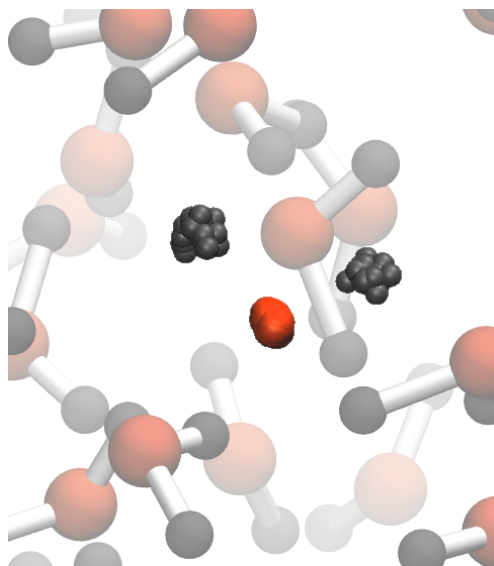


# Ring polymer molecular dynamics

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Mariapfarr Workshop 2019, Lecture II

# I. Quantum mechanical correlation functions

Many dynamical properties of condensed phase systems can be related to real-time correlation functions of the form

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

where

$$Q = \text{tr} \left[ e^{-\beta \hat{H}} \right],$$

and

$$\hat{B}(t) = e^{+i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar}.$$

For example, the diffusion coefficient of a molecule  $i$  in a liquid is given by

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

chemical reaction rate coefficients can be calculated from

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

and dipole absorption spectra from

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

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

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

whereas the *Kubo-transformed* correlation function is<sup>1</sup>

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

There are a number of 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 that

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

where

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

So standard correlation functions can easily be reconstructed from Kubo-transformed correlation functions, and vice versa.

Proof (I):

$$\begin{aligned}c_{AB}(t) &= \frac{1}{Q} \text{tr} \left[ e^{-\beta \hat{H}} \hat{A}(0) \hat{B}(t) \right] \\&= \frac{1}{Q} \text{tr} \left[ e^{-\beta \hat{H}} \hat{A} e^{+i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} \right] \\&= \frac{1}{Q} \sum_{jk} e^{-\beta E_j} \langle j | \hat{A} | k \rangle e^{+iE_k t/\hbar} \langle k | \hat{B} | j \rangle e^{-iE_j t/\hbar} \\&= \frac{1}{Q} \sum_{jk} e^{-\beta E_j} A_{jk} B_{kj} e^{+i(E_k - E_j)t/\hbar}.\end{aligned}$$

$$\begin{aligned}\therefore C_{AB}(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} c_{AB}(t) dt \\&= \frac{1}{Q} \sum_{jk} e^{-\beta E_j} A_{jk} B_{kj} \cdot \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i(\omega - [E_k - E_j]/\hbar)t} dt \\&= \frac{1}{Q} \sum_{jk} e^{-\beta E_j} A_{jk} B_{kj} \delta(\omega - [E_k - E_j]/\hbar).\end{aligned}$$

**Proof (II):**

$$\begin{aligned}\tilde{c}_{AB}(t) &= \frac{1}{\beta Q} \int_0^\beta d\lambda \operatorname{tr} \left[ e^{-(\beta-\lambda)\hat{H}} \hat{A} e^{-\lambda\hat{H}} e^{+i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} \right] \\ &= \frac{1}{\beta Q} \int_0^\beta d\lambda \sum_{jk} e^{-\beta E_j} A_{jk} B_{kj} e^{-\lambda(E_k - E_j)} e^{+i(E_k - E_j)t/\hbar}.\end{aligned}$$

$$\begin{aligned}\therefore \tilde{C}_{AB}(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \tilde{c}_{AB}(t) dt \\ &= \frac{1}{\beta Q} \int_0^\beta d\lambda \sum_{jk} e^{-\beta E_j} A_{jk} B_{kj} e^{-\lambda(E_k - E_j)} \delta(\omega - [E_k - E_j]/\hbar) \\ &= \frac{1}{\beta} \int_0^\beta e^{-\lambda\hbar\omega} d\lambda \cdot \frac{1}{Q} \sum_{jk} e^{-\beta E_j} A_{jk} B_{kj} \delta(\omega - [E_k - E_j]/\hbar) \\ &\equiv \frac{(1 - e^{-\beta\hbar\omega})}{\beta\hbar\omega} \cdot C_{AB}(\omega).\end{aligned}$$

## Alternatively (I):

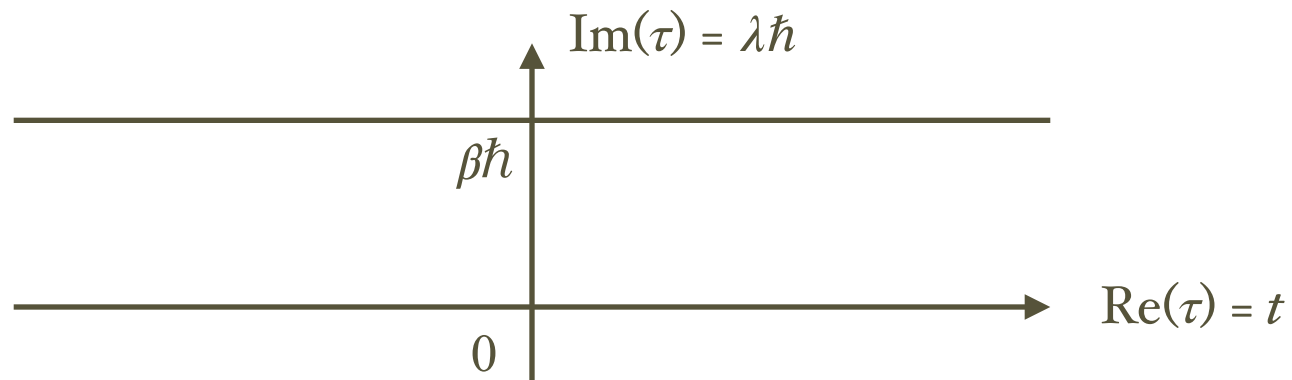
Note that

$$\begin{aligned}\tilde{c}_{AB}(t) &= \frac{1}{\beta Q} \int_0^\beta d\lambda \operatorname{tr} \left[ e^{-(\beta-\lambda)\hat{H}} \hat{A} e^{-\lambda\hat{H}} e^{+i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} \right] \\ &= \frac{1}{\beta Q} \int_0^\beta d\lambda \operatorname{tr} \left[ e^{-\beta\hat{H}} \hat{A} e^{+i\hat{H}(t+i\lambda\hbar)/\hbar} \hat{B} e^{-i\hat{H}(t+i\lambda\hbar)/\hbar} \right] \\ &\equiv \frac{1}{\beta} \int_0^\beta d\lambda c_{AB}(t + i\lambda\hbar),\end{aligned}$$

where

$$c_{AB}(\tau) = \frac{1}{Q} \operatorname{tr} \left[ e^{-\beta\hat{H}} \hat{A} e^{+i\hat{H}\tau/\hbar} \hat{B} e^{-i\hat{H}\tau/\hbar} \right]$$

is an analytic function of  $\tau$  in the strip  $0 \leq \operatorname{Im}(\tau) \leq \beta\hbar$ :

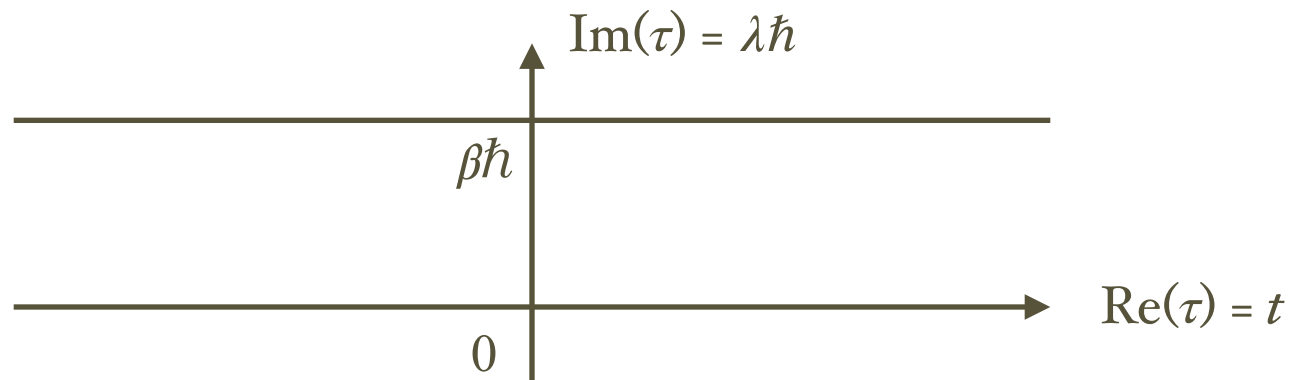




## Alternatively (II):

So

$$\begin{aligned}\tilde{C}_{AB}(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \tilde{c}_{AB}(t) dt \\ &= \frac{1}{\beta} \int_0^{\beta} d\lambda \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} c_{AB}(t + i\lambda\hbar) dt \\ &= \frac{1}{\beta} \int_0^{\beta} e^{-\lambda\omega\hbar} d\lambda \frac{1}{2\pi} \int_{-\infty+i\lambda\hbar}^{+\infty+i\lambda\hbar} e^{-i\omega\tau} c_{AB}(\tau) d\tau \\ &= \frac{1}{\beta} \int_0^{\beta} e^{-\lambda\omega\hbar} d\lambda \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega\tau} c_{AB}(\tau) d\tau \\ &= \frac{(1 - e^{-\beta\hbar\omega})}{\beta\hbar\omega} \cdot C_{AB}(\omega).\end{aligned}$$



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

For example:

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

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

and

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

where

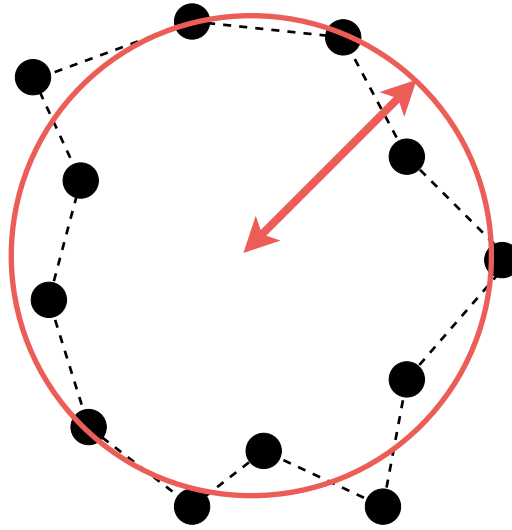
$$\tilde{C}_{\mu \cdot \mu}(\omega) = \frac{1}{2\pi} \int_{-\infty}^\infty e^{-i\omega t} \tilde{c}_{\mu \cdot \mu}(t) dt.$$

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

## 2. Ring polymer molecular dynamics<sup>2</sup>

Recall that:

$$Q = \text{tr} \left[ e^{-\beta \hat{H}} \right]$$



$$\Delta q = \Lambda(T) / \sqrt{8\pi}$$

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

$$\Delta p = \sqrt{m k T}$$

$$\Rightarrow \Delta p \Delta q = \frac{\hbar}{2}.$$

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

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

## Path integral molecular dynamics:

PIMD uses the ring polymer trajectories

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

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

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

## Ring polymer molecular dynamics:

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

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

where

$$\hat{B}(t) = e^{+i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} .$$

## Ring polymer molecular dynamics:

The RPMD approximation to

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

is simply

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

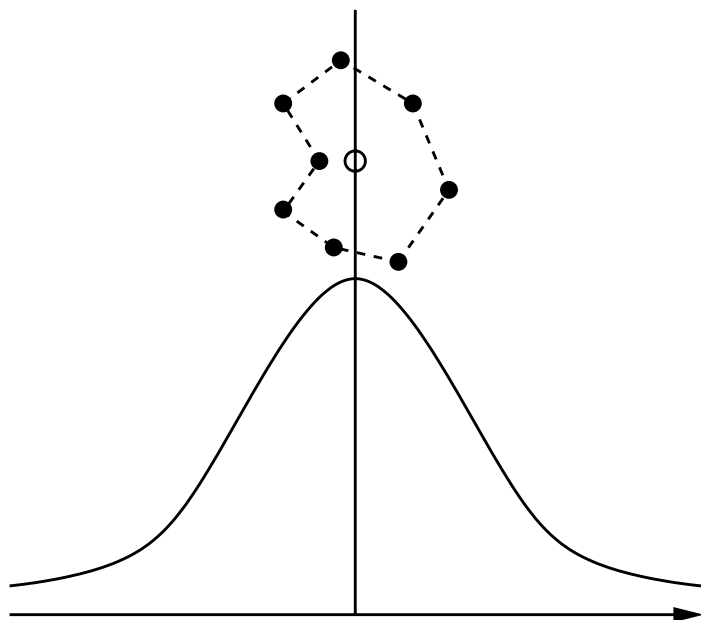
where

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

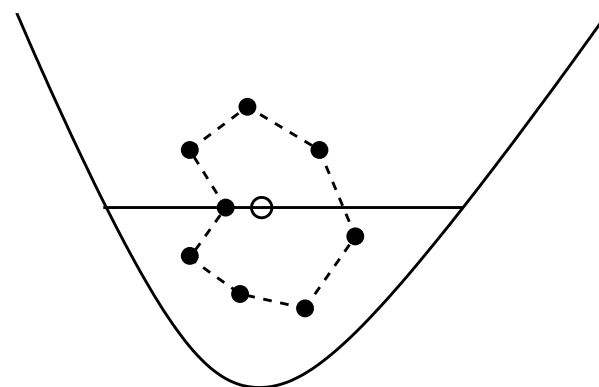
*Classical molecular dynamics in an extended phase space!*

*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<sup>3</sup>
3. Exact in the harmonic limit (for linear  $\hat{A}$  or  $\hat{B}$ )<sup>2</sup>
4. Exact for  $\hat{A} = \hat{1}$  (the unit operator)
5. Faithful to all QM symmetries<sup>2</sup>
6. Consistent with the QM equilibrium distribution

E.g.: when  $\hat{A} = \hat{1}$  we have

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



And in RPMD we also have

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

where we have used Liouville's theorem ( $d\mathbf{p}_0 d\mathbf{q}_0 = d\mathbf{p}_t d\mathbf{q}_t$ ) and the fact that RPMD trajectories conserve  $H_n(\mathbf{p}_t, \mathbf{q}_t)$ .

## Non-local operators

So far, we have only considered local operators  $\hat{A} = A(\hat{q})$  and  $\hat{B} = B(\hat{q})$ . But

$$\begin{aligned}\frac{d^2}{dt^2} Q c_{qq}(t) &= \frac{d^2}{dt^2} \text{tr} \left[ e^{-\beta \hat{H}} \hat{q} e^{+i\hat{H}t/\hbar} \hat{q} e^{-i\hat{H}t/\hbar} \right] \\ &= \frac{d}{dt} \text{tr} \left[ e^{-\beta \hat{H}} \hat{q} e^{+i\hat{H}t/\hbar} \frac{i}{\hbar} [\hat{H}, \hat{q}] e^{-i\hat{H}t/\hbar} \right] \\ &= \frac{d}{dt} \text{tr} \left[ e^{-\beta \hat{H}} \hat{q} e^{+i\hat{H}t/\hbar} \hat{v} e^{-i\hat{H}t/\hbar} \right] \\ &= \frac{d}{dt} \text{tr} \left[ e^{-\beta \hat{H}} e^{-i\hat{H}t/\hbar} \hat{q} e^{+i\hat{H}t/\hbar} \hat{v} \right] \\ &= -\text{tr} \left[ e^{-\beta \hat{H}} e^{-i\hat{H}t/\hbar} \frac{i}{\hbar} [\hat{H}, \hat{q}] e^{+i\hat{H}t/\hbar} \hat{v} \right] \\ &= -\text{tr} \left[ e^{-\beta \hat{H}} e^{-i\hat{H}t/\hbar} \hat{v} e^{+i\hat{H}t/\hbar} \hat{v} \right] \\ &= -\text{tr} \left[ e^{-\beta \hat{H}} \hat{v} e^{+i\hat{H}t/\hbar} \hat{v} e^{-i\hat{H}t/\hbar} \right] \\ &\equiv -Q c_{vv}(t).\end{aligned}$$

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

Thus the velocity autocorrelation function can be calculated in RPMD as  $\tilde{c}_{vv}(t) = -\frac{d^2}{dt^2} \tilde{c}_{qq}(t)$ , which gives (entirely naturally!)

$$\begin{aligned}
(2\pi\hbar)^n Q c_{vv}(t) &= -\frac{d^2}{dt^2} \int d\mathbf{p}_0 \int d\mathbf{q}_0 e^{-\beta_n H_n(\mathbf{p}_0, \mathbf{q}_0)} \bar{q}_0 \bar{q}_t \\
&= -\frac{d}{dt} \int d\mathbf{p}_0 \int d\mathbf{q}_0 e^{-\beta_n H_n(\mathbf{p}_0, \mathbf{q}_0)} \bar{q}_0 \bar{v}_t \\
&= -\frac{d}{dt} \int d\mathbf{p}_t \int d\mathbf{q}_t e^{-\beta_n H_n(\mathbf{p}_t, \mathbf{q}_t)} \bar{q}_0 \bar{v}_t \\
&= -\frac{d}{dt} \int d\mathbf{p}_0 \int d\mathbf{q}_0 e^{-\beta_n H_n(\mathbf{p}_0, \mathbf{q}_0)} \bar{q}_{-t} \bar{v}_0 \\
&= \int d\mathbf{p}_0 \int d\mathbf{q}_0 e^{-\beta_n H_n(\mathbf{p}_0, \mathbf{q}_0)} \bar{v}_{-t} \bar{v}_0 \\
&= \int d\mathbf{p}_t \int d\mathbf{q}_t e^{-\beta_n H_n(\mathbf{p}_t, \mathbf{q}_t)} \bar{v}_0 \bar{v}_t \\
&= \int d\mathbf{p}_0 \int d\mathbf{q}_0 e^{-\beta_n H_n(\mathbf{p}_0, \mathbf{q}_0)} \bar{v}_0 \bar{v}_t.
\end{aligned}$$

That is,  $\tilde{c}_{vv}(t) = \langle \bar{v}_0 \bar{v}_t \rangle$ , where  $\bar{q} = \frac{1}{n} \sum_{j=1}^n q_j$  and  $\bar{v} = \frac{d}{dt} \bar{q} = \frac{1}{n} \sum_{j=1}^n \frac{p_j}{m}$ .

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

For example, chemical reaction rate coefficients can be calculated from

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

where

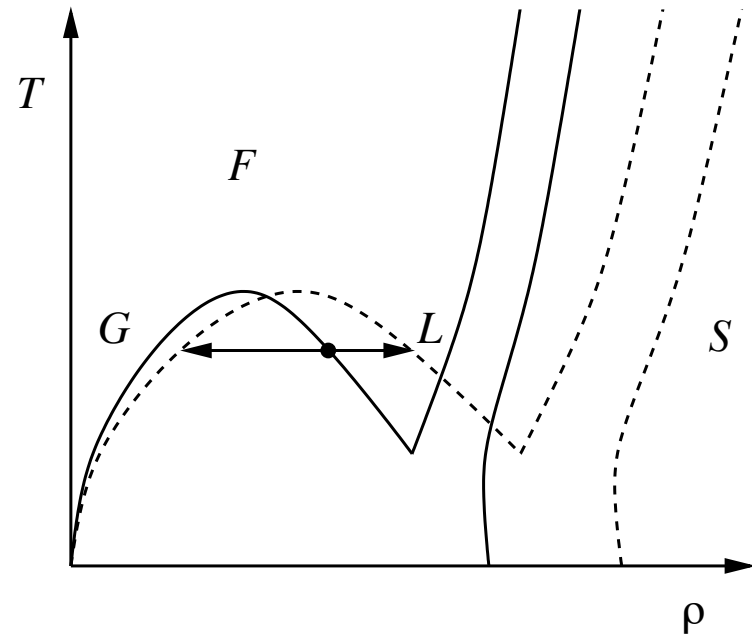
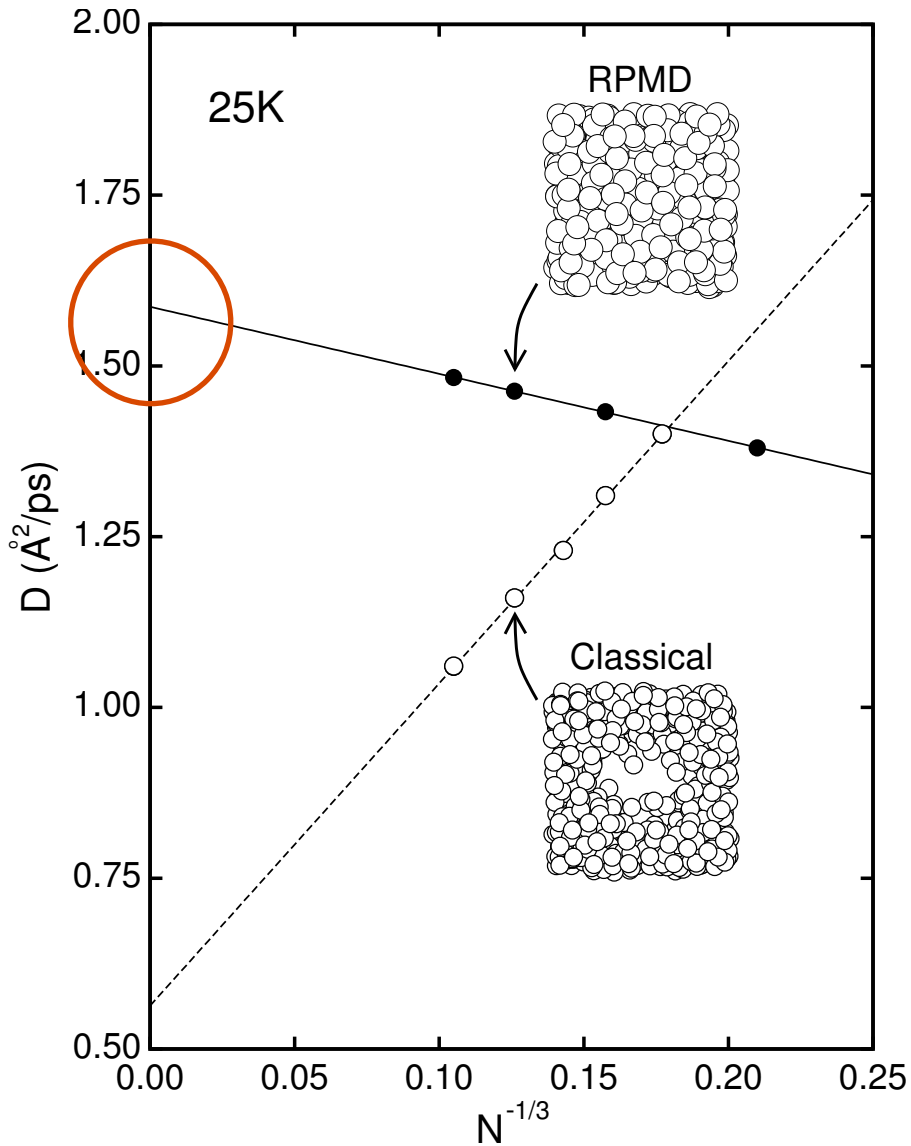
$$\tilde{c}_{ff}(t) = \frac{d}{dt} \tilde{c}_{fs}(t) = - \frac{d^2}{dt^2} \tilde{c}_{ss}(t),$$

both in QM and in RPMD.

But I shall not discuss this any further here, as it is the subject of Lecture III.

### 3. Example applications

#### A. Quantum diffusion in liquid para-hydrogen<sup>4</sup>



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

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

### Consistency check:

Recall that  $C_{vv}(\omega) = \frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}} \tilde{C}_{vv}(\omega)$ . So (in 1d notation)

$$\begin{aligned}\langle T \rangle &= \frac{1}{Q} \text{tr} \left[ e^{-\beta\hat{H}} \hat{T} \right] = \frac{m}{2} \frac{1}{Q} \text{tr} \left[ e^{-\beta\hat{H}} \hat{v}\hat{v} \right] \\ &= \frac{m}{2} c_{vv}(0) = \frac{m}{2} \int_{-\infty}^{\infty} d\omega C_{vv}(\omega) \\ &= \frac{m}{2} \int_{-\infty}^{\infty} d\omega \frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}} \tilde{C}_{vv}(\omega) \\ &= \frac{m}{4\pi} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} dt \frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}} e^{-i\omega t} \tilde{c}_{vv}(t) \\ &= \frac{m}{2} \left[ \tilde{c}_{vv}(0) + \int_0^{\infty} dt \frac{2}{1 - e^{+2\pi t/\beta\hbar}} \frac{d\tilde{c}_{vv}(t)}{dt} \right],\end{aligned}$$

in which the last line is obtained by evaluating the integral over  $\omega$ .<sup>5</sup>

By comparing this with the exact  $\langle T \rangle = \langle \mathcal{T}_{\text{CV}}(\mathbf{q}) \rangle$ , one has a way to check the accuracy of the RPMD approximation to  $\tilde{c}_{vv}(t)$ .

For the 25 K liquid para-hydrogen example given above, this consistency check gives the following kinetic energies per atom (in 3d):<sup>4</sup>

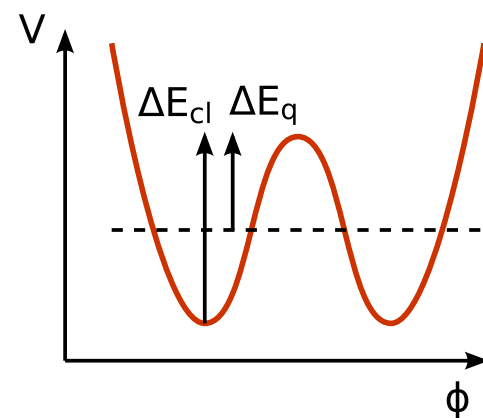
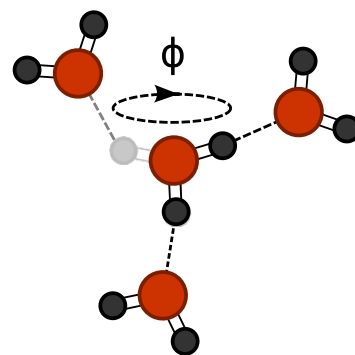
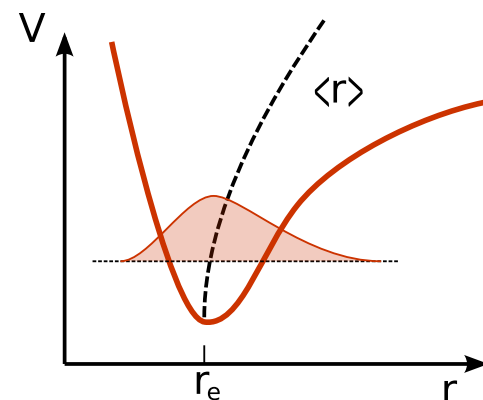
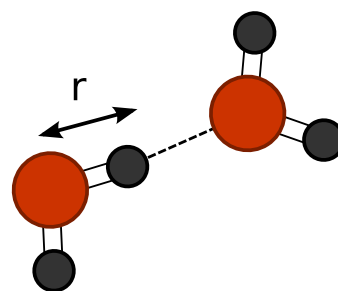
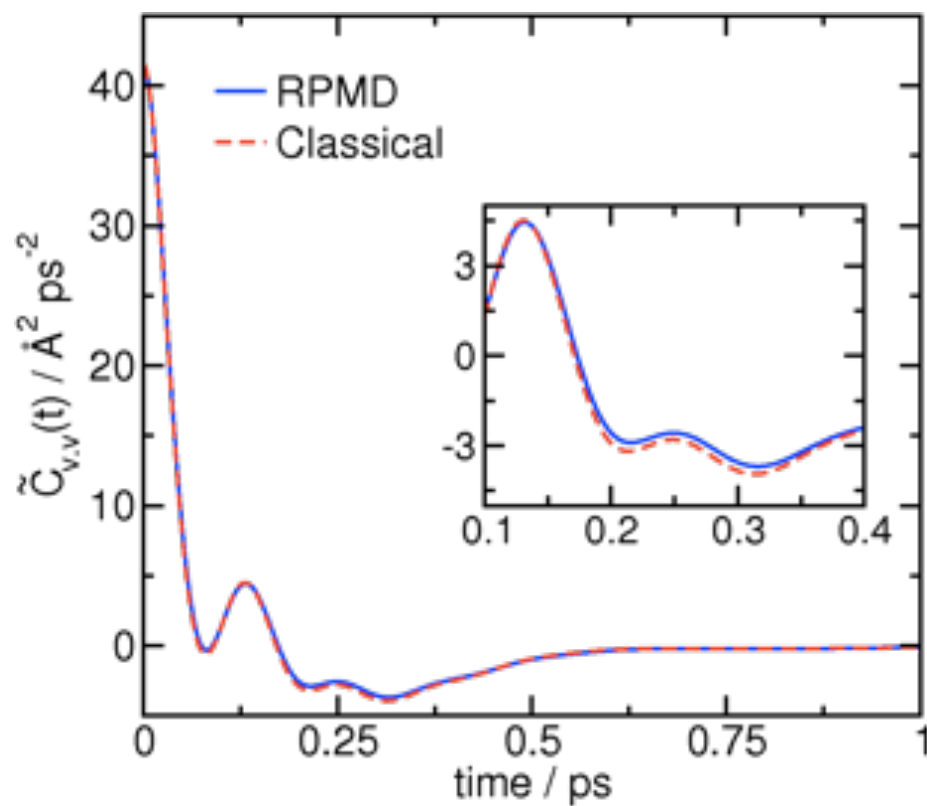
Kinetic energy (K)		
Exact	RPMD	Classical
62.0	64.5	37.5

Not bad – the RPMD approximation to  $\tilde{c}_{vv}(t)$  overestimates the quantum contribution to the kinetic energy by less than 10%. But not perfect – RPMD is just an approximation to real-time quantum dynamics, after all!

This is actually quite a stringent test, because the thermal time  $\beta\hbar$  at 25 K is  $\sim 0.3$  ps, which is comparable to the decay time of the p-H<sub>2</sub> velocity autocorrelation function. So it provides some reason to have faith in RPMD for other (less quantum mechanical) problems:

## B. Competing quantum effects in liquid water<sup>6</sup>

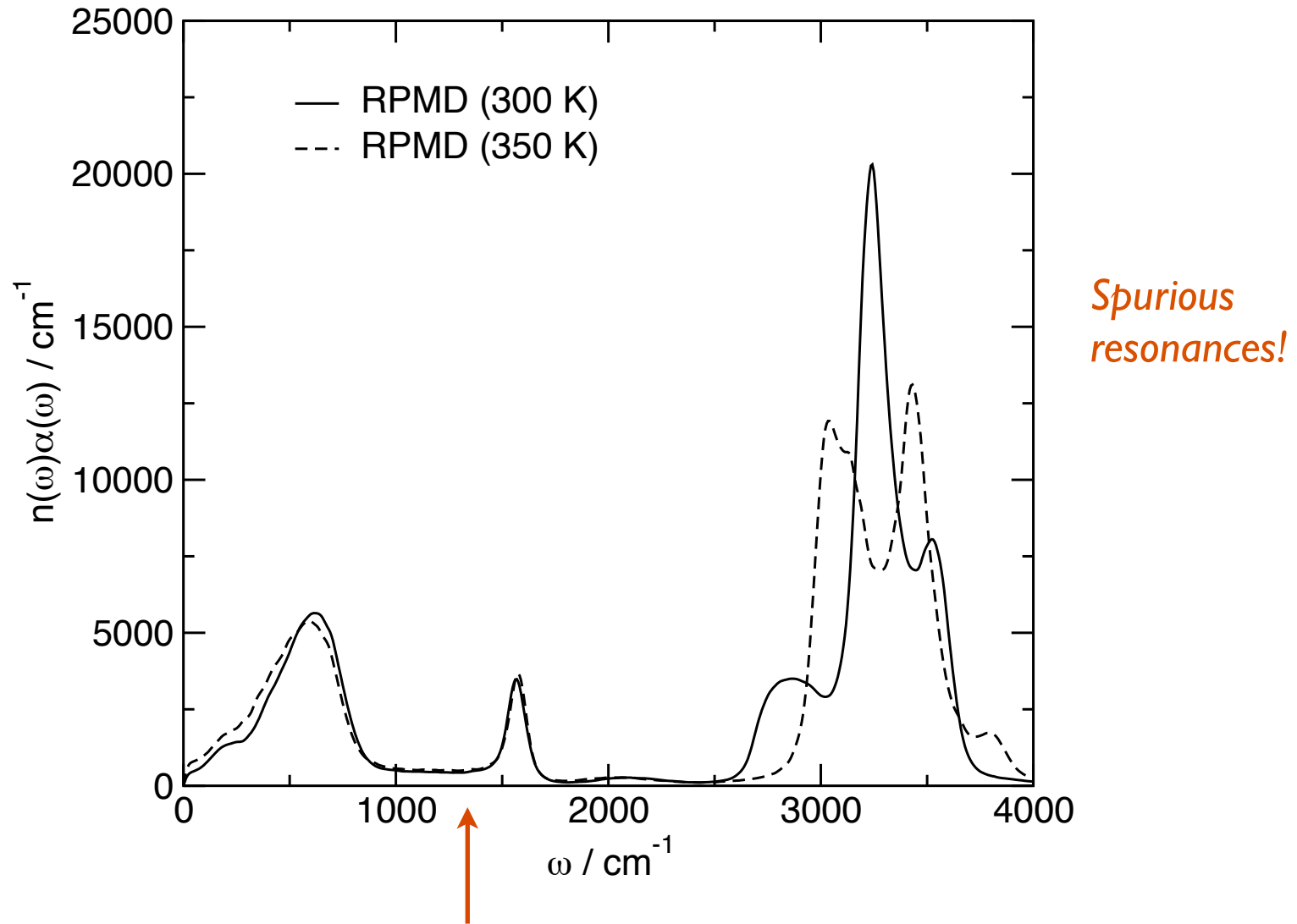
q-TIP4P/F



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



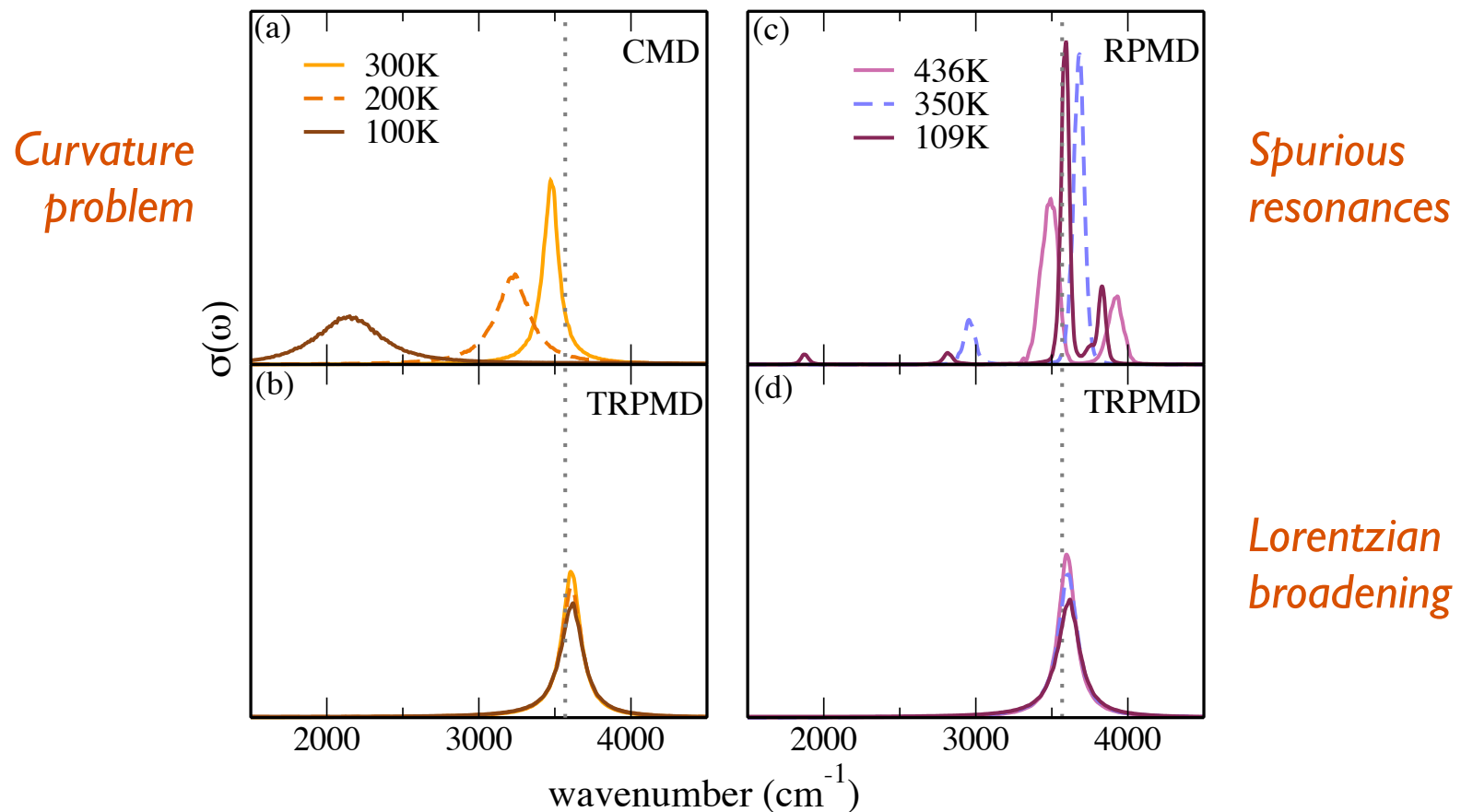
### C. The vibrational spectrum of liquid water<sup>7</sup>



$$\omega_1 = (2n/\beta\hbar) \sin(\pi/n) \simeq (2\pi/\beta\hbar) = 1300 \text{ cm}^{-1} \text{ at } 300 \text{ K.}$$

## D. Thermostatted RPMD<sup>8</sup>

None of the established properties of RPMD is affected when a PILE thermostat is attached to the internal modes of the ring polymer during the dynamics (TRPMD), which seems to be a good idea for calculating vibrational spectra:



Vibrational spectra of an anharmonic OH molecule ( $2\omega_e x_e = 170 \text{ cm}^{-1}$ ).

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# Ring-Polymer Molecular Dynamics: Quantum Effects in Chemical Dynamics from Classical Trajectories in an Extended Phase Space

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## Abstract

This article reviews the ring-polymer molecular dynamics model for condensed-phase quantum dynamics. This model, which involves classical evolution in an extended ring-polymer phase space, provides a practical approach to approximating the effects of quantum fluctuations on the dynamics of condensed-phase systems. The review covers the theory, implementation, applications, and limitations of the approximation.