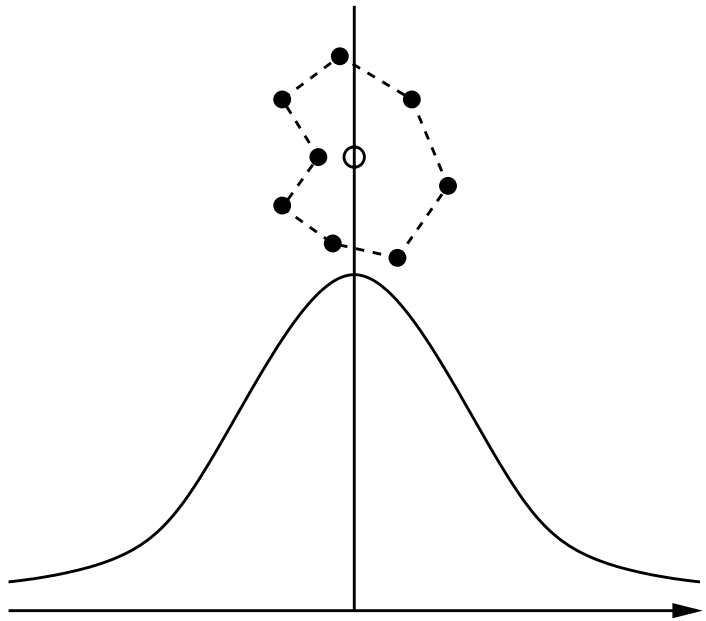
where

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

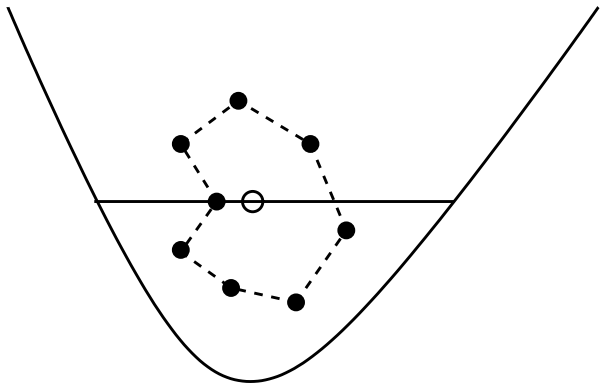
Classical molecular dynamics in an extended phase space!

In short, the RPMD approximation includes both:

tunneling and



zero point energy



But it neglects QM interference effects in the real-time dynamics.

One can show that RPMD is:

1. Exact in the high temperature limit
2. Exact in the short time limit
3. Exact in the harmonic limit (for linear A or B)
4. Exact for $A = 1$ (the unit operator)
5. Faithful to all QM symmetries
6. Consistent with the QM equilibrium distribution

Eg: when $A = 1$, we have

$$\begin{aligned}
\tilde{c}_{1B}(t) &= \frac{1}{\beta Z}\int_0^\beta d\lambda \,\mathrm{tr}\left[e^{-(\beta-\lambda)H}1\, e^{-\lambda H}B(t)\right] \\
&= \frac{1}{\beta Z}\int_0^\beta d\lambda \,\mathrm{tr}\left[e^{-\beta H}B(t)\right] \\
&= \frac{1}{Z}\mathrm{tr}\left[e^{-\beta H}B(t)\right] \\
&= \frac{1}{Z}\mathrm{tr}\left[e^{-\beta H}e^{+iHt/\hbar}Be^{-iHt/\hbar}\right] \\
&= \frac{1}{Z}\mathrm{tr}\left[e^{-iHt/\hbar}e^{-\beta H}e^{+iHt/\hbar}B\right] \\
&= \frac{1}{Z}\mathrm{tr}\left[e^{-\beta H}B\right] \equiv \langle B\rangle\,,
\end{aligned}$$

And in RPMD,

$$
\begin{aligned}
\tilde{c}_{1B}(t) &= \frac{1}{(2\pi\hbar)^n Z} \int d\mathrm{p}_0 \int d\mathrm{q}_0 \, e^{-\beta_n H_n(\mathrm{p}_0,\mathrm{q}_0)} \, B_n(\mathrm{q}_t) \\
&= \frac{1}{(2\pi\hbar)^n Z} \int d\mathrm{p}_t \int d\mathrm{q}_t \, e^{-\beta_n H_n(\mathrm{p}_0,\mathrm{q}_0)} \, B_n(\mathrm{q}_t) \\
&= \frac{1}{(2\pi\hbar)^n Z} \int d\mathrm{p}_t \int d\mathrm{q}_t \, e^{-\beta_n H_n(\mathrm{p}_t,\mathrm{q}_t)} \, B_n(\mathrm{q}_t) \\
&= \frac{1}{(2\pi\hbar)^n Z} \int d\mathrm{p}_0 \int d\mathrm{q}_0 \, e^{-\beta_n H_n(\mathrm{p}_0,\mathrm{q}_0)} \, B_n(\mathrm{q}_0) \\
&\equiv \langle B \rangle \,,
\end{aligned}
$$

where we have used Liouville's theorem and the conservation of $H_n(\mathrm{p}_t, \mathrm{q}_t)$.

Non-local operators

So far we have only considered local operators. But (e.g.),

$$\begin{aligned}
\frac{d^2}{dt^2}\mathrm{tr}\left[e^{-\beta H}\,q\,e^{+iHt/\hbar}q\,e^{-iHt/\hbar}\right] &= \frac{d}{dt}\mathrm{tr}\left[e^{-\beta H}\,q\,e^{+iHt/\hbar}\,\frac{i}{\hbar}\,[H,q]\,e^{-iHt/\hbar}\right] \\
&= \frac{d}{dt}\mathrm{tr}\left[e^{-\beta H}\,q\,e^{+iHt/\hbar}v\,e^{-iHt/\hbar}\right] \\
&= \frac{d}{dt}\mathrm{tr}\left[e^{-\beta H}\,e^{-iHt/\hbar}q\,e^{+iHt/\hbar}v\right] \\
&= -\mathrm{tr}\left[e^{-\beta H}\,e^{-iHt/\hbar}\,\frac{i}{\hbar}\,[H,q]\;e^{+iHt/\hbar}v\right] \\
&= -\mathrm{tr}\left[e^{-\beta H}\,e^{-iHt/\hbar}v\,e^{+iHt/\hbar}v\right] \\
&= -\mathrm{tr}\left[e^{-\beta H}\,v\,e^{+iHt/\hbar}v\,e^{-iHt/\hbar}\right],
\end{aligned}$$

$$\therefore\; c_{vv}(t) = -\frac{d^2}{dt^2}c_{qq}(t) \text{ and (similarly) } \tilde{c}_{vv}(t) = -\frac{d^2}{dt^2}\tilde{c}_{qq}(t).$$

So in RPMD,

$$\begin{aligned}
\tilde{c}_{vv}(t) = -\frac{d^2}{dt^2}\tilde{c}_{qq}(t) &\sim -\frac{d^2}{dt^2}\int d\mathrm{p}_0 \int d\mathrm{q}_0\, e^{-\beta_n H_n(\mathrm{p}_0,\mathrm{q}_0)}\, \overline{q}_0 \overline{q}_t \\
&\sim -\frac{d}{dt}\int d\mathrm{p}_0 \int d\mathrm{q}_0\, e^{-\beta_n H_n(\mathrm{p}_0,\mathrm{q}_0)}\, \overline{q}_0 \overline{v}_t \\
&\sim -\frac{d}{dt}\int d\mathrm{p}_t \int d\mathrm{q}_t\, e^{-\beta_n H_n(\mathrm{p}_t,\mathrm{q}_t)}\, \overline{q}_0 \overline{v}_t \\
&\sim -\frac{d}{dt}\int d\mathrm{p}_0 \int d\mathrm{q}_0\, e^{-\beta_n H_n(\mathrm{p}_0,\mathrm{q}_0)}\, \overline{q}_{-t} \overline{v}_0 \\
&\sim \int d\mathrm{p}_0 \int d\mathrm{q}_0\, e^{-\beta_n H_n(\mathrm{p}_0,\mathrm{q}_0)}\, \overline{v}_{-t} \overline{v}_0 \\
&\sim \int d\mathrm{p}_t \int d\mathrm{q}_t\, e^{-\beta_n H_n(\mathrm{p}_t,\mathrm{q}_t)}\, \overline{v}_0 \overline{v}_t \\
&\sim \int d\mathrm{p}_0 \int d\mathrm{q}_0\, e^{-\beta_n H_n(\mathrm{p}_0,\mathrm{q}_0)}\, \overline{v}_0 \overline{v}_t,
\end{aligned}$$

$$\text{where } \overline{q} = \frac{1}{n}\sum_{j=1}^{n} q_j \text{ and } \overline{v} = \dot{\overline{q}} = \frac{1}{n}\sum_{j=1}^{n} \frac{p_j}{m}.$$

The same argument applies to correlation functions involving other non-local operators.

E.g., chemical reaction rate coefficients can be calculated from

$$Q_r(T)k(T) = \int_0^\infty \tilde{c}_{ff}(t)\,dt = \lim_{t\to\infty} \tilde{c}_{fs}(t) = -\lim_{t\to\infty} \frac{d}{dt}\tilde{c}_{ss}(t),$$

where

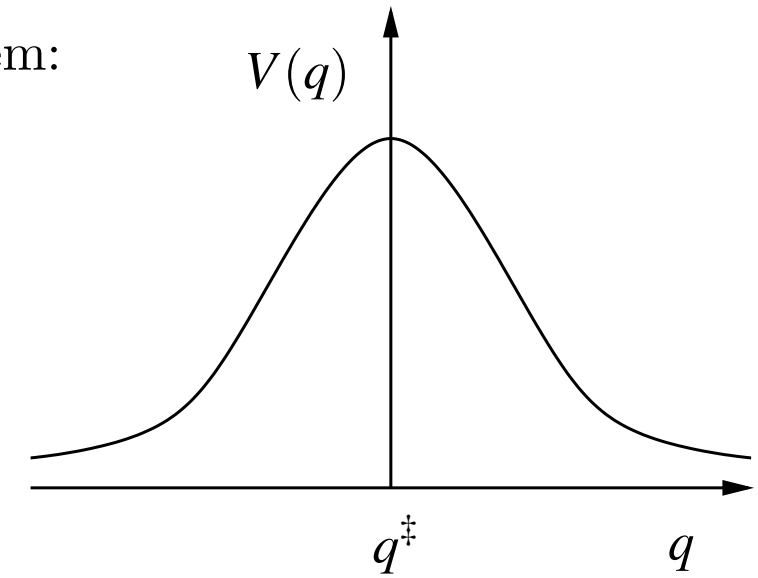
$$\tilde{c}_{ff}(t) = \frac{d}{dt}\tilde{c}_{fs}(t) = -\frac{d^2}{dt^2}\tilde{c}_{ss}(t),$$

both in QM and in RPMD.

Which brings me on to...

Ring polymer reaction rate theory

Consider a simple 1d barrier transmission problem:



The exact QM rate coefficient is

$$k(T) = \frac{1}{Q_r(T)} \lim_{t\to\infty} \tilde{c}_{fs}(t)$$

where

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

with

$$F = \frac{i}{\hbar}[H,h] \quad \text{and} \quad h = h(q - q^{\ddagger}).$$

(Flux) (Side)

NB:

1. $k(T)$ is independent of $q^{\ddagger}$.
2. $\tilde{c}_{fs}(t \to 0_+) \sim at^{1/2} \sim 0$.

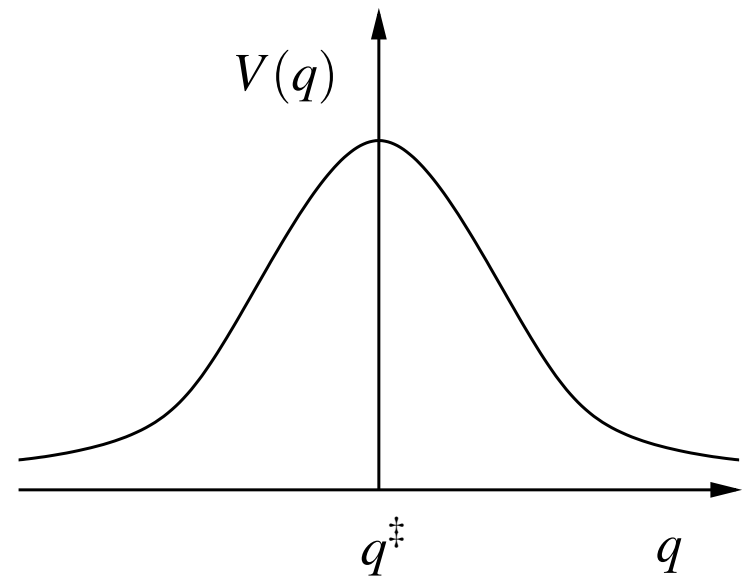
The classical limit:

The classical limit rate coefficient is

$$k^{cl}(T) = \frac{1}{Q_r(T)} \lim_{t\to\infty} c_{fs}^{cl}(t)$$

where

$$c_{fs}^{cl}(t) = \frac{1}{2\pi\hbar} \int dp_0 \int dq_0 \, e^{-\beta H(p_0,q_0)} \times \underbrace{\delta(q_0 - q^{\ddagger}) \frac{p_0}{m}}_{\text{Flux } (t=0)} \times \underbrace{h(q_t - q^{\ddagger})}_{\text{Side } (t>0)}.$$

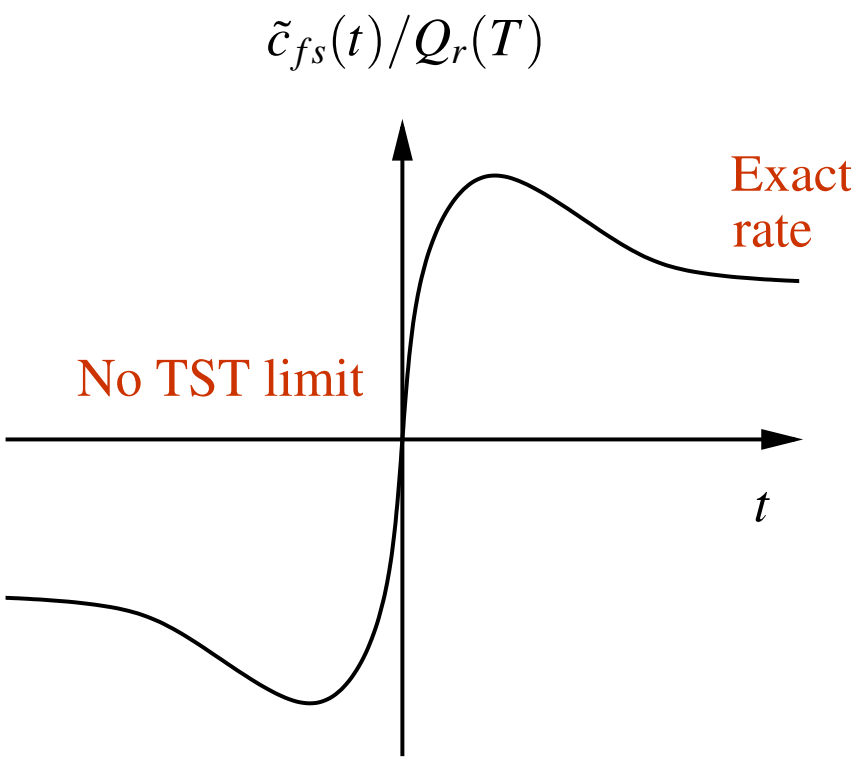


NB:

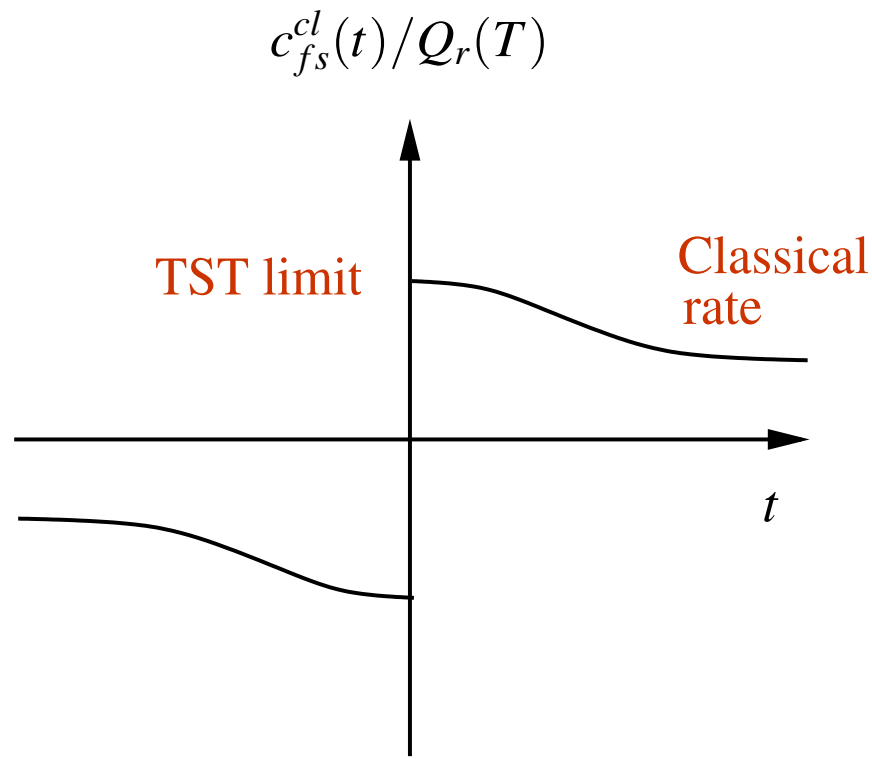
1. $k^{cl}(T)$ is independent of $q^{\ddagger}$.
2. As $t \to 0_+$, $h(q_t - q^{\ddagger}) \to h(p_0)$, giving

$$k^{cl,TST}(T) = c_{fs}^{cl}(t \to 0_+)/Q_r(T) = \frac{1}{2} \langle |\dot{q}| \rangle_{cl} \, e^{-\beta V(q^{\ddagger})}.$$

Quantum



Classical



$$k^{cl,TST}(T) = \frac{1}{2}\,\langle|\dot{q}|\rangle_{cl}\, e^{-\beta V(q^{\ddagger})}$$

"Quantum transition state theory":

The centroid density QTST rate is

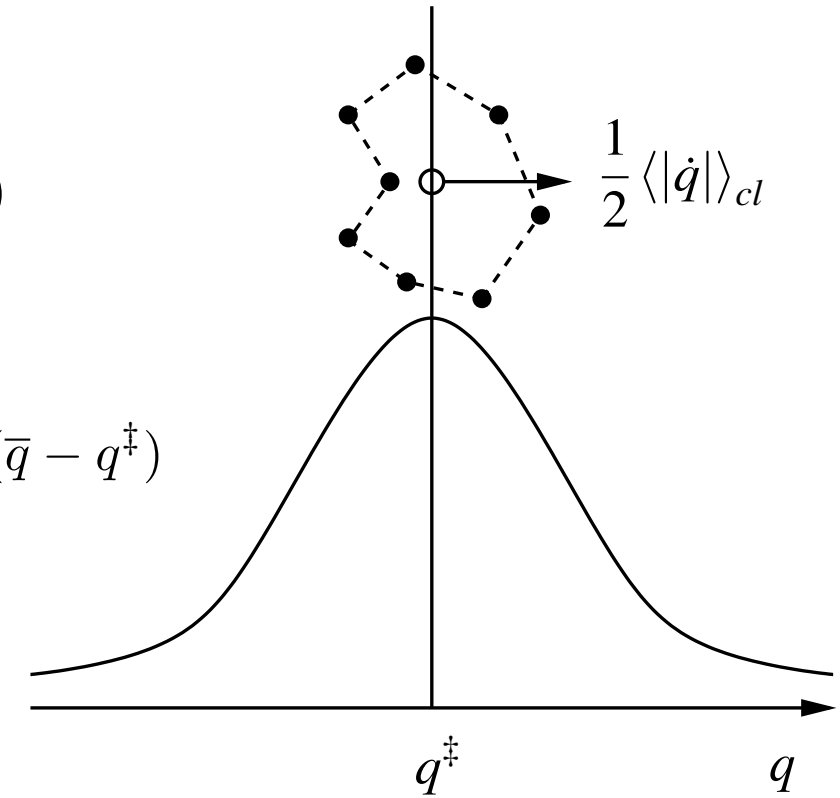
$$k^{\mathrm{QTST}}(T) = \frac{1}{2}\,\langle|\dot{q}|\rangle_{cl}\,Q(q^{\ddagger})/Q_r(T)$$

where

$$Q(q^{\ddagger}) = \frac{1}{(2\pi\hbar)^n}\int d\mathrm{p}\int d\mathrm{q}\, e^{-\beta_n H_n(\mathrm{p},\mathrm{q})}\delta(\overline{q}-q^{\ddagger})$$

with

$$\overline{q} = \frac{1}{n}\sum_{j=1}^{n} q_j\,.$$



NB:

1. $e^{-\beta V(q^{\ddagger})} \rightarrow Q(q^{\ddagger})/Q_r(T)$ includes (some) QM tunneling (good).
2. However, $k^{QTST}(T)$ is *exponentially* sensitive to $q^{\ddagger}$ (bad).

Ring polymer reaction rate theory:

The RPMD rate coefficient is

$$k^{\mathrm{RPMD}}(T) = \frac{1}{Q_r(T)} \lim_{t\to\infty} \bar{c}_{fs}(t)$$

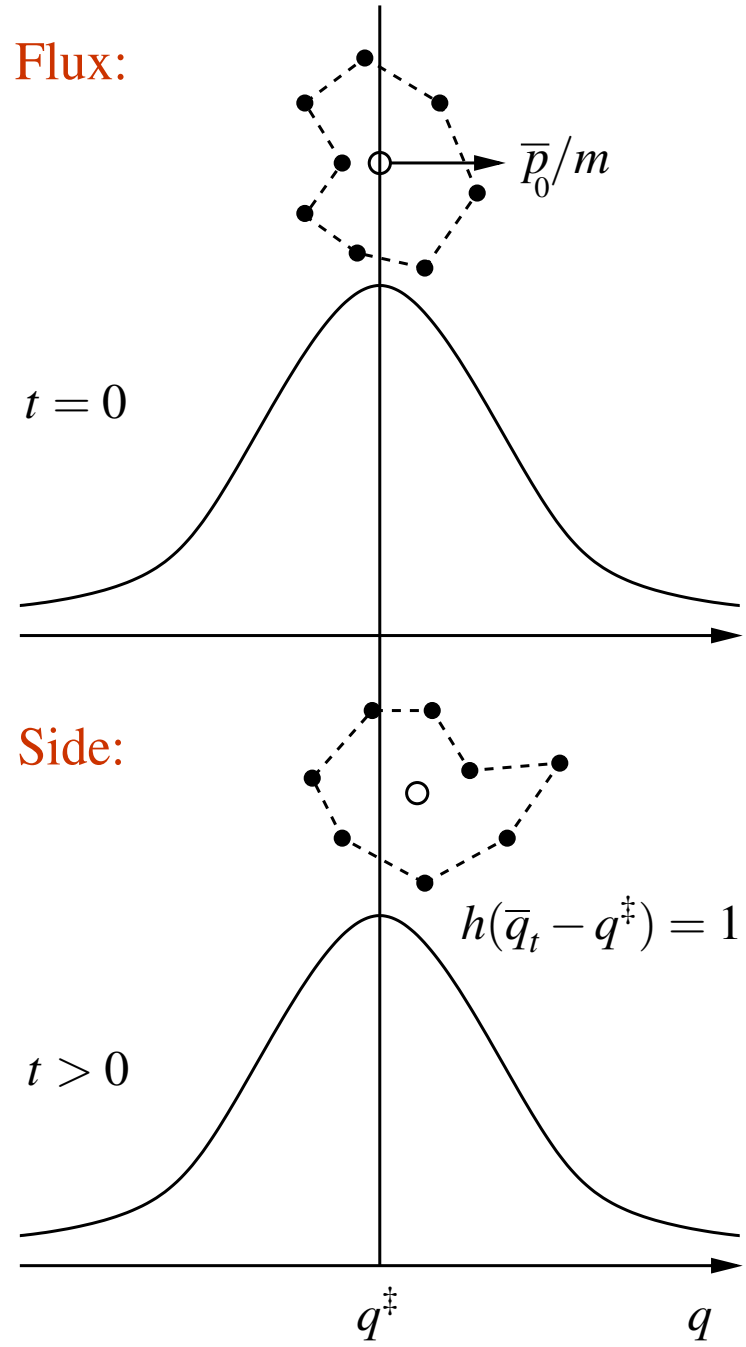
where

$$\bar{c}_{fs}(t) = \frac{1}{(2\pi\hbar)^n} \int d\mathrm{p}_0 \int d\mathrm{q}_0 \; e^{-\beta_n H_n(\mathrm{p}_0,\mathrm{q}_0)}$$

$$\times \delta(\bar{q}_0 - q^{\ddagger}) \frac{\bar{p}_0}{m} h(\bar{q}_t - q^{\ddagger})$$

with

$$\bar{q} = \frac{1}{n}\sum_{j=1}^{n} q_j, \quad \bar{p} = \frac{1}{n}\sum_{j=1}^{n} p_j.$$



$k^{\mathrm{RPMD}}(T)$ is...

1. Simple to compute
2. Exact in the high temperature limit
3. Exact for a parabolic barrier
4. Equal to $k^{\mathrm{QTST}}(T)$ in the limit as $t \to 0_+$
5. Bounded from above by $k^{\mathrm{QTST}}(T)$
6. *Independent of* $q^{\ddagger}$

...so $k^{\mathrm{RPMD}}(T)$ is to $k^{\mathrm{QTST}}(T)$ what $k^{\mathrm{cl}}(T)$ is to $k^{\mathrm{cl,TST}}(T)$!

Some tricks of the trade

Integrating the RPMD equations of motion:

The standard (symplectic) velocity Verlet method for the Hamiltonian

$$H(p,q) = \frac{p^2}{2m} + V(q) = H_0 + V$$

is

$$p \leftarrow p - \frac{dt}{2}V'(q) \qquad \textit{exact} \text{ evolution under } V \text{ for time } dt/2$$

$$q \leftarrow q + dt\frac{p}{m} \qquad \textit{exact} \text{ evolution under } H_0 \text{ for time } dt$$

$$p \leftarrow p - \frac{dt}{2}V'(q) \qquad \textit{exact} \text{ evolution under } V \text{ for time } dt/2$$

We can do the same thing with the ring polymer Hamiltonian

$$H = \sum_{j=1}^{n} \left[\frac{p_j^2}{2m} + \frac{1}{2} m\omega_n^2 (q_j - q_{j-1})^2 \right] + \sum_{j=1}^{n} V(q_j) = H_0 + V.$$

Since H_0 is harmonic, its evolution involves the normal modes

$$\tilde{p}_k = \sum_{j=1}^{n} p_j C_{jk} \qquad \text{and} \qquad \tilde{q}_k = \sum_{j=1}^{n} q_j C_{jk},$$

where

$$C_{jk} = \begin{cases} \sqrt{1/n}, & k = 0 \\ \sqrt{2/n}\cos(2\pi jk/n), & 0 < k < n/2 \\ \sqrt{1/n}(-1)^j, & k = n/2 \\ \sqrt{2/n}\sin(2\pi jk/n), & n/2 < k < n. \end{cases}$$

In the normal mode representation, H_0 becomes

$$H_0 = \sum_{k=0}^{n-1} \left[\frac{\tilde{p}_k^2}{2m} + \frac{1}{2} m \omega_k^2 \tilde{q}_k^2 \right]$$

with $\omega_k = 2\omega_n \sin(k\pi/n)$.

The time evolution through dt is therefore

$$\begin{pmatrix} \tilde{p}_k \\ \tilde{q}_k \end{pmatrix} \leftarrow \begin{pmatrix} \cos \omega_k dt & -m\omega_k \sin \omega_k dt \\ (1/m\omega_k) \sin \omega_k dt & \cos \omega_k dt \end{pmatrix} \begin{pmatrix} \tilde{p}_k \\ \tilde{q}_k \end{pmatrix},$$

followed by a transformation back to the bead representation

$$p_j = \sum_{k=0}^{n-1} C_{jk} \tilde{p}_k \qquad \text{and} \qquad q_j = \sum_{k=0}^{n-1} C_{jk} \tilde{q}_k.$$

Aside on centroid molecular dynamics:

The adiabatic implementation of CMD can be obtained simply by changing H_0 in the normal mode representation to

$$H_0 = \sum_{k=0}^{n-1} \left[\frac{\tilde{p}_k^2}{2m_k} + \frac{1}{2} m\omega_k^2 \tilde{q}_k^2 \right]$$

where $m_0 = m$ and $m_{k>1} \ll m$.

This adiabatically separates the internal modes of the ring polymer from the centroid mode. It is necessary to use a smaller time step dt to correctly follow the motion of the internal modes and it is also desirable to attach these modes to a thermostat to ensure canonical sampling.

The net result is classical molecular dynamics on a free energy surface: the centroid potential of mean force.

Ring polymer contraction:

The real bottleneck of the calculation is the evaluation of the forces associated with the potential

$$V_n(\mathrm{q}) = \sum_{j=1}^{n} V(q_j),$$

which seems to require n times the effort of classical MD.

However, most empirical potentials can be split into two parts,

$$V(q) = V_S(q) + V_L(q),$$

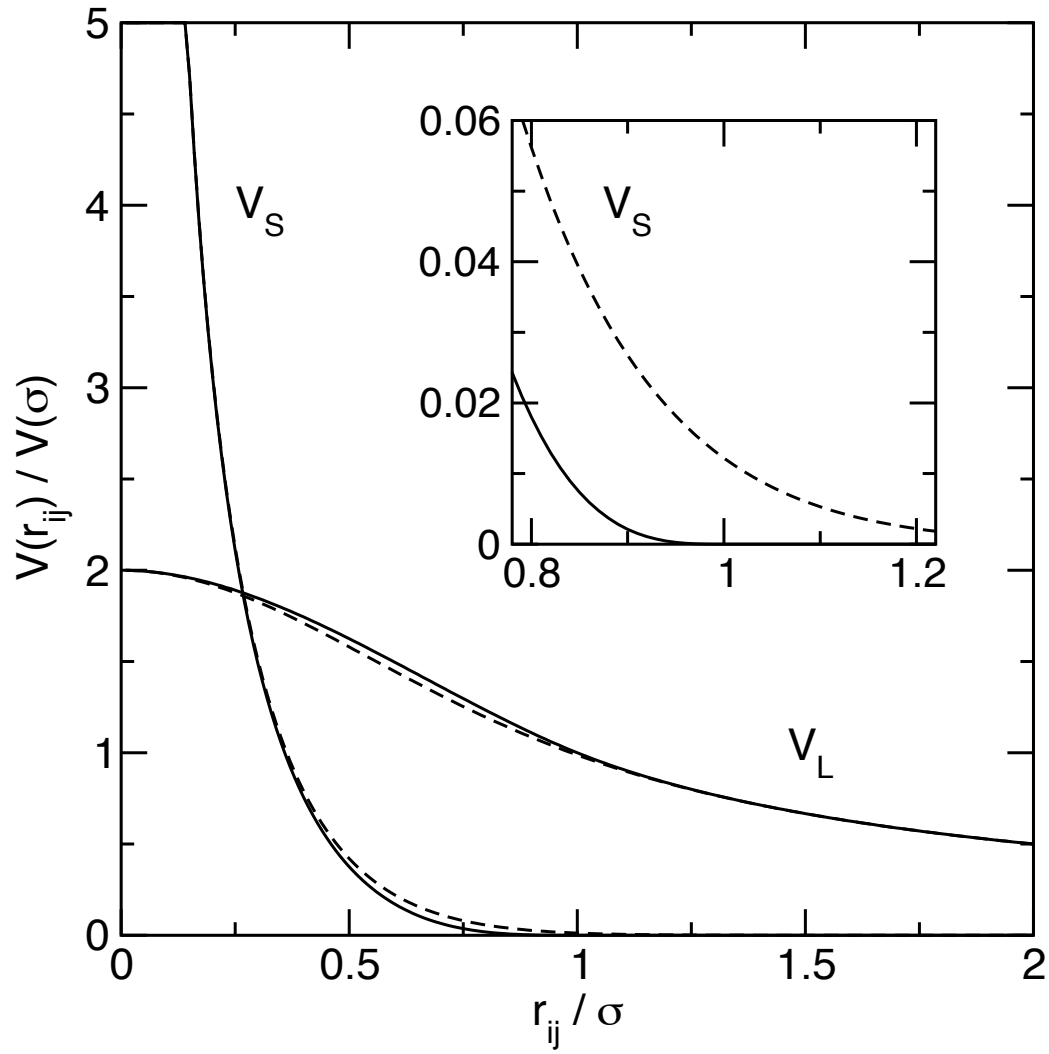
where $V_S(q)$ is short-range and rapidly-varying and $V_L(q)$ is long-range and slowly-varying.

E.g.: The Coulomb potential is often split into short- and long-range parts

$$V(r) = V_S(r) + V_L(r)$$

$$V_S(r) = [1 - f(r)]V(r)$$

$$V_L(r) = f(r)V(r)$$



$$f(r) = \mathrm{erf}(\sqrt{\pi} r/\sigma) \qquad (dashed)$$

$$f(r < \sigma) = 2(r/\sigma) - 2(r/\sigma)^3 + (r/\sigma)^4 \qquad (solid)$$

Now if $V_L(q)$ is sufficiently slowly varying over the length scale of the ring polymer ($\left\langle r^2 \right\rangle^{1/2} \simeq \Lambda(T)/\sqrt{8\pi}$), we can write

$$V_n(\mathrm{q}) \simeq \sum_{j=1}^{n} V_S(q_j) + n V_L(\bar{q}) \qquad \text{where} \qquad \bar{q} = \frac{1}{n}\sum_{j=1}^{n} q_j .$$

Within this approximation, the forces are

$$-\frac{\partial V_n(\mathrm{q})}{\partial q_j} = -\frac{dV_S(q_j)}{dq_j} - n\frac{dV_L(\bar{q})}{d\bar{q}} \cdot \frac{\partial \bar{q}}{\partial q_j},$$

I.e.,

$$-\frac{\partial V_n(\mathrm{q})}{\partial q_j} = -\frac{dV_S(q_j)}{dq_j} - \frac{dV_L(\bar{q})}{d\bar{q}}.$$

Note that the RPMD equations of motion with these forces will exactly conserve the RPMD Hamiltonian with the approximate $V_n(\mathrm{q})$.

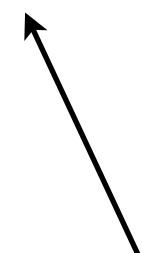
In practice, the contraction can be implemented as follows:

$$V_n(\mathrm{q}) = \sum_{j=1}^{n} V_S(q_j) + nV_L(\bar{q})$$

$$= \sum_{j=1}^{n} V_S(q_j) + n\left[V(\bar{q}) - V_S(\bar{q})\right]$$

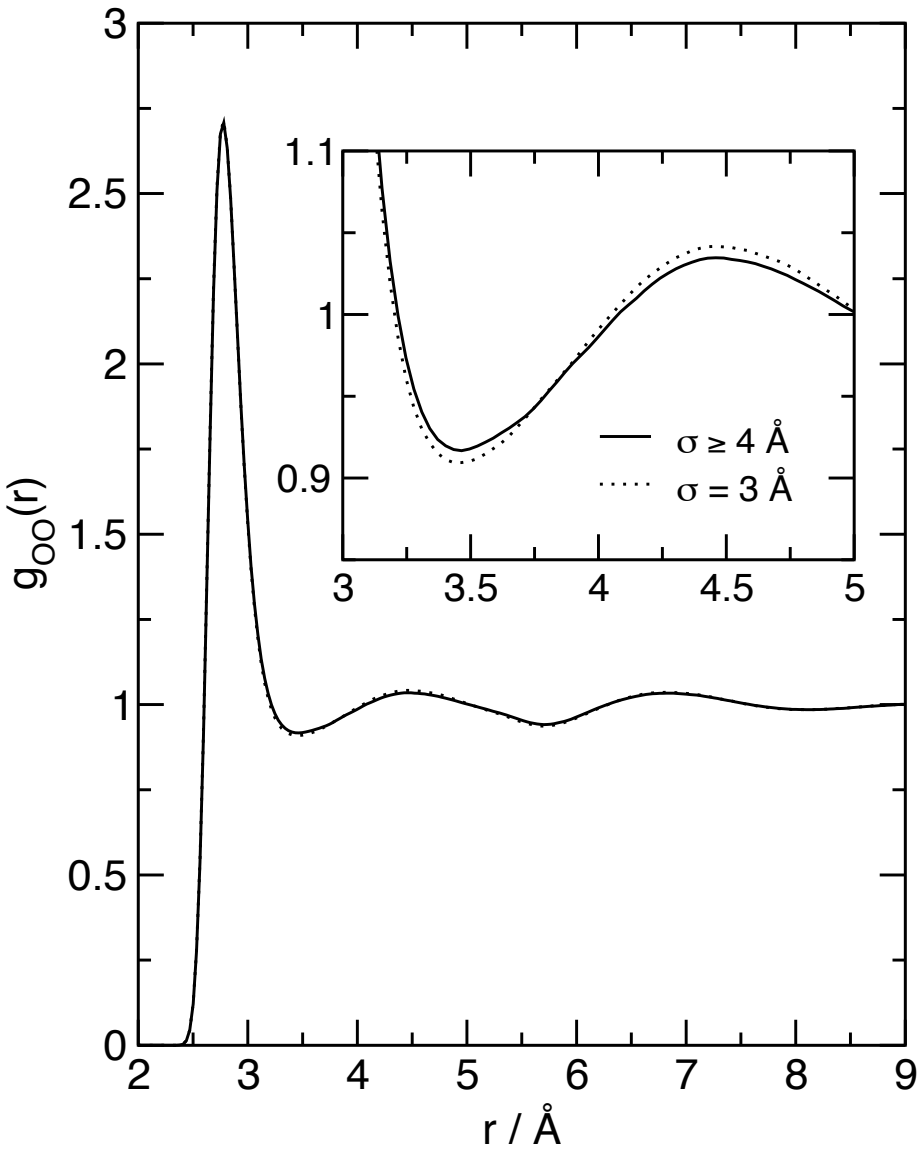
$$= nV(\bar{q}) + \sum_{j=1}^{n} \left[V_S(q_j) - V_S(\bar{q})\right].$$

Full potential on centroid
(just one Ewald sum)



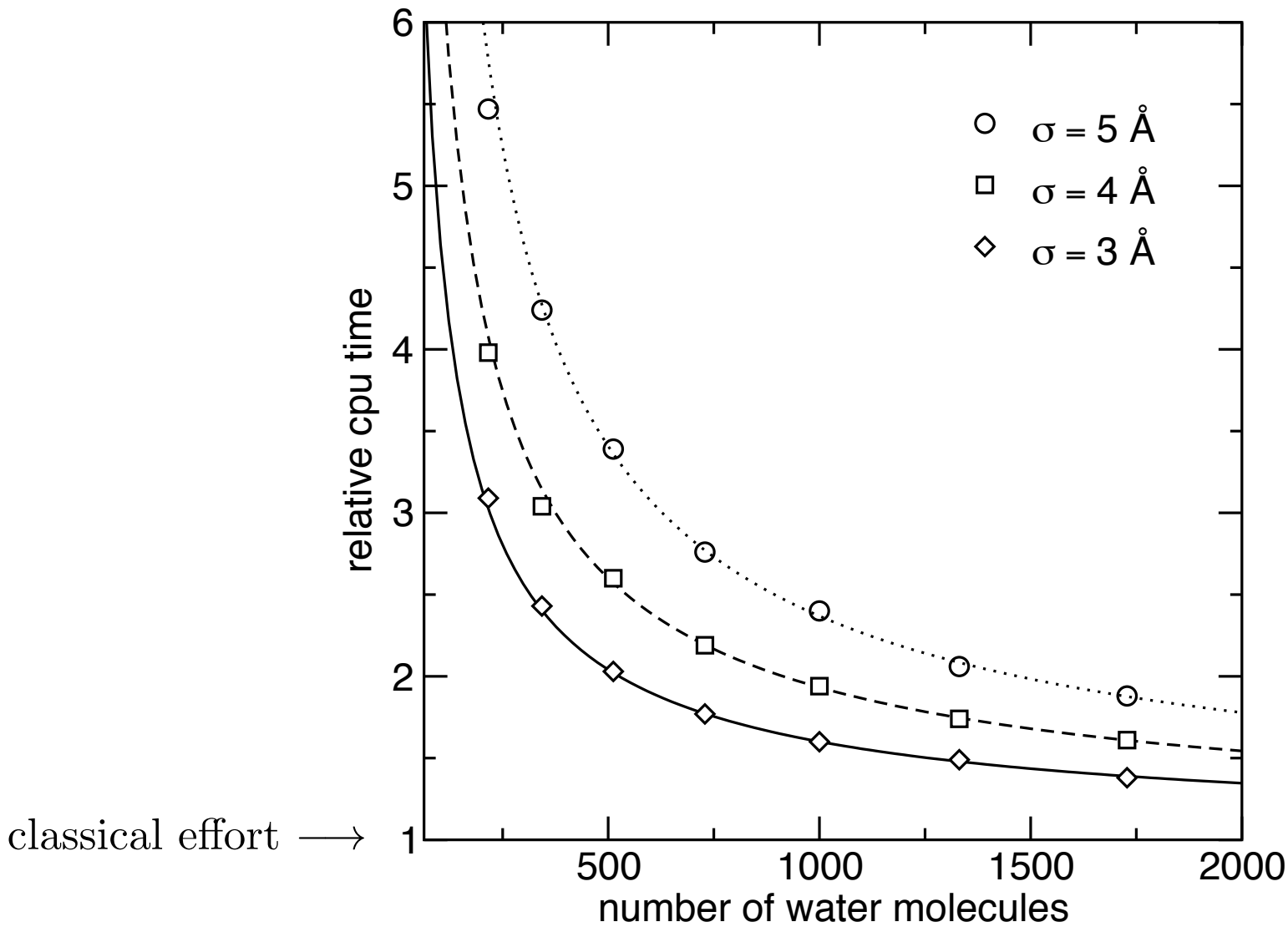
Plus a short-range correction
on each bead (zero beyond σ)

This works extremely well. E.g.:



σ (Å)	D (Å^2 ps^{-1})
3	0.402(3)
4	0.397(3)
5	0.399(3)
∞	0.400(3)

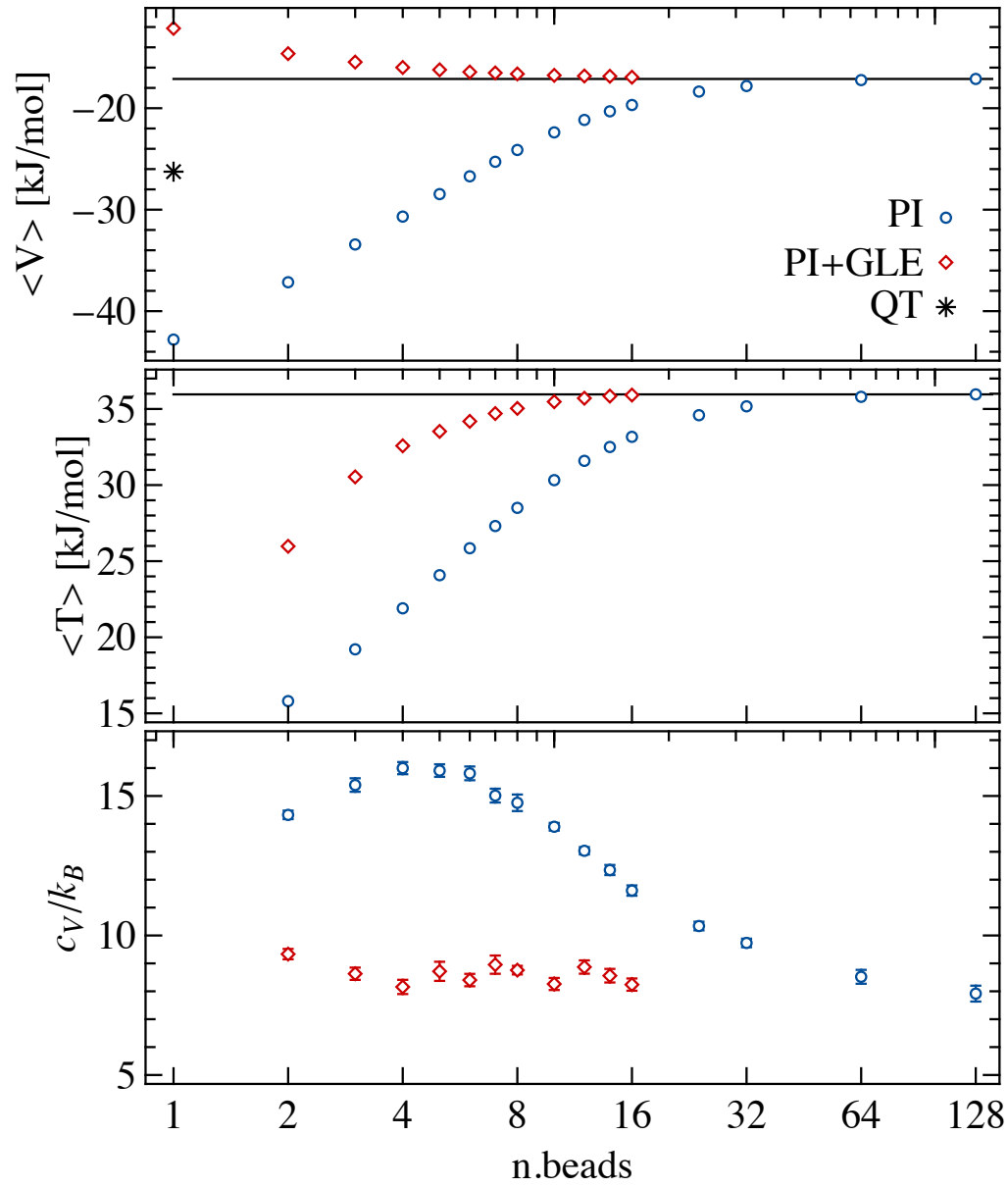
And it gives a method with purely classical computational effort in the limit of infinite system size:



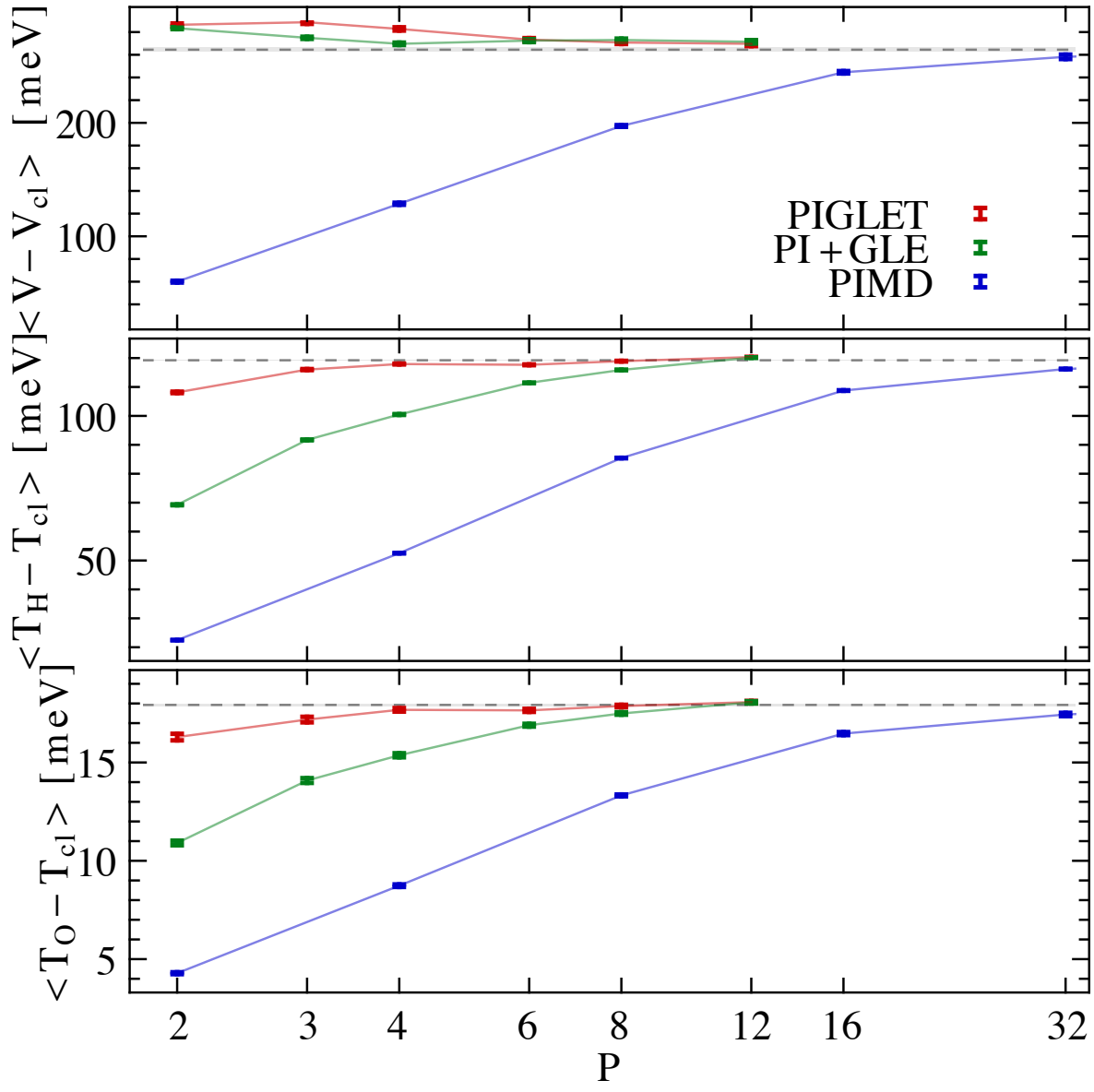
Aside on PI+GLE and PIGLET:

Here are the PI+GLE results for liquid water that Joe Morrone showed you on Tuesday evening:

Notice how the PI+GLE $\langle V \rangle$ converges more rapidly than $\langle T \rangle$.



We have recently fixed this by designing a new PIGLET method that converges $\langle T \rangle$ just as rapidly as $\langle V \rangle$:



M. Ceriotti *at el.*
submitted to PRL.

And finally:

All of the equations in these notes have been given for a simple one-dimensional model problem.

However the multidimensional generalisation is entirely straightforward when identical particle exchange effects can be ignored.

E.g., For a system with N Cartesian degrees of freedom the partition function becomes

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

where

$$H_n(\mathrm{p},\mathrm{q}) = \sum_{i=1}^{N}\sum_{j=1}^{n}\left[\frac{p_{i.j}^2}{2m_i} + \frac{1}{2}m_i\omega_n^2(q_{i,j} - q_{i,j-1})^2\right] + \sum_{j=1}^{n} V(q_{1,j},\ldots,q_{N,j}).$$

Example applications

Quantum diffusion in liquid para-hydrogen (2005)

Quantum diffusion in liquid water (2005)

Neutron scattering from liquid para-hydrogen (2006)

Proton transfer in a polar solvent (2008)

Diffusion of H and Mu in water and ice (2008)

The IR spectrum of liquid water (2008)

Gas phase chemical reaction rates (2009)

Competing quantum effects in liquid water (2009)

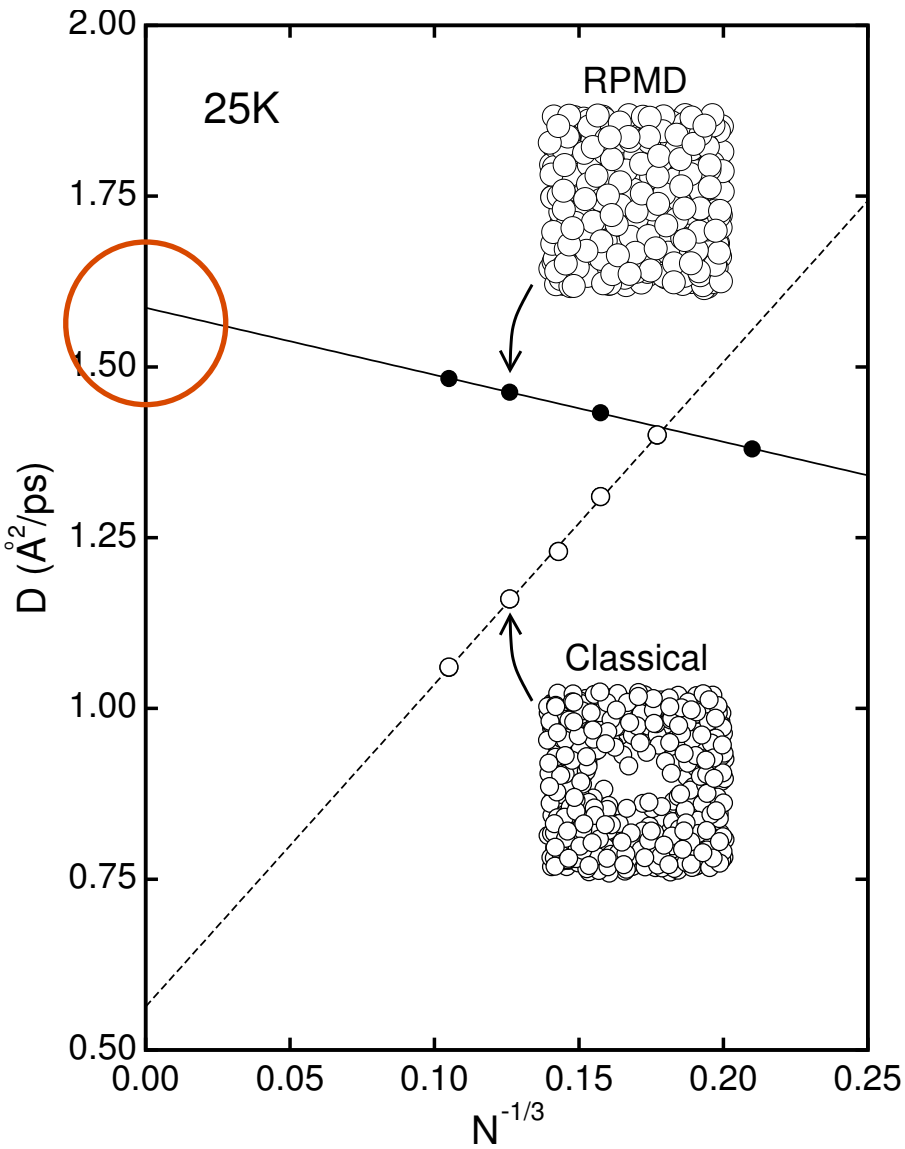
The dynamics of the solvated electron (2010)

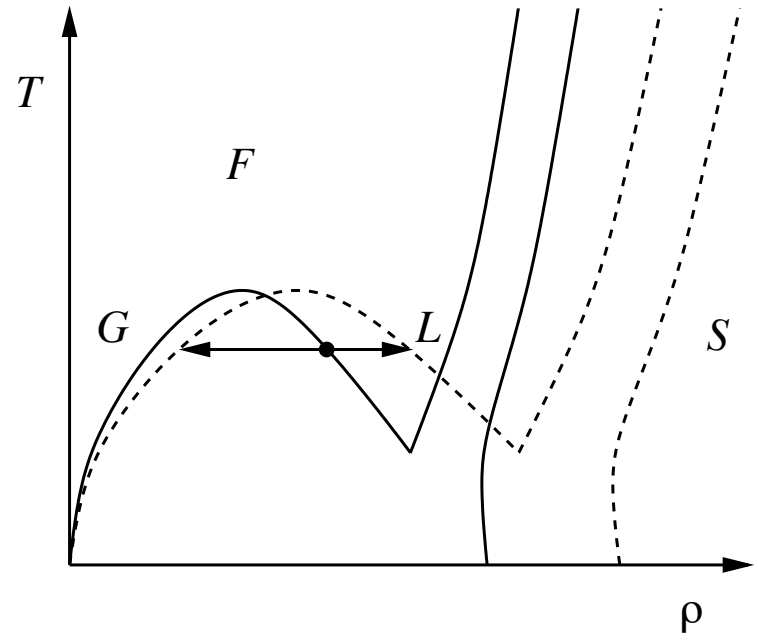
A re-entrant quantum glass transition (2011)

Enzyme-catalysed hydride transfer (2011)

Aqueous electron transfer (2011)

Quantum diffusion in liquid para-hydrogen





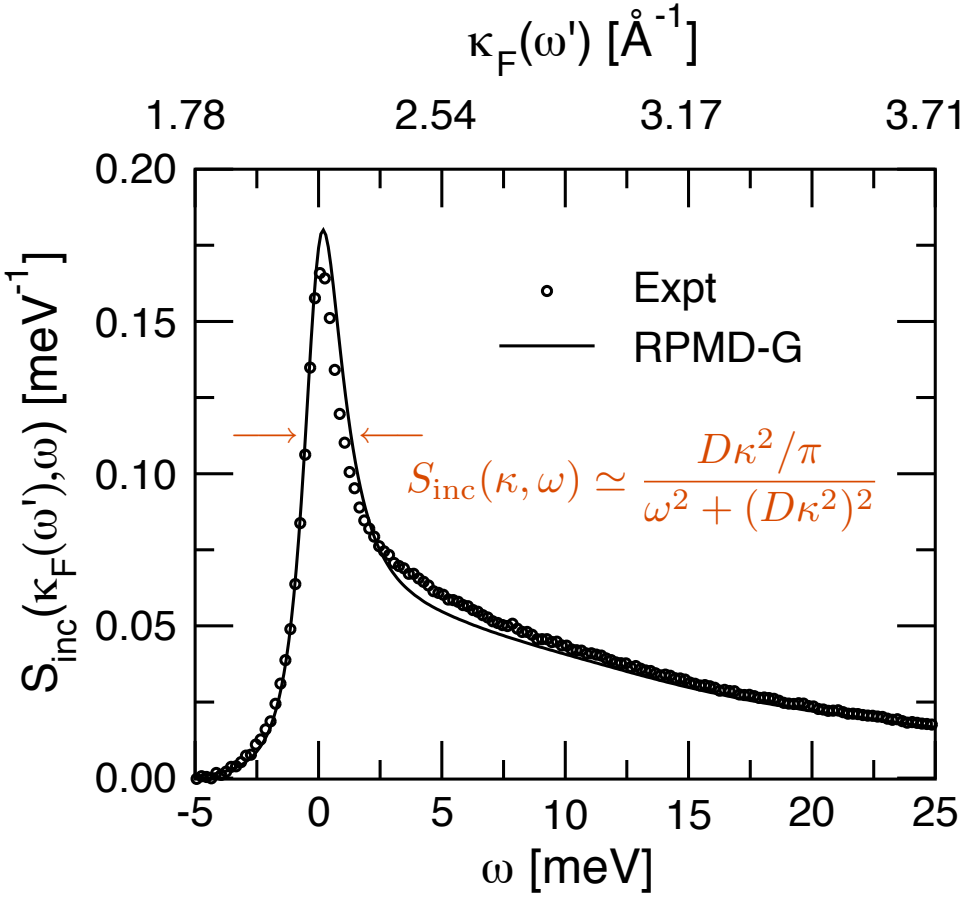
$$D = \frac{1}{3}\int_0^\infty \tilde{c}_{\mathbf{v}\cdot\mathbf{v}}(t)\,dt$$

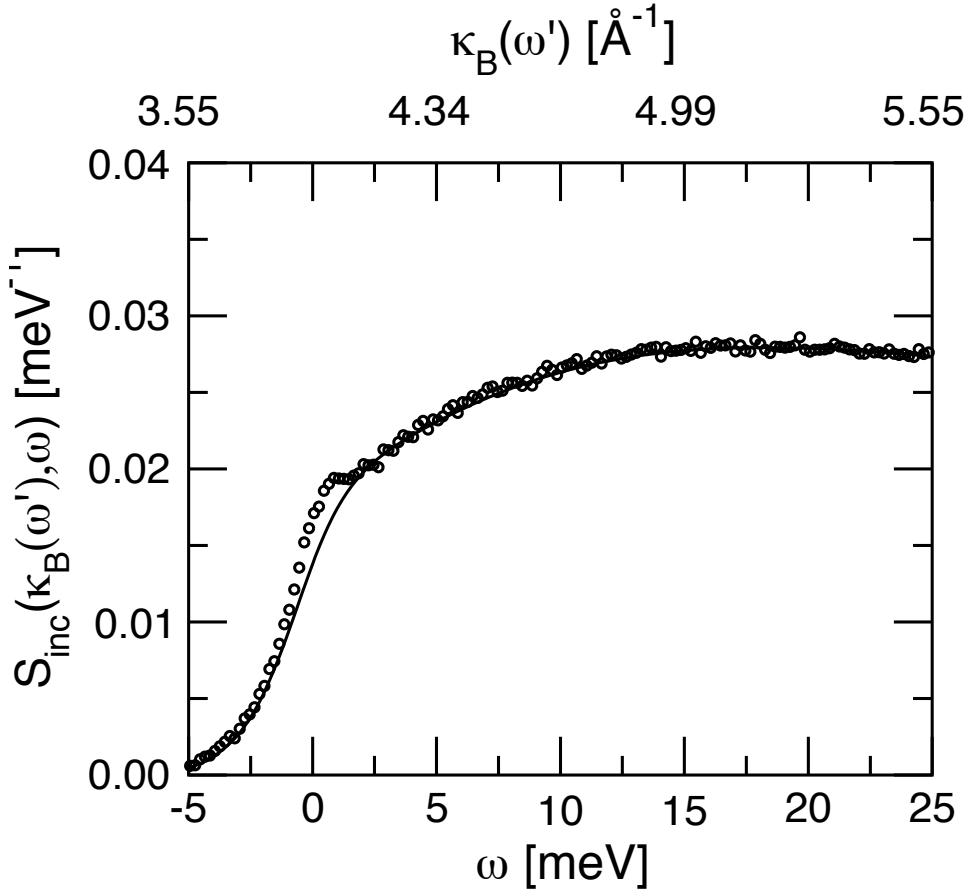
$$D(L) = D(\infty) - \xi\frac{k_\mathrm{B}T}{6\pi\eta L}$$

Inelastic neutron scattering from liquid para-hydrogen (at 14 K)

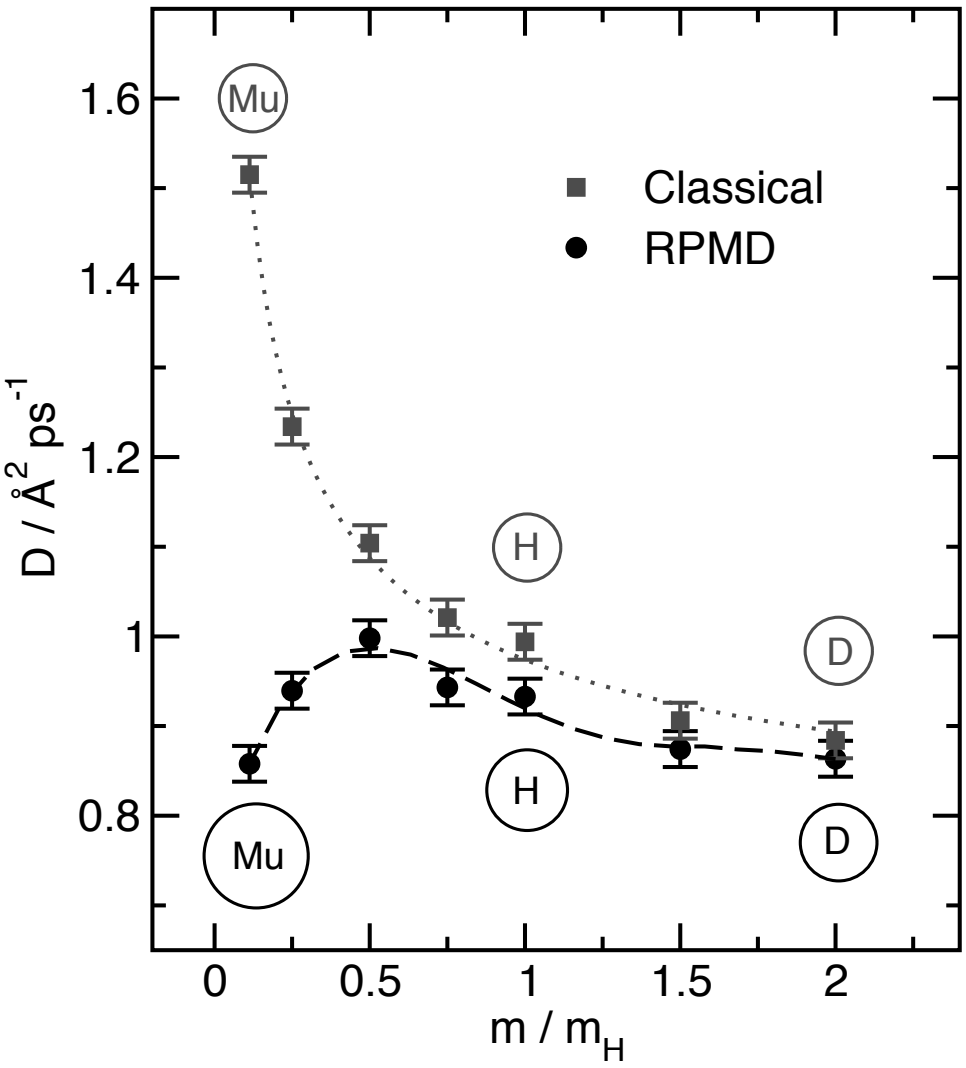
$$S_{\rm inc}(\kappa,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t} F_s(\kappa,t)\,dt;$$

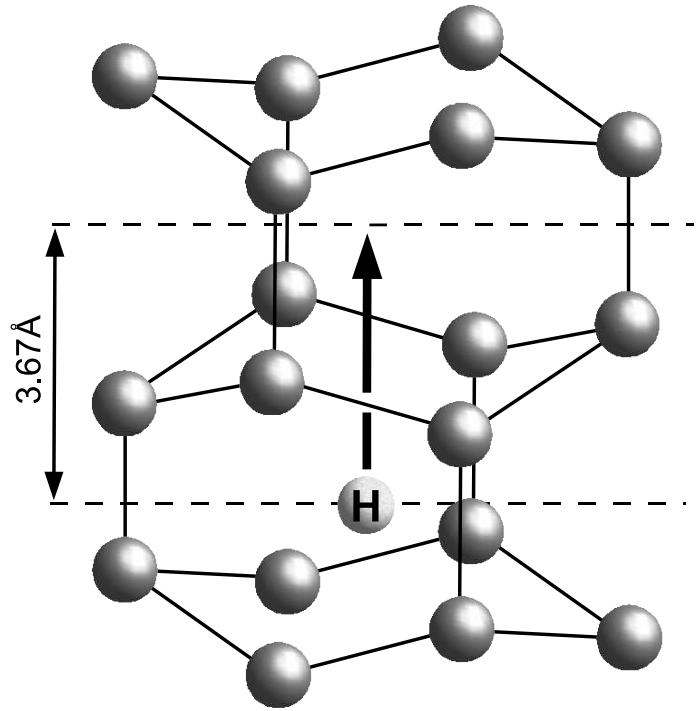
$$F_s(\kappa,t) \simeq e^{-\kappa^2\gamma(t)}; \qquad \gamma(t) = -i\frac{\hbar t}{2m} + \frac{1}{3}\int_0^t (t-t')c_{\mathbf{v}\cdot\mathbf{v}}(t')\,dt'.$$





Quantum diffusion of Mu, H, D in liquid water

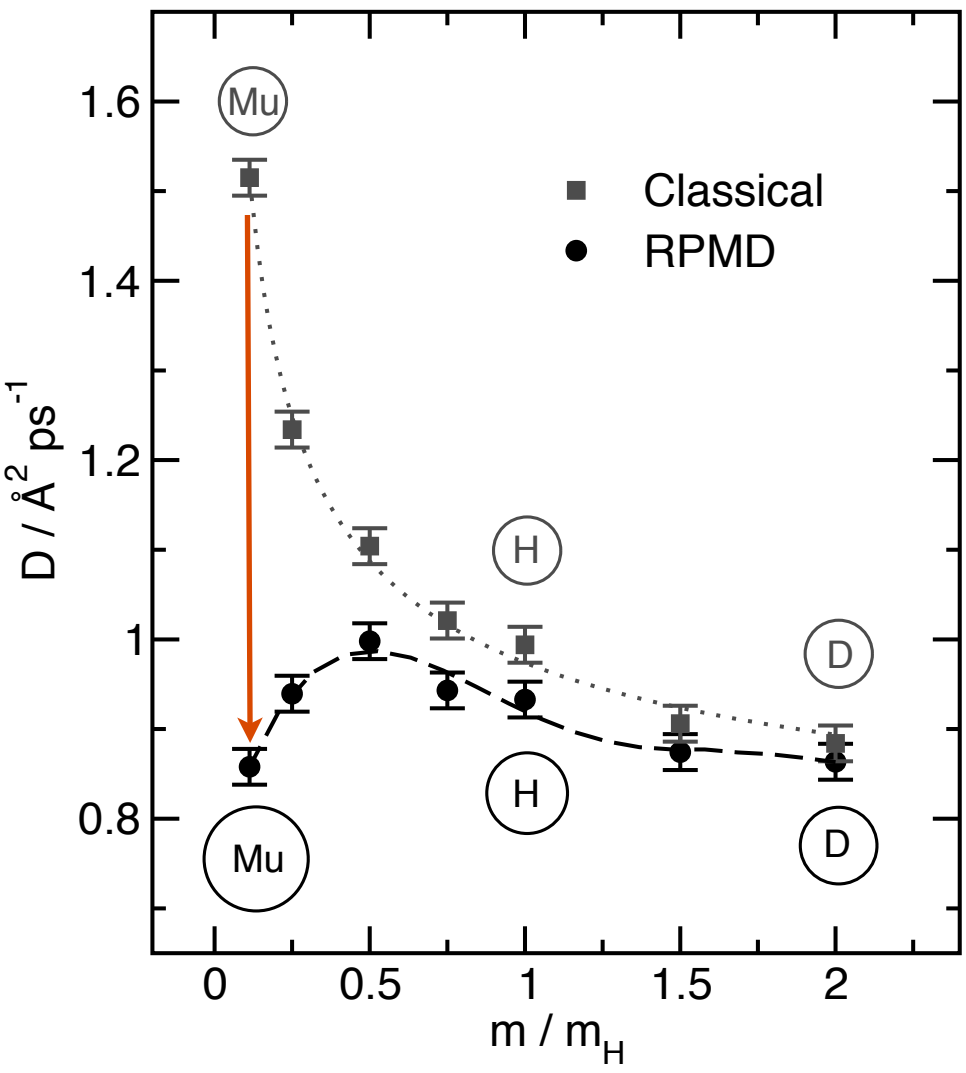




The classical results satisfy

$$D(m) = (m_H/m)^{1/2}\, D_{\rm hop} + D_{\rm cav}$$

Quantum diffusion of Mu, H, D in liquid water



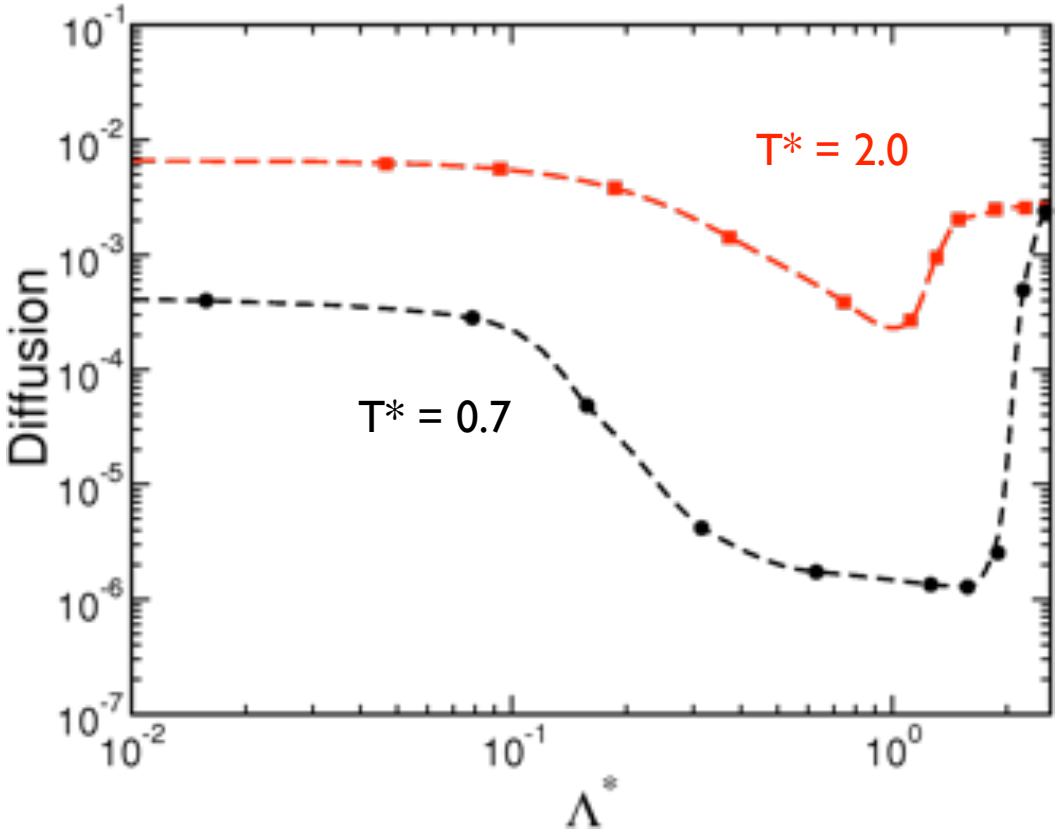
But thermal QM "swelling" strongly inhibits the inter-cavity hopping of Mu:

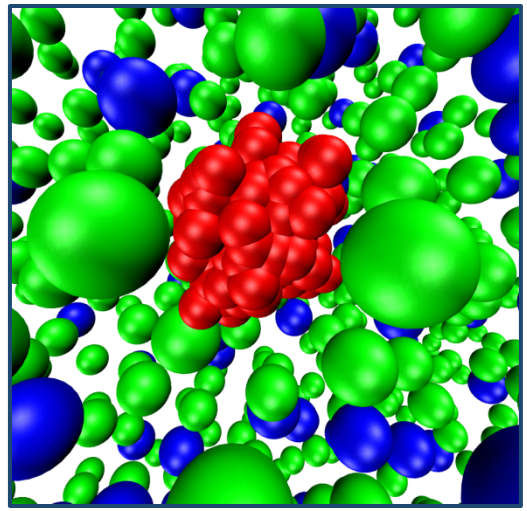
$$\langle r^2 \rangle^{1/2} \sim \Lambda(T)/\sqrt{8\pi}$$

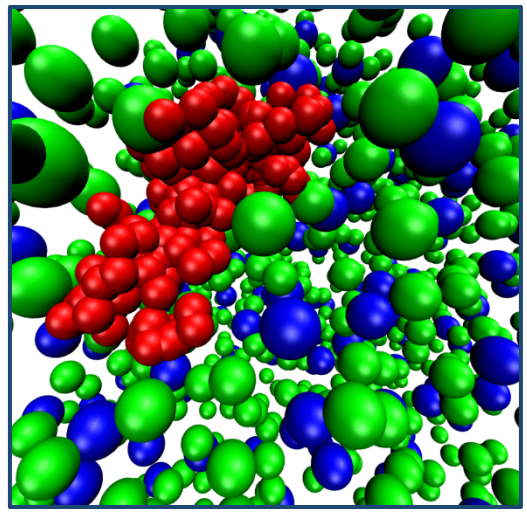
$$\Lambda(T) = h/\sqrt{2\pi m k T}$$

The net result is hardly any isotope effect in the RPMD diffusion coefficients of Mu, H and D - in good qualitative agreement with experiment.

"Quantum fluctuations can promote or inhibit glass formation"



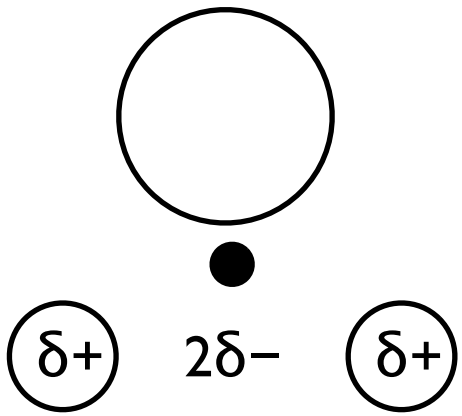




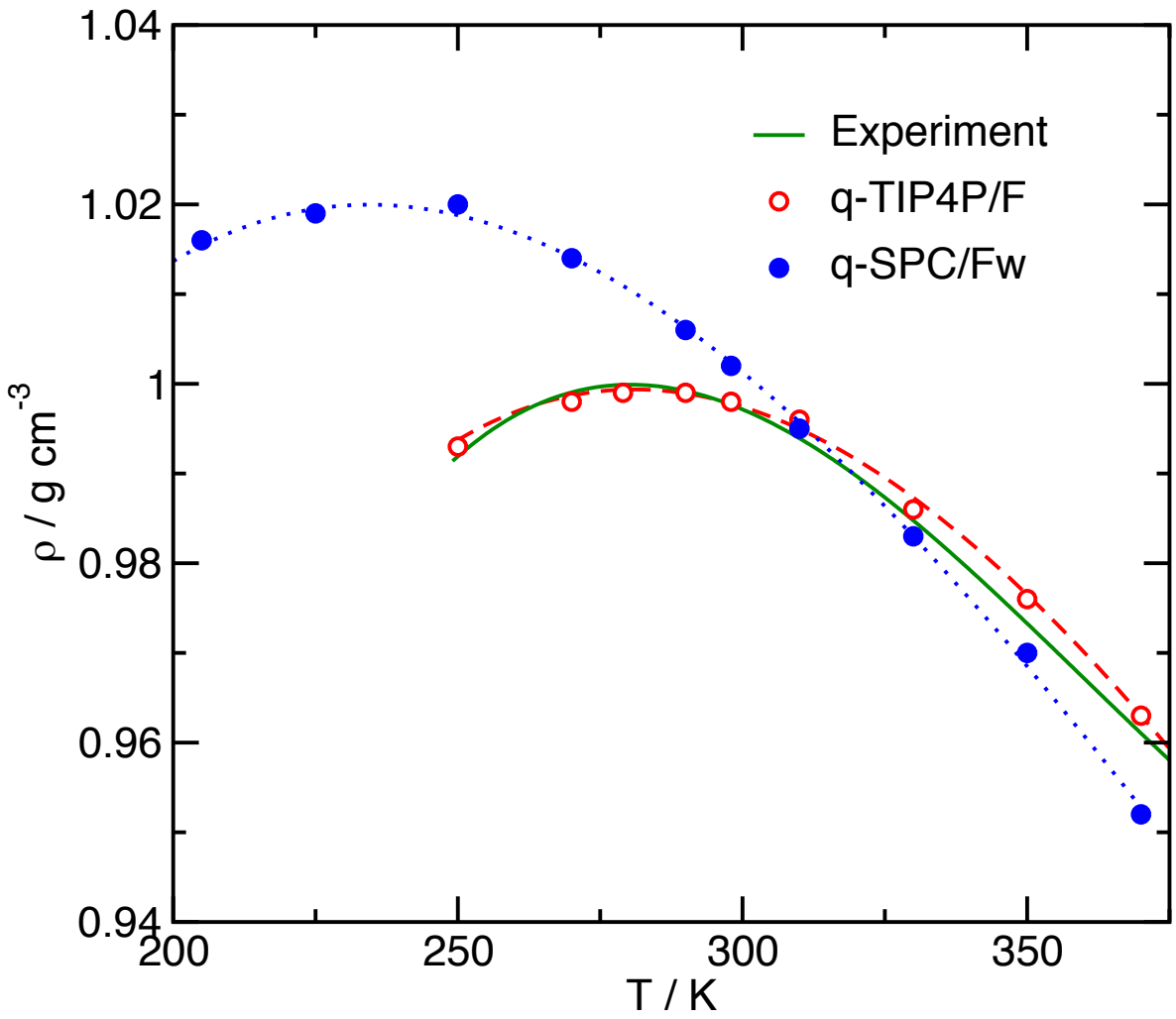
T. E. Markland *et al.*
Nature Physics 7, 99 (2011)

Competing quantum effects in liquid water

q-TIP4P/F

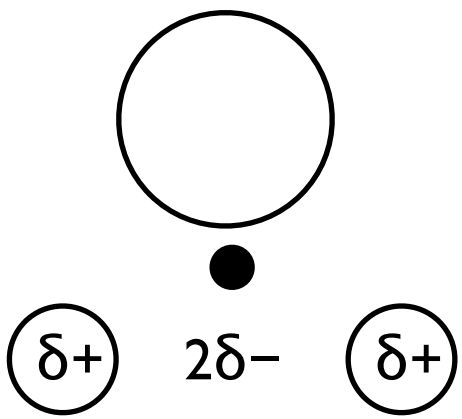


$V_{OH}(r)$ = quartic



Competing quantum effects in liquid water

q-TIP4P/F



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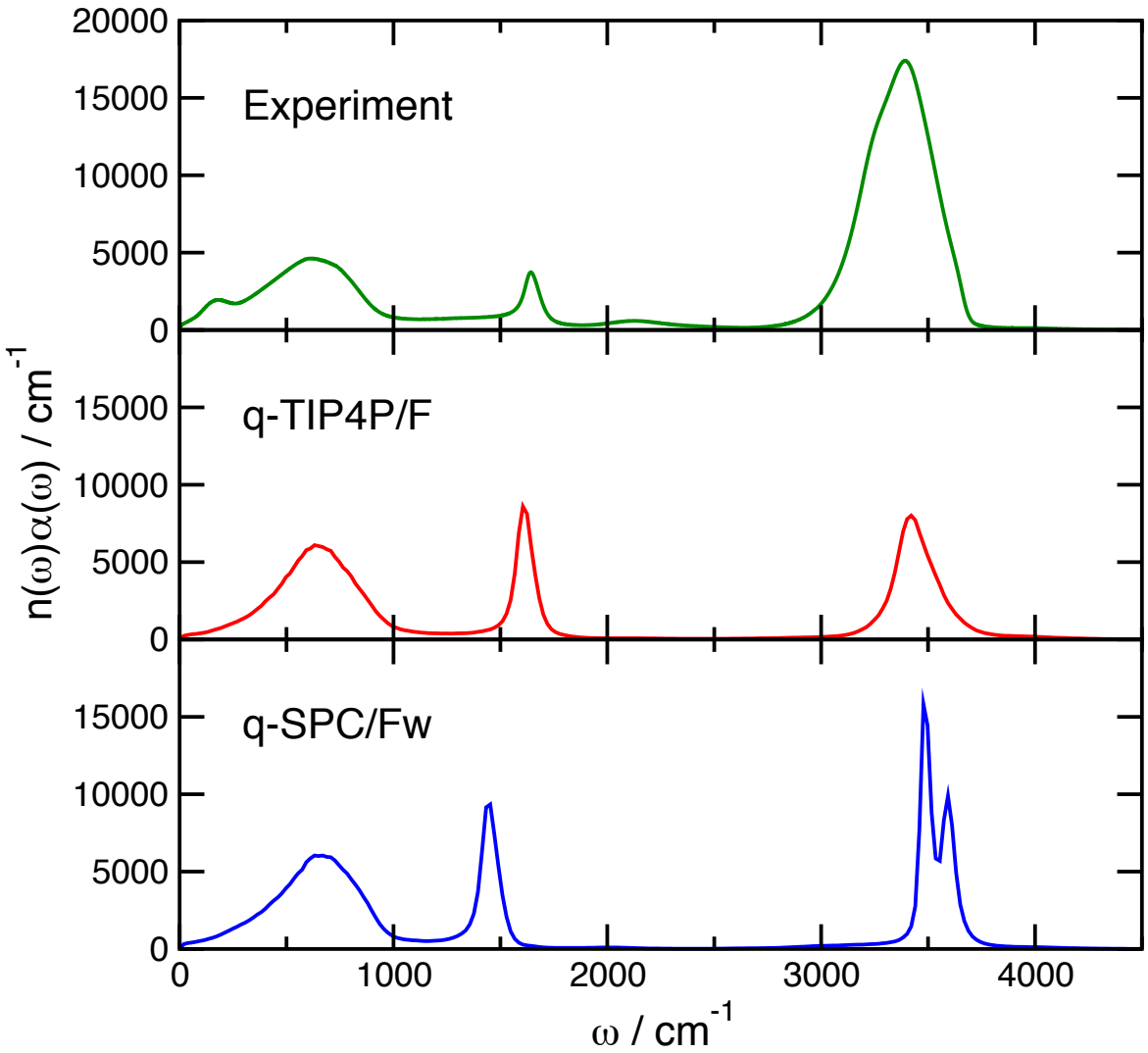
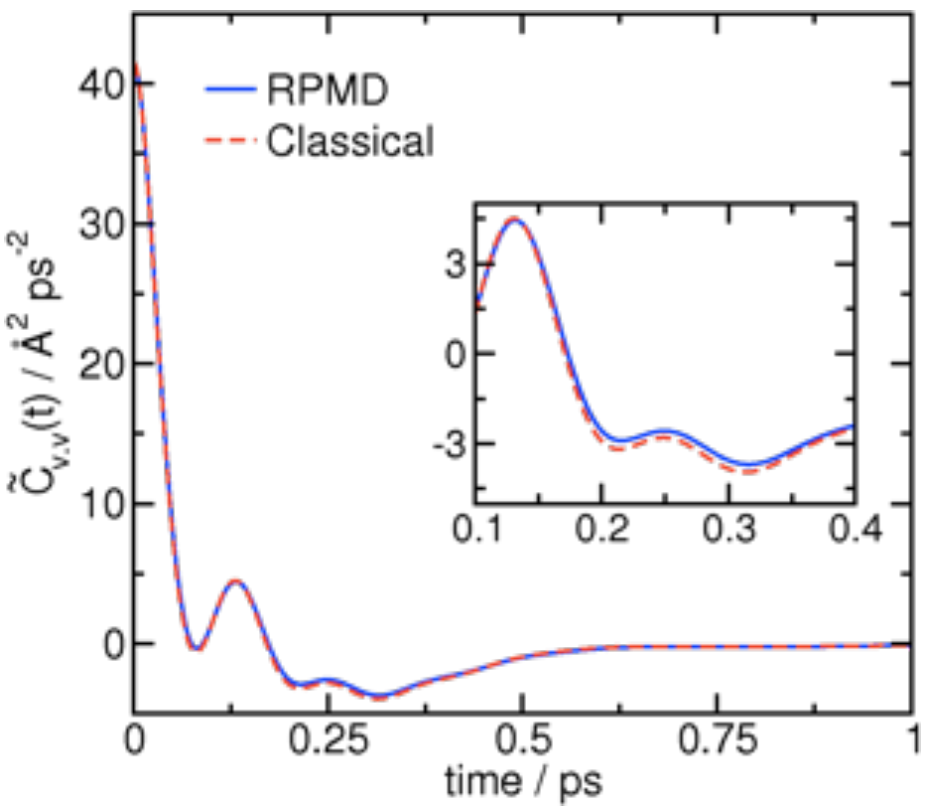
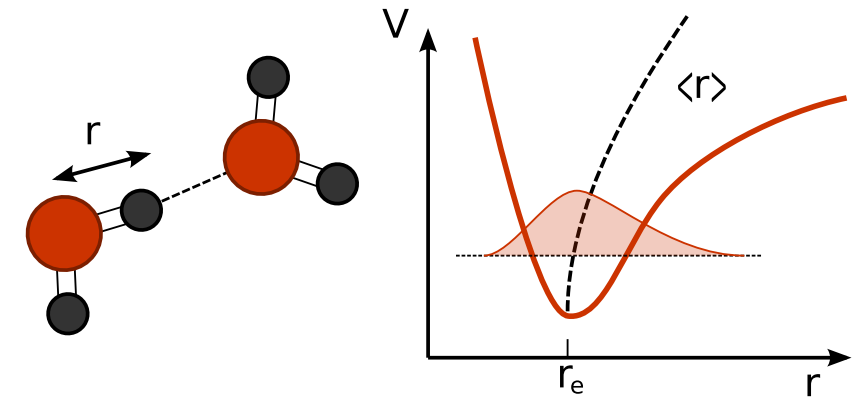
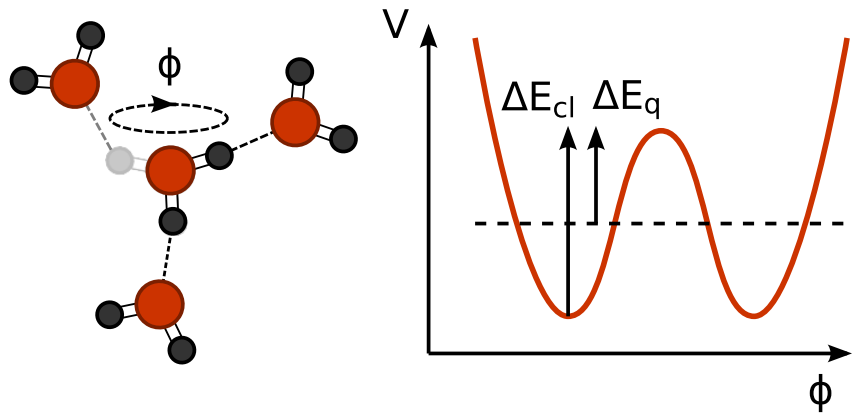


Competing quantum effects in liquid water

q-TIP4P/F

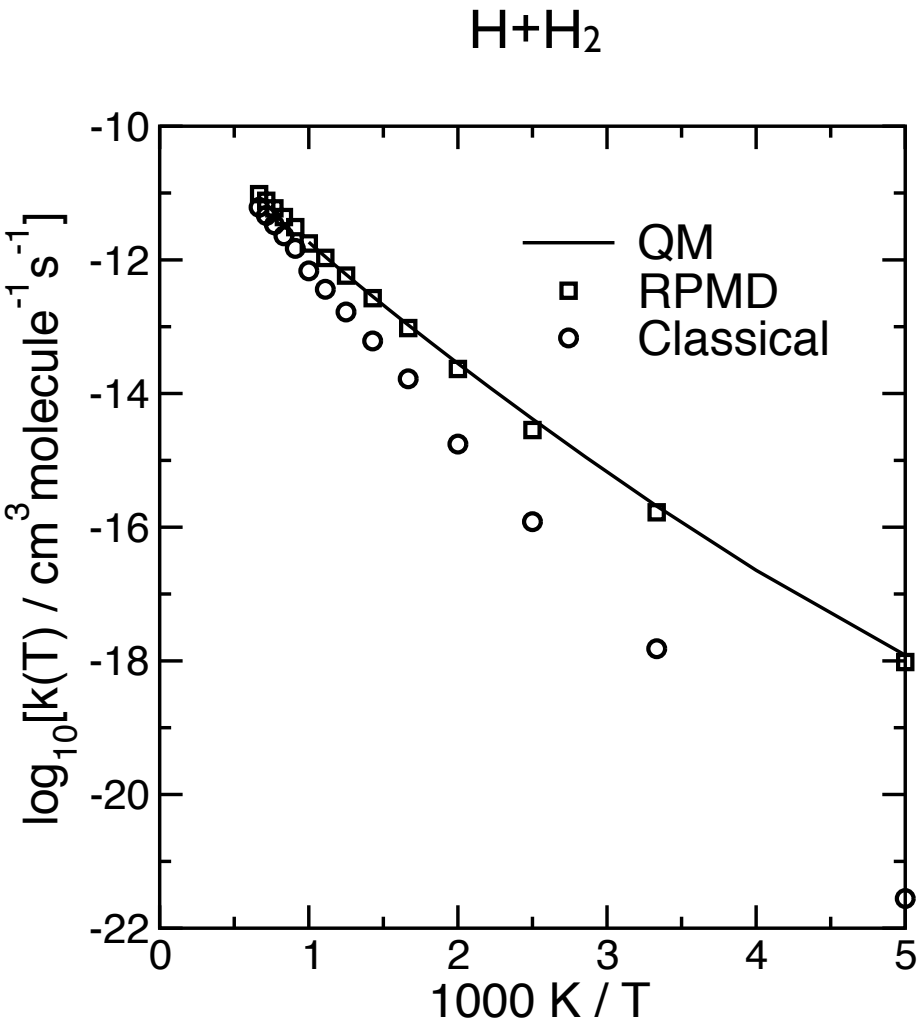






D_{QM}/D_{cl} = 1.1

Gas phase chemical reaction rates

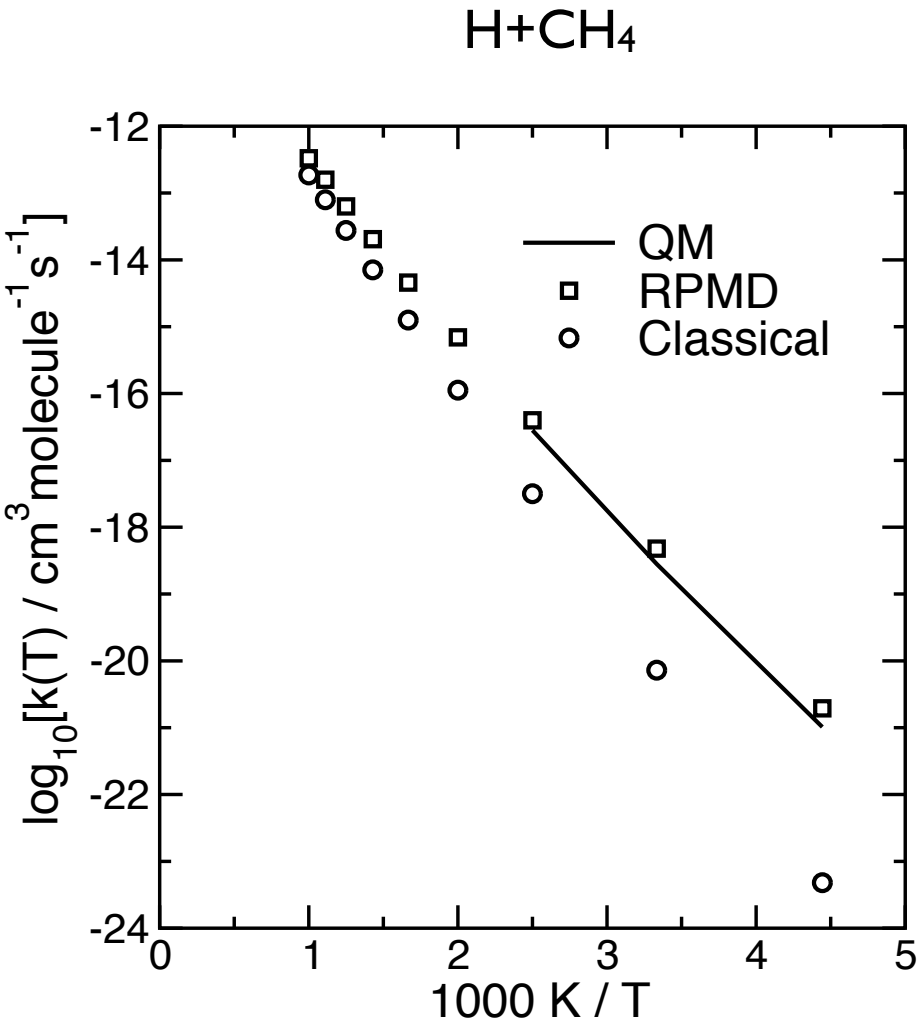


$$k(T)Q_r(T) = \int_0^\infty \tilde{c}_{ff}(t)\,dt$$

Symmetric barrier. T_c = 345 K.

RPMD is out by -29% at 200 K.

Gas phase chemical reaction rates

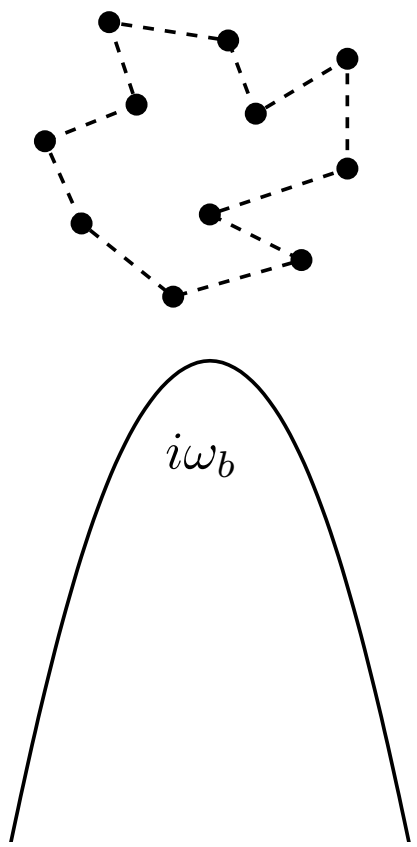


$$k(T)Q_r(T) = \int_0^\infty \tilde{c}_{ff}(t)\,dt$$

Asymmetric barrier. T_c = 296 K.

RPMD is out by +92% at 225 K.

The deep tunneling regime



$F.T.$

$(etc.)$

$\omega_{\pm 3} = \sqrt{(6\pi/\beta\hbar)^2 - \omega_b^2}$

$\omega_{\pm 2} = \sqrt{(4\pi/\beta\hbar)^2 - \omega_b^2}$

$\omega_{\pm 1} = \sqrt{(2\pi/\beta\hbar)^2 - \omega_b^2}$

$\omega_0 = i\omega_b$

Qualitative change in behaviour for

$$\beta > \beta_c = \frac{2\pi}{\hbar\omega_b}$$

$$T < T_c = \frac{\hbar\omega_b}{2\pi k_{\mathrm{B}}}$$

THE JOURNAL OF CHEMICAL PHYSICS **131**, 214106 (2009)

Ring-polymer molecular dynamics rate-theory in the deep-tunneling regime: Connection with semiclassical instanton theory

Jeremy O. Richardson and Stuart C. Althorpe
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

(Received 14 October 2009; accepted 4 November 2009; published online 3 December 2009)

We demonstrate that the ring-polymer molecular dynamics (RPMD) method is equivalent to an automated and approximate implementation of the "Im F" version of semiclassical instanton theory when used to calculate reaction rates in the deep-tunneling regime. This explains why the RPMD method is often reliable in this regime and also shows how it can be systematically improved. The geometry of the beads at the transition state on the ring-polymer potential surface describes a finite-difference approximation to the "instanton" trajectory (a periodic orbit in imaginary time $\beta\hbar$ on the inverted potential surface). The deep-tunneling RPMD rate is an approximation to the rate obtained by applying classical transition-state theory (TST) in ring-polymer phase-space using the optimal dividing surface; this TST rate is in turn an approximation to a free-energy version of the Im F instanton rate. The optimal dividing surface is in general a function of several modes of the ring polymer, which explains why centroid-based quantum-TSTs break down at low temperatures for asymmetric reaction barriers. Numerical tests on one-dimensional models show that the RPMD rate tends to overestimate deep-tunneling rates for asymmetric barriers and underestimate them for symmetric barriers, and we explain that this is likely to be a general trend. The ability of the RPMD method to give a dividing-surface-independent rate in the deep-tunneling regime is shown to be a consequence of setting the bead-masses equal to the physical mass. [doi:10.1063/1.3267318]

THE JOURNAL OF CHEMICAL PHYSICS **131**, 214106 (2009)

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geometry of the beads at the transit
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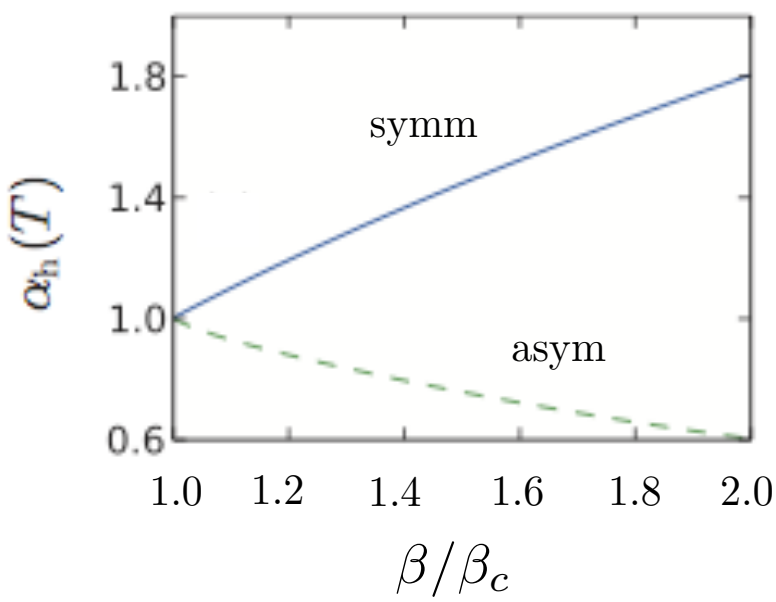
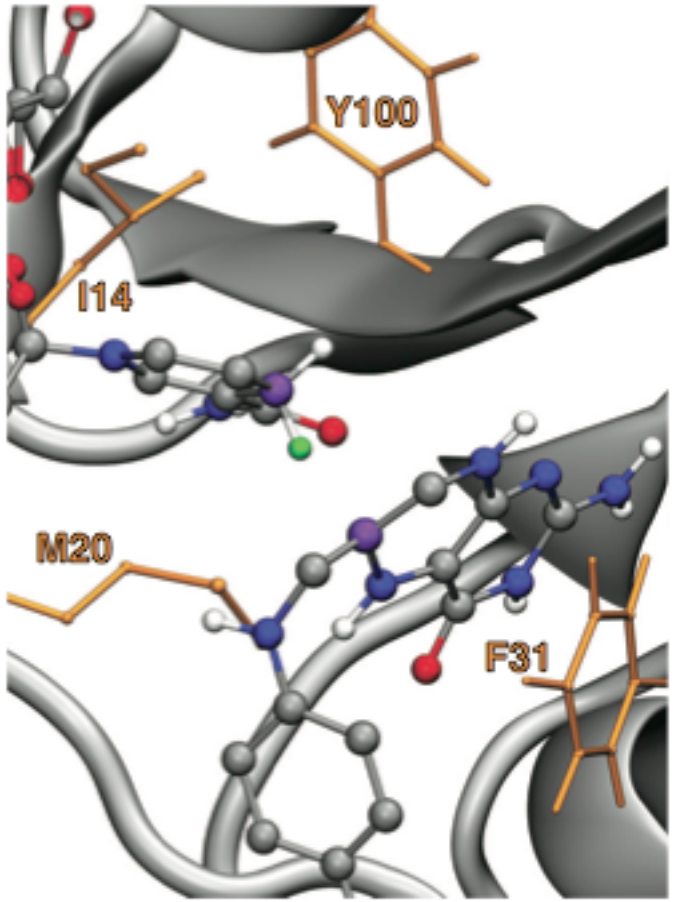
obtained by applying classical transiti
optimal dividing surface; this TST rat
Im F instanton rate. The optimal divi
ring polymer, which explains why ce
for asymmetric reaction barriers. Num
rate tends to overestimate deep-tunnel
symmetric barriers, and we explain tha
method to give a dividing-surface-ind
consequence of setting the bead-mass
Physics. [doi:10.1063/1.3267318]

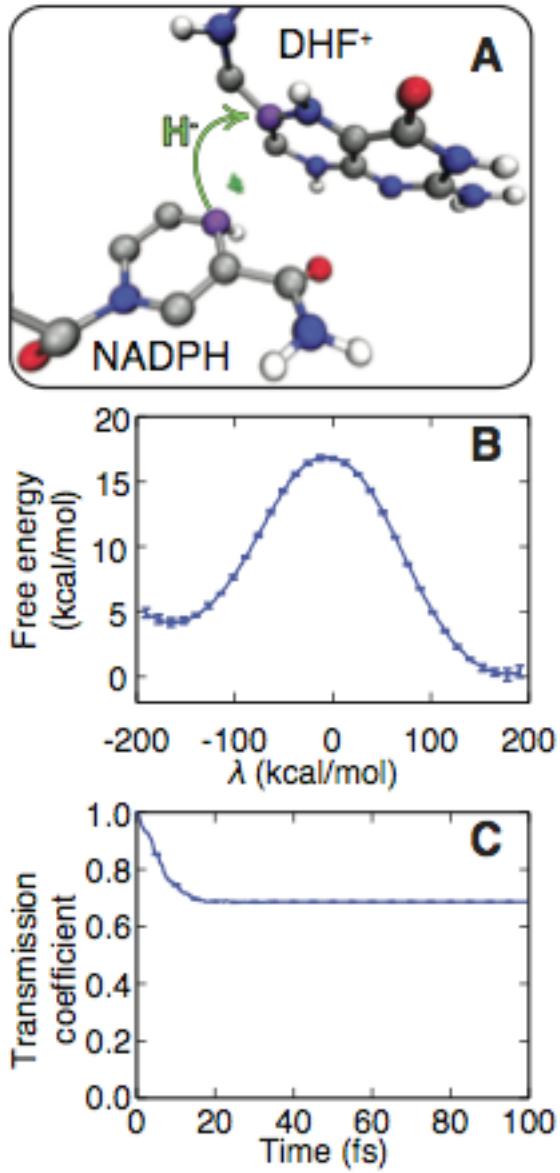


$$k^{\rm oTST}_{\rm RPMD}(T) = \frac{1}{\alpha(T)} k_{\rm inst}(T)$$

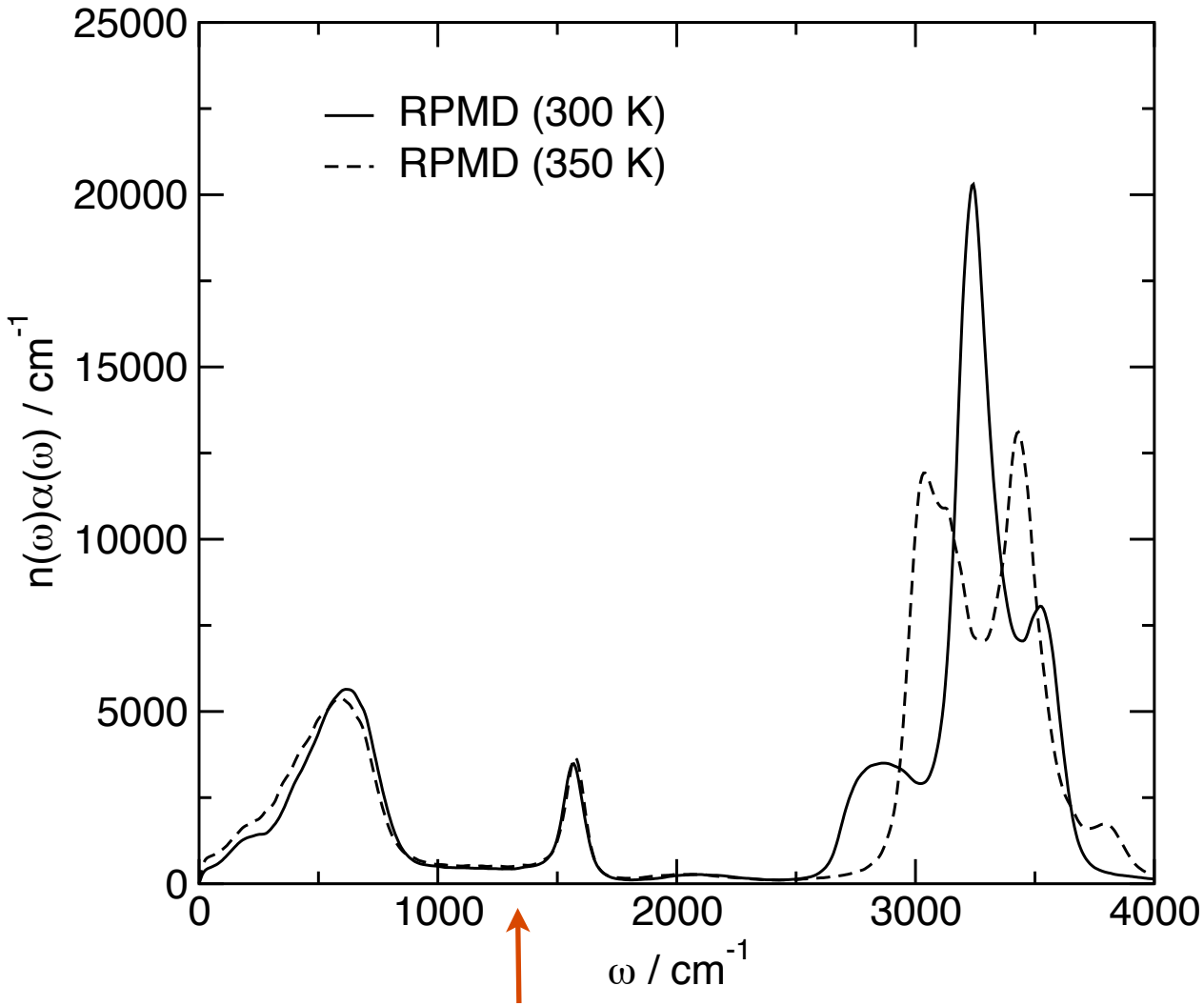
"Dynamics and dissipation in enzyme catalysis"



N. Boekelheide *et al.*
PNAS 108, 16159 (2011)



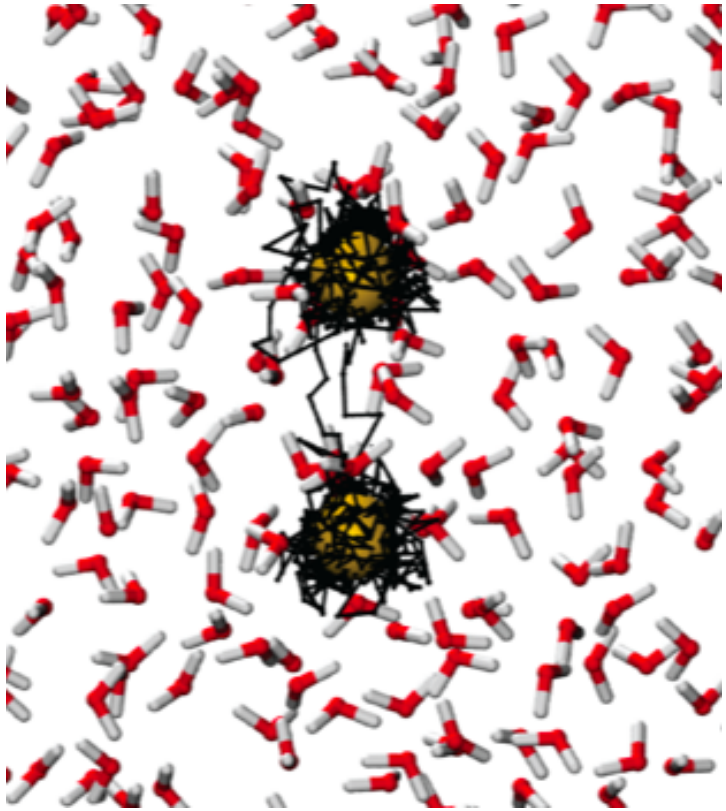
Limitations



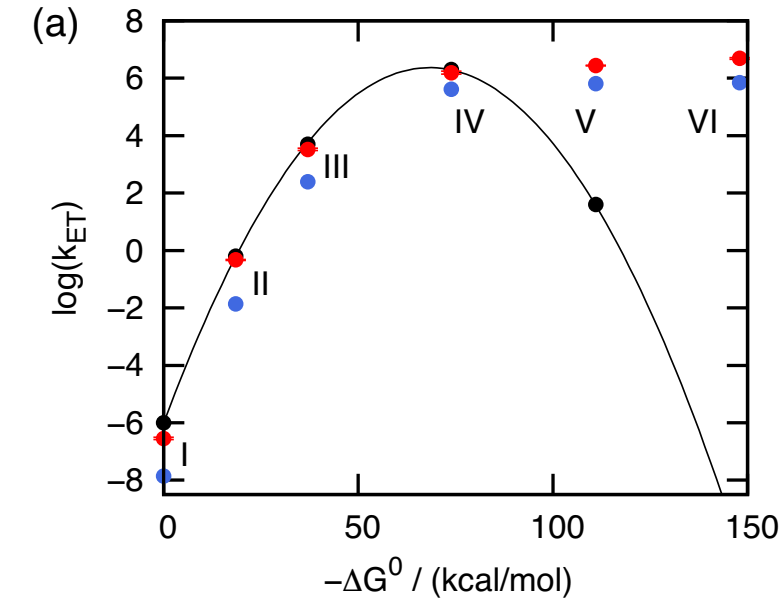
Infrared spectroscopy of liquid water

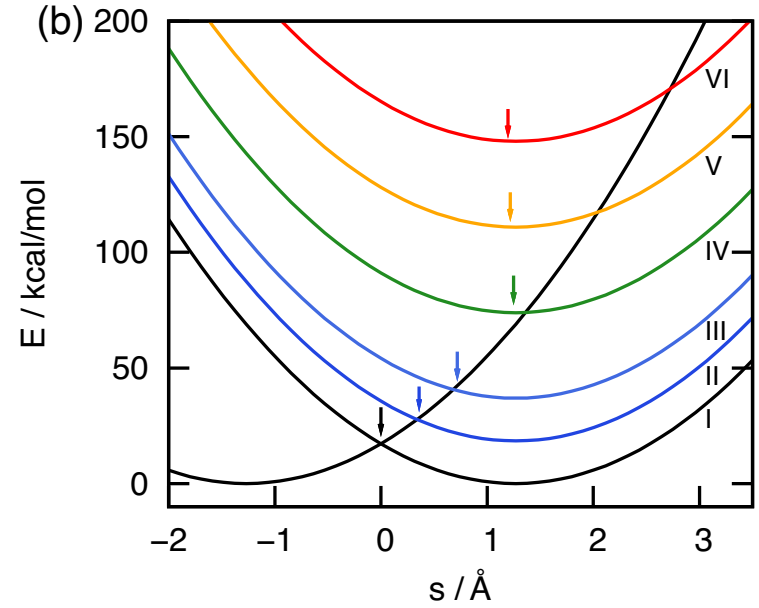
$\omega_1 = 2\pi/\beta\hbar = 1300\ \mathrm{cm}^{-1}$ at 300 K

The Marcus inverted regime



A. R. Menzeleev *et al.*
JCP 135, 074106 (2011)





References

I have only included references in these slides to work done by other groups.

A complete list of our own publications on RPMD can be found at

http://physchem.ox.ac.uk/~mano/publications.html