Which quantum statistics–classical dynamics method is best for water?

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There are a variety of methods for including nuclear quantum effects in dynamics simulations by combining quantum Boltzmann statistics with classical dynamics. Among them are thermostatted ring-polymer molecular dynamics (TRPMD), centroid molecular dynamics (CMD), quasi-centroid molecular dynamics (QCMD), and the linearised semi-classical initial value representation (LSC-IVR). Here we make a systematic comparison of these methods by calculating the infrared spectrum of water in the gas phase, and in the liquid and ice phases (using the q-TIP4P/F model potential). Some of these results are taken from previous work, some of them are new (including the LSC-IVR calculations for ice, and extensions of all the spectra into the near-infrared region dominated by overtone and combination bands). Our results suggest that QCMD is the best method for reproducing fundamental transitions in the spectrum, and that LSC-IVR gives the best overall description of the spectrum (albeit with large errors in the bend fundamental band caused by zero-point-energy leakage). The TRPMD method gives damped spectra that line up with the QCMD spectra, and is by far the cheapest method.

1 Introduction

Two approaches are commonly used to include nuclear quantum effects in condensed-phase dynamics simulations. One approach is to solve the Schrödinger equation for a smaller, decoupled part of the system.^{1–5} The other approach, which is the one we will consider here, is to treat the Boltzmann statistics quantally and the dynamics classically.^{6–32}

The oldest such ‘quantum statistics–classical dynamics’ method goes back to Wigner, but was developed into a practical simulation method much more recently; this method is usually referred to as the linearised semiclassical initial value representation (LSC-IVR).^{6–12} The LSC-IVR method has now been used to calculate a variety of condensed-phase observables, including infrared (IR)^{13–15} and Raman¹⁶ spectra for liquid water. The drawback of LSC-IVR is that the Newtonian dynamics

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that it employs does not conserve the quantum Boltzmann distribution, which introduces errors into the time-correlation functions (typically in the form of artificially rapid decorrelation).^{12,15,17–19}

There is a newer family of quantum statistics–classical dynamics methods, each of which uses ‘ring polymers’ (*i.e.* imaginary-time Feynman paths)^{33–35} to describe the quantum Boltzmann statistics, and obtains classical trajectories from a Liou-villian that conserves the ring-polymer phase-space density. These ‘ring-polymer methods’ include centroid molecular dynamics (CMD)^{20–25} and (thermostatted) ring-polymer molecular dynamics ((T)RPMD).^{18,26–32} Unlike LSC-IVR, the ring-polymer methods conserve the quantum Boltzmann distribution by construction. Ring-polymer methods were initially considered to be heuristic, but have recently been shown to be approximations to ‘Matsubara dynamics’,^{36–39} which is the classical dynamics that results without further approximation when the exact path-integral formulation of quantum dynamics is mean-field averaged about the smooth paths.¹⁹ Ring-polymer methods cannot treat non-linear operators at low temperatures^{21,29} and have other drawbacks, which can cause errors in the dynamics. When used to compute the IR spectrum of water, CMD gives redshifts and broadening in the stretch band,^{40–42} and RPMD gives spurious resonances;⁴³ TPRMD damps out these resonances, but gives artificially broadened spectral line-shapes.³⁰

Recently, we developed a ring-polymer method, called quasi-centroid molecular dynamics (QCMD),⁴⁴ which appears to avoid most of these errors, by making a better mean-field approximation to Matsubara dynamics than CMD, without artificially damping the dynamics as in TRPMD. The QCMD method is expensive, but not prohibitively so, and has recently yielded IR spectra for liquid water and ice described by the simple q-TIP4P/F potential energy surface. The QCMD spectra for gas-phase water are close to the exact quantum results, suggesting that the QCMD condensed phase spectra are of comparable quality.⁴⁴

Given these new developments, it is timely to ask which is better at describing the dynamics of liquid water and ice (and related systems): LSC-IVR, or ring-polymer methods such as QCMD? We present here new LSC-IVR spectra, computed for liquid water at 300 K and ice at 150 K, which are compared with recently calculated CMD, TRPMD and QCMD results from ref. 44. We also extend the range of the calculated spectrum from the 0–4700 cm^{−1} of ref. 44 to 0–8000 cm^{−1}, in order to test the ability of these methods to describe overtones and combination bands. To our knowledge, these are the first LSC-IVR calculations on ice, and we pay particular attention to the rate at which the quantum Boltzmann distribution is degraded by the dynamics. Section 2 summarises the various methodologies used; Section 4 presents the numerical results; Section 5 concludes the article with some suggestions for discussion.

2 Background theory

2.1 Infrared spectrum time-correlation functions

From Fermi's Golden rule, the IR absorption spectrum of a system at thermal equilibrium is given by^{43,45}

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

where $n(\omega)$ is the refractive index, $\alpha(\omega)$ the Beer-Lambert absorption coefficient, $\beta = (k_B T)^{-1}$, V is the volume of the system, and $G_{\dot{\mu}\dot{\mu}}(\omega)$ is the Fourier transform of the standard quantum dipole-derivative autocorrelation function (ATCF),

$$G_{\dot{\mu}\dot{\mu}}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} C_{\dot{\mu}\dot{\mu}}(t), \quad (2)$$

where

$$C_{\dot{\mu}\dot{\mu}}(t) = \frac{1}{Z} \text{Tr} \left[e^{-\beta\hat{H}} \hat{\dot{\mu}} \cdot e^{i\hat{H}t/\hbar} \hat{\dot{\mu}} e^{-i\hat{H}t/\hbar} \right]. \quad (3)$$

Here $\hat{H}$ is the Hamiltonian of the system, $\hat{\dot{\mu}} = i\hbar^{-1}[\hat{H}, \hat{\mu}]$ is the dipole-derivative operator, and $Z = \text{Tr}[e^{-\beta\hat{H}}]$ is the quantum mechanical partition function.

If the dynamics is evaluated exactly, the spectrum can be obtained equivalently from only the real part of the standard ATCF,

$$C_{\dot{\mu}\dot{\mu}}^{[R]}(t) = \text{Re} [C_{\dot{\mu}\dot{\mu}}(t)] \quad (4)$$

using³⁹

$$n(\omega)\alpha(\omega) = \frac{\pi\beta}{3cV\epsilon_0} \frac{\tanh(\beta\hbar\omega/2)}{\beta\hbar\omega/2} \tilde{G}_{\dot{\mu}\dot{\mu}}^{[R]}(\omega), \quad (5)$$

or from the Kubo-transformed ATCF

$$\tilde{C}_{\dot{\mu}\dot{\mu}}(t) = \frac{1}{\beta\hbar} \int_0^{\beta\hbar} d\tau C_{\dot{\mu}\dot{\mu}}(t + i\tau), \quad (6)$$

using⁴³

$$n(\omega)\alpha(\omega) = \frac{\pi\beta}{3cV\epsilon_0} \tilde{G}_{\dot{\mu}\dot{\mu}}(\omega). \quad (7)$$

In most of what follows we discuss approximate dynamics, for which these various ATCFs are *not* equivalent. For the LSC-IVR calculations we will use the standard ATCF of eqn (1) (since this was found to give better quality spectra—see Section 2.6). For the ring-polymer method (TRPMD, CMD and QCMD) calculations we will use the Kubo-transformed ATCF of eqn (6) (since these methods derive from the Matusbara dynamics approximation to the Kubo-transformed ATCF of eqn (6)³⁶).

2.2 Ring polymers

The ring polymers used in the approximate dynamics methods TRPMD, CMD, QCMD are taken from path-integral molecular dynamics (PIMD), where they have long been used to compute static properties.^{33,34} For example, to compute the quantum partition function Z , one splits the reciprocal temperature β into N equally

spaced imaginary-time segments $\beta_N = \beta/N$, giving

$$Z = \lim_{N \rightarrow \infty} Z_N \quad (8)$$

with

$$Z_N = \frac{1}{(2\pi\hbar)^{3Nn}} \iint \prod_{i=1}^n \prod_{l=1}^N d^3 \mathbf{p}_i^{(l)} d^3 \mathbf{q}_i^{(l)} \exp \left\{ -\beta_N R_N \left(\{ \mathbf{p}_i^{(l)} \}, \{ \mathbf{q}_i^{(l)} \} \right) \right\}, \quad (9)$$

and

$$\begin{aligned} R_N \left(\{ \mathbf{p}_i^{(l)} \}, \{ \mathbf{q}_i^{(l)} \} \right) &= \frac{1}{2} \sum_{i=1}^n \sum_{l=1}^N \sum_{l'=1}^N [\mathbf{M}_i^{-1}]^{(l,l')} \mathbf{p}_i^{(l)} \cdot \mathbf{p}_i^{(l')} \\ &+ \frac{1}{2} \sum_{i=1}^n \sum_{l=1}^N \frac{m_i}{(\beta_N \hbar)^2} \left| \mathbf{q}_i^{(l)} - \mathbf{q}_i^{(l-1)} \right|^2 + \sum_{l=1}^N V \left(\mathbf{q}_1^{(l)}, \dots, \mathbf{q}_n^{(l)} \right). \end{aligned} \quad (10)$$

where $\mathbf{p}_i^{(l)}$ and $\mathbf{q}_i^{(l)}$ denote the momentum and position of the l -th replica (or ‘bead’) of particle i . The replica indices are defined modulo N (i.e. $\mathbf{p}_i^{(0)} \equiv \mathbf{p}_i^{(N)}$ and $\mathbf{q}_i^{(0)} \equiv \mathbf{q}_i^{(N)}$), hence each of the n particles is connected cyclically to its N replicas and forms a classical ‘ring polymer’ in the extended phase space $(\mathbf{p}_i^{(l)}, \mathbf{q}_i^{(l)})$, $l = 1, \dots, N$. Whereas m_i must be the physical mass of particle i , the $N \times N$ Parrinello-Rahman mass matrix $\mathbf{M}_i$ is required only to be symmetric and positive definite.³⁴

Using the ring-polymer Hamiltonian R_N , one can therefore evaluate static averages over $e^{-\beta \hat{H}}$ using classical MD (as is done in PIMD) or Monte Carlo (as in PIMC). The various ring-polymer dynamics methods investigated here ((T)RPMD, CMD, QCMD) go beyond this in using R_N also to generate an approximation to the dynamics in the Kubo ATCF of eqn (6).

2.3 Thermostatted ring-polymer molecular dynamics

In (unthermostatted) ring-polymer molecular dynamics (RPMD)^{26,29}, one sets the Parrinello-Rahman masses to the physical masses of the system (i.e. $M_i^{(l,l')} = m_i \delta_{ll'}$), and uses the ring-polymer Hamiltonian R_N to propagate classical trajectories. This gives a classical ATCF in the extended ring-polymer phase-space $(\mathbf{p}_i^{(l)}, \mathbf{q}_i^{(l)})$, $l = 1, \dots, N$, which is taken to be an approximation to the Kubo ATCF. In particular, the dipole-derivative ATCF of eqn (6) is approximated by¹⁴

$$\begin{aligned} \tilde{C}_{\mu\mu}(t) &\simeq \frac{1}{(2\pi\hbar)^{3Nn} Z_N} \iint \prod_{i=1}^n \prod_{l=1}^N d^3 \mathbf{p}_i^{(l)} d^3 \mathbf{q}_i^{(l)} \exp \left\{ -\beta_N R_N \left(\{ \mathbf{p}_i^{(l)} \}, \{ \mathbf{q}_i^{(l)} \} \right) \right\} \\ &\times \dot{\boldsymbol{\mu}}_N \left(\{ \mathbf{p}_i^{(l)} \}, \{ \mathbf{q}_i^{(l)} \} \right) \cdot \dot{\boldsymbol{\mu}}_N \left(\{ \mathbf{p}_i^{(l)}(t) \}, \{ \mathbf{q}_i^{(l)}(t) \} \right), \end{aligned} \quad (11)$$

where

$$\dot{\boldsymbol{\mu}}_N \left(\{ \mathbf{q}_i^{(l)} \} \right) = \frac{1}{N} \sum_{l=1}^N \dot{\boldsymbol{\mu}} \left(\mathbf{q}_1^{(l)}, \dots, \mathbf{q}_n^{(l)} \right), \quad (12)$$

and $(\mathbf{p}_i^{(l)}(t), \mathbf{q}_i^{(l)}(t))$ denotes the phase-space point $(\mathbf{p}_i^{(l)}, \mathbf{q}_i^{(l)})$ at time t .

The initial justification for RPMD was heuristic (namely, RPMD gives the correct zero-time, harmonic and high-temperature limits of the quantum Kubo ATCF for lin-

ear operators); it was subsequently found that the ring-polymer ‘springs’ corrupt the IR spectrum, giving spurious resonance peaks.⁴³ Thermostatted RPMD (TRPMD) was developed to solve this problem.^{30,31} The bead coordinates are converted to free-ring-polymer normal mode coordinates

$$\mathbf{Q}_i^{(k)} = \sum_{l=1}^N T_{lk} \mathbf{q}_i^{(l)}, \quad (13)$$

which resemble Fourier modes (see ref. 30 for the definition of T_{lk}). The lowest-frequency modes,

$$\mathbf{Q}_i^{(0)} = \frac{1}{\sqrt{N}} \sum_{l=1}^N \mathbf{q}_i^{(l)}, \quad (14)$$

are proportional to the centres of mass or ‘centroids’ of the bead coordinates $\mathbf{q}_i^{(l)}$. In TRPMD, white-noise Langevin thermostats are attached independently to each of the non-centroid (fluctuation) modes, $k \neq 0$.³⁰ This damps off the spurious resonance peaks, but artificially broadens the spectral lineshapes as the temperature is lowered.³⁰ It is now understood that, by damping the fluctuation modes, TRPMD gives a short-time approximation to the Matsubara dynamics of the centroid.^{36–38}

2.4 Centroid molecular dynamics

In CMD the ring-polymer centroids, $\mathbf{Q}_i = N^{-1/2} \mathbf{Q}_i^{(0)}$, undergo classical dynamics on an effective classical potential $W(\mathbf{Q}_1, \dots, \mathbf{Q}_n)$, defined so that $A(\mathbf{Q}_1, \dots, \mathbf{Q}_n)$ gives the correct, unbiased estimator for $\langle A \rangle$ when $\hat{A}$ is a position-dependent linear operator.^{20,21} The force on the centroid can be calculated as a mean-field average over the fluctuation modes,

$$-\frac{\partial W(\mathbf{Q}_1, \dots, \mathbf{Q}_n)}{\partial \mathbf{Q}_i} = -\frac{1}{N} \sum_{l=1}^N \left\langle \frac{\partial V(\mathbf{q}_1^{(l)}, \dots, \mathbf{q}_n^{(l)})}{\partial \mathbf{q}_i^{(l)}} \right\rangle_{\mathbf{Q}_1, \dots, \mathbf{Q}_n} \quad (15)$$

where $\langle \dots \rangle_{\mathbf{Q}_1, \dots, \mathbf{Q}_n}$ denotes an average over the ring-polymer phase space with the centroid constrained at $N^{-1} \sum_{i=1}^N \mathbf{q}_i^{(l)} = \mathbf{Q}_i$. Thus W can be regarded as a free energy, and is often called the centroid potential of mean force. Kubo-transformed dipole-derivative ATCFs can be approximated using

$$\begin{aligned} \tilde{C}_{\dot{\mu}\dot{\mu}}(t) \simeq & \frac{1}{(2\pi\hbar)^{3n} Z_N} \iint \prod_{i=1}^n d^3 \mathbf{P}_i d^3 \mathbf{Q}_i e^{-\beta H_0(\mathbf{P}_1, \dots, \mathbf{P}_n; \mathbf{Q}_1, \dots, \mathbf{Q}_n)} \\ & \times \dot{\boldsymbol{\mu}}(\mathbf{P}_1, \dots, \mathbf{P}_n; \mathbf{Q}_1, \dots, \mathbf{Q}_n) \cdot \dot{\boldsymbol{\mu}}(\mathbf{P}_1(t), \dots, \mathbf{P}_n(t); \mathbf{Q}_1(t), \dots, \mathbf{Q}_n(t)), \end{aligned} \quad (16)$$

where

$$H_0(\mathbf{P}_1, \dots, \mathbf{P}_n; \mathbf{Q}_1, \dots, \mathbf{Q}_n) = \frac{1}{2} \sum_{i=1}^n m_i |\mathbf{P}_i|^2 + W(\mathbf{Q}_1, \dots, \mathbf{Q}_n), \quad (17)$$

and the equations of motion are defined accordingly.

The (partially) adiabatic implementation of CMD, called (P)A-CMD, is algorithmically similar to TRPMD, but differs crucially in the choice of the mass matrices $\mathbf{M}_i$, which are now only diagonal in the normal mode basis.^{43,46–48} The mass of each fluctuation mode is scaled to yield a natural frequency of $\Omega = \Gamma/(\beta_N \hbar)$, so

the fluctuations become adiabatically separated from the (much slower) centroid motion in the limit $\Gamma \rightarrow \infty$.

The CMD approximation is exact in the classical limit, and also in the short-time and harmonic limits if $\hat{\mu}$ is linear.²¹ CMD is a mean-field approximation to Matsubara dynamics.^{36,38,42} At high temperatures, the mean-field approximation works well because the ring-polymer distribution around the centroid is compact; at lower temperatures, the mean-field approximation breaks down because the polymers spread around curves in the potential, causing CMD to give artificial redshifts and broadening in the stretch region of the IR spectrum.^{40–42}

2.5 Quasi-centroid molecular dynamics

QCMD was developed recently by Trenins *et al.*⁴⁴ to resolve the CMD curvature problem. The method resembles CMD, except that the potential of mean force is obtained by constraining the centroids of curvilinear rather than cartesian bead coordinates. In water, these curvilinear coordinates are simply the bond-angle coordinates of the water monomers. By constraining the bond-angle centroids, one obtains compact ring-polymer distributions unaffected by the curvature problem.

The curvilinear centroid constraints define a set of points in configuration space which are close to (but not precisely at) the overall centroids (*i.e.* ring-polymer centres-of-mass) of the water monomers, and which we refer to as the *quasi-centroid* coordinates $\{\bar{\mathbf{Q}}_i\}$. The potential of mean force is then given by

$$-\frac{\partial \bar{W}(\bar{\mathbf{Q}}_1, \dots, \bar{\mathbf{Q}}_n)}{\partial \bar{\mathbf{Q}}_i} = -\frac{1}{N} \sum_{l=1}^N \left\langle \frac{\partial V(\mathbf{q}_1^{(l)}, \dots, \mathbf{q}_n^{(l)})}{\partial \mathbf{q}_i^{(l)}} \right\rangle_{\bar{\mathbf{Q}}_1, \dots, \bar{\mathbf{Q}}_n}, \quad (18)$$

where $\langle \dots \rangle_{\bar{\mathbf{Q}}_1, \dots, \bar{\mathbf{Q}}_n}$ denotes an average over the ring-polymer phase space subject to quasi-centroid (curvilinear) constraints.

In QCMD, the dynamics is generated in cartesian quasi-centroid coordinates, and the Kubo-transformed dipole-derivative ATCFs are calculated just as in CMD, except that the terms appearing in eqn (16) are modified to

$$\begin{aligned} \tilde{C}_{\hat{\mu}\hat{\mu}}(t) \simeq & \frac{1}{(2\pi\hbar)^{3n}\bar{Z}_N} \iint \prod_{i=1}^n d^3\bar{\mathbf{P}}_i d^3\bar{\mathbf{Q}}_i e^{-\beta\bar{H}_0(\bar{\mathbf{P}}_1, \dots, \bar{\mathbf{P}}_n; \bar{\mathbf{Q}}_1, \dots, \bar{\mathbf{Q}}_n)} \\ & \times \hat{\mu}(\bar{\mathbf{P}}_1, \dots, \bar{\mathbf{P}}_n; \bar{\mathbf{Q}}_1, \dots, \bar{\mathbf{Q}}_n) \cdot \hat{\mu}(\bar{\mathbf{P}}_1(t), \dots, \bar{\mathbf{P}}_n(t); \bar{\mathbf{Q}}_1(t), \dots, \bar{\mathbf{Q}}_n(t)), \end{aligned} \quad (19)$$

where

$$\bar{H}_0(\bar{\mathbf{P}}_1, \dots, \bar{\mathbf{P}}_n; \bar{\mathbf{Q}}_1, \dots, \bar{\mathbf{Q}}_n) = \frac{1}{2} \sum_{i=1}^n m_i |\bar{\mathbf{P}}_i|^2 + \bar{W}(\bar{\mathbf{Q}}_1, \dots, \bar{\mathbf{Q}}_n), \quad (20)$$

and the partition function $\bar{Z}_N$ is defined accordingly.

QCMD is new, and has not yet been formally derived. However, it seems likely that it works because it gives a better mean-field approximation to Matsubara dynamics than CMD, especially at temperatures low enough to cause the CMD curvature problem. In obtaining eqn (19), one makes various approximations to the quantum Boltzmann distribution, and also assumes that the distribution is compact enough for the quasi-centroid to be close to the centroid. In ref. 44, it is found that these approximations appear to be minor in gas-phase water, liquid water and ice,

across the entire 150–800 K temperature range tested.

2.6 Linearised semiclassical initial-value representation

Unlike the ring-polymer methods discussed so far, LSC-IVR uses plain classical dynamics on the system potential V .^{6–12} The LSC-IVR approximation to the standard dipole-derivative ATCF is¹⁵

$$C_{\mu\mu}(t) \simeq \frac{1}{(2\pi\hbar)^{3n}Z} \iint d^{3n}\mathbf{p} d^{3n}\mathbf{q} \rho_W(\mathbf{p}, \mathbf{q}) \mathbf{f}_{\mu}(\mathbf{p}, \mathbf{q}) \cdot \dot{\boldsymbol{\mu}}(\mathbf{p}(t), \mathbf{q}(t)), \quad (21)$$

where

$$\rho_W(\mathbf{p}, \mathbf{q}) = \left[e^{-\beta\hat{H}} \right]_W(\mathbf{p}, \mathbf{q}), \quad (22)$$

and

$$\mathbf{f}_{\mu}(\mathbf{p}, \mathbf{q}) = \frac{\left[e^{-\beta\hat{H}} \hat{\boldsymbol{\mu}} \right]_W(\mathbf{p}, \mathbf{q})}{\rho_W(\mathbf{p}, \mathbf{q})}. \quad (23)$$

The variables $(\mathbf{p}, \mathbf{q})$ represent a point in $3n$ -dimensional phase-space; $(\mathbf{p}(t), \mathbf{q}(t))$ are the coordinates of this point after the system has evolved classically on V for a time t . The nomenclature $[\hat{O}]_W$ denotes the Wigner transform of the operator $\hat{O}$,

$$[\hat{O}]_W(\mathbf{p}, \mathbf{q}) = \int d^{3n}\boldsymbol{\Delta} \langle \mathbf{q} - \boldsymbol{\Delta}/2 | \hat{O} | \mathbf{q} + \boldsymbol{\Delta}/2 \rangle e^{(i/\hbar)\boldsymbol{\Delta} \cdot \mathbf{p}}. \quad (24)$$

An analogous expression can also be written out for the Kubo ATCF,^{13,15} but we employ throughout the standard expression in eqn (21), which is found to give fewer artefacts in the IR spectrum.

The quantum Boltzmann distribution is not conserved by the classical trajectories $(\mathbf{p}(t), \mathbf{q}(t))$, so detailed balance is not satisfied and thermal expectation values calculated by LSC-IVR are not time-invariant.^{12,15,17,18} As a result, spectral line-shapes can be contaminated by zero-point energy ‘leakage’, where energy flows artificially from high-frequency intramolecular modes to low-frequency intermolecular modes.¹⁸

Evaluating the Wigner quasi-probability distribution ρ_W requires some level of approximation for any system with more than a few degrees of freedom. One approach that has been applied successfully to liquid water is the local Gaussian approximation (LGA) due to Liu and Miller,^{11,13,15,16,18} which is based on the local harmonic approximation (LHA) introduced earlier by Shi and Geva.⁹

The LGA (like the LHA) makes a locally harmonic approximation to the off-diagonal matrix elements of $e^{-\beta\hat{H}}$, allowing the Fourier transforms in ρ_W to be evaluated analytically.^{9,11} The potential V is Taylor expanded to second order about a point $\mathbf{q}$, giving

$$V(\mathbf{q} + \delta\mathbf{q}) \simeq V(\mathbf{q}) + \delta\mathbf{q} \cdot \frac{\partial V(\mathbf{q})}{\partial \mathbf{q}} + \frac{1}{2} \delta\mathbf{q} \cdot \mathbf{M}^{1/2} \boldsymbol{\Omega}^2(\mathbf{q}) \mathbf{M}^{1/2} \delta\mathbf{q}, \quad (25)$$

where $\mathbf{M}$ is the diagonal mass matrix and $\boldsymbol{\Omega}^2$ is the mass-weighted Hessian,

$$\Omega_{ij}^2(\mathbf{q}) = \frac{1}{\sqrt{M_{ii}M_{jj}}} \frac{\partial^2 V(\mathbf{q})}{\partial q_i \partial q_j}. \quad (26)$$

This can be shown^{9,11} to give

$$\frac{\langle \mathbf{q} - \Delta/2 | e^{-\beta \hat{H}} | \mathbf{q} + \Delta/2 \rangle}{\langle \mathbf{q} | e^{-\beta \hat{H}} | \mathbf{q} \rangle} \simeq \exp \left\{ -\frac{1}{2\beta \hbar^2} \Delta \cdot \mathbf{M}^{1/2} \Phi(\mathbf{q}) \mathbf{M}^{1/2} \Delta \right\} \quad (27)$$

where the ‘quantum correction factor’ (QCF) Φ is defined by

$$\Phi(\mathbf{q}) = f(\Omega(\mathbf{q})); \quad (28)$$

$$f(\omega) = \frac{\beta \hbar \omega}{2} \coth \left(\frac{\beta \hbar \omega}{2} \right). \quad (29)$$

Evaluating the Fourier transforms over Δ leads to

$$\frac{\rho_W(\mathbf{p}, \mathbf{q})}{\langle \mathbf{q} | e^{-\beta \hat{H}} | \mathbf{q} \rangle} \simeq \frac{\exp \left\{ -\frac{\beta}{2} \mathbf{p} \cdot \mathbf{M}^{-1/2} \Phi^{-1}(\mathbf{q}) \mathbf{M}^{-1/2} \mathbf{p} \right\}}{\sqrt{\beta^{-1} \det(2\pi \mathbf{M}^{1/2} \Phi(\mathbf{q}) \mathbf{M}^{1/2})}}, \quad (30)$$

Equation (30) is the LHA approximation to $\rho_W(\mathbf{p}, \mathbf{q})$. To obtain the LGA approximation, one simply replaces $f(\omega_i)$ by $1/f(|\omega_i|)$, for each eigenvalue ω_i^2 of $\Omega^2(\mathbf{q})$ that is negative and for which $\beta \hbar |\omega_i| > \pi$. This *ad hoc* approximation ensures that the LGA approximation to $\rho_W(\mathbf{p}, \mathbf{q})$ does not diverge at barriers. In a typical LSC-IVR simulation using the LGA, the position distribution $\langle \mathbf{q} | e^{-\beta \hat{H}} | \mathbf{q} \rangle$ is sampled using PIMD;¹² the momenta are then sampled from the distribution in eqn (30). To obtain a tractable expression for $\mathbf{f}_\mu$ (eqn (23)), one expands to first order in Δ to obtain¹⁵

$$\text{Re}[\mathbf{f}_\mu(\mathbf{p}, \mathbf{q})] \simeq \dot{\boldsymbol{\mu}}(\mathbf{p}, \mathbf{q}), \quad (31)$$

which is exact in the case that $\boldsymbol{\mu}$ is linear.

3 Computational details

3.1 Gas-phase water

Gas-phase water simulations were carried out at $T = 300$ K and $T = 150$ K, using the potential energy⁴⁹ and dipole moment⁵⁰ surfaces due to Partridge and Schwenke. The numbers of replicas used for the path-integral simulations were $N = 32$ at 300 K and $N = 64$ at 150 K.

The reader is referred to Section III of ref. 44 for further details of the TRPMD, CMD and QCMD simulations. Exact quantum ATCFs were also calculated as in ref. 44, using the DVR3D package of Tennyson and co-workers.⁵¹ The classical MD simulations were carried out analogously to TRPMD, but with the number of beads N reduced to one.

For LSC-IVR, the ring polymers were thermalised under PILE-L,⁵² with the bead masses equal to the physical masses and a time step of $\Delta t = 0.125$ fs. For the thermostat, the non-centroid friction coefficients were set to the natural frequencies of the free ring polymer; the centroid time constant was $\tau_0 = 100$ fs. At each temperature, 10^5 initial configurations of the water molecule were obtained by selecting one of the replicas randomly at intervals of 125 fs. The mass-weighted Hessian Ω^2 was evaluated and diagonalised at each of these configurations, allowing a set of initial momenta to be sampled from the LGA distribution (eqn (30)). Five mo-

menta were sampled independently for each initial configuration, yielding a total of 5×10^5 initial phase-space points. In order to mitigate artefacts in the spectrum caused by treating free rotations of the molecule harmonically, the eigenvalues ω_i corresponding to free rotation were reset to zero, such that the LGA distribution reduced to the classical Maxwell-Boltzmann distribution for these modes. A classical *NVE* trajectory of length 1 ps ($\Delta t = 0.125$ fs) was propagated from each initial phase-space point in order to calculate the real part of the standard dipole-moment ATCF, given by eqn (21) with eqn (31). Note that since the Partridge-Schwenke dipole moment surface is non-linear,⁵⁰ eqn (31) is an approximation to the true estimator for $\hat{\mu}$ at time $t = 0$.

3.2 Condensed-phase water

Condensed-phase water simulations were carried out for the liquid at $T = 300$ K and ice I_h at $T = 150$ K, using the q-TIP4P/F potential energy and dipole moment surfaces.¹⁸ Both of these regimes have been studied in previous literature,^{14,18,31,39,44} although to the best of our knowledge, no LSC-IVR results for the IR spectrum of ice have yet been published. The q-TIP4P/F surfaces are too approximate to reproduce the experimental spectra of water and ice quantitatively, but have the advantage of being cheap, and are realistic enough to test how well the various approximate methods are likely to perform on more accurate (and expensive) water surfaces such as those of refs. 23–25. The densities used for liquid water and ice were $\rho = 1000.82$ kg m⁻³ and $\rho = 917.240$ kg m⁻³, respectively. Each simulation employed periodic boundary conditions and a simulation box containing 128 molecules for the liquid, and 96 for ice. The numbers of replicas used for the path-integral simulations were $N = 32$ for the liquid and $N = 64$ for ice.

The reader is referred to Section V of ref. 44 for further details of the TRPMD, CMD and QCMD simulations. We note that in each case, the total propagation time (excluding thermalisation) required to converge the ATCFs was no more than 800 ps. The classical MD simulations were carried out analogously to TRPMD, but with the number of beads N reduced to one.

For LSC-IVR in the condensed phase, many more trajectories are generally required to converge the ATCFs than for the other methods, since one cannot exploit horizontal statistics (*i.e.* time-averaging) when the Boltzmann distribution is not conserved.⁵³ At each temperature, the LSC-IVR calculation began by propagating eight independently equilibrated ring-polymer configurations for approximately 40 ns under PILE-G,⁵² with the bead masses equal to the physical masses and a time step of $\Delta t = 0.125$ fs. For the thermostat, the non-centroid friction coefficients were set to the natural frequencies of the free ring polymer; the centroid time constant was $\tau_0 = 100$ fs. The positions $\mathbf{q}_1^{(1)}, \dots, \mathbf{q}_n^{(1)}$ of the first replica were recorded at intervals of 1 ps, yielding about 40000 independent initial configurations for the LGA. At each of these configurations, the mass-weighted Hessian Ω^2 was evaluated and diagonalised, allowing a set of initial momenta to be sampled from the LGA distribution. Finally, classical *NVE* trajectories of length 1 ps ($\Delta t = 0.125$ fs) were propagated from each set of initial conditions in order to calculate the real part of the standard dipole-moment ATCF. Note in this case that eqn (31) is exact, since the q-TIP4P/F dipole moment surface is linear.

The classical, TRPMD, CMD and QCMD simulations, as well as the long ther-

$n(\omega)\alpha(\omega)$ [arb. units]

Fig. 1 Calculated IR absorption spectra for gas-phase water at 300 K, obtained after damping each ATCF with a Hann window of width $\tau = 750$ fs. Each approximate spectrum is superimposed on the exact spectrum, filled in light grey. The TRPMD, CMD and QCMD results in the $\omega < 4250$ cm^{-1} region are taken from ref. 44.

malisation runs required for LSC-IVR, were performed using an in-house code. The subsequent LGA sampling and classical propagation required for LSC-IVR were carried out using a modified version of the i-PI package of Ceriotti *et al.* with the included q-TIP4P/F driver.⁵⁴

4 Results and discussion

4.1 Gas-phase water spectra

Figures 1 and 2 show the IR spectra calculated for gas-phase water at 300 K and 150 K, obtained after damping each ATCF with a Hann window⁵⁵ of width $\tau = 750$ fs. The TRPMD, CMD and QCMD results in the $\omega < 4250$ cm^{-1} region are taken from ref. 44. We use the notation $v_1v_2v_3$ to denote a band due to the vibrational transition $|v_1v_2v_3\rangle \leftarrow |000\rangle$, where the quantum numbers v_1 , v_2 and v_3 label the symmetric stretch, bend and antisymmetric stretch respectively.

The behaviour of the various ring-polymer methods in the mid- to far-IR region

$n(\omega)\alpha(\omega)$ [arb. units]

Fig. 2 Same as Fig. 1 for gas-phase water at 150 K.

($\omega < 4250 \text{ cm}^{-1}$) of the spectrum has already been discussed in ref. 44. In summary, CMD gives artificial redshifts in the stretch band, QCMD gives overall excellent agreement with the exact quantum result, TRPMD gives a broadened version of the QCMD spectrum; none of the ring-polymer methods captures the internal structure of the stretch, which is presumably the result of real-time coherence. Figures 1 and 2 show that LSC-IVR behaves similarly to TRPMD in this region, giving artificially broadened spectra that line up with the QCMD results. Obviously the causes of the artificial broadening in the methods are different (in TRPMD it is the thermostat, in LSC-IVR it is violation of quantum detailed balance).

A striking advantage of the LSC-IVR method emerges when we turn to the near-IR ($\omega > 4700 \text{ cm}^{-1}$) region of the spectrum. This part of the spectrum is dominated by two combination bands, 011 at 5300 cm^{-1} and 101 at 7300 cm^{-1} .⁴⁹ All of the ring-polymer methods reproduce only a small fraction of the intensity of these bands, doing no better than classical MD in this respect. LSC-IVR, by contrast, reproduces over 80% of the total integrated intensity in this region. The LSC-IVR peaks are artificially broadened, and we have no way of telling whether this is solely the result of not satisfying quantum detailed balance. However, the result shows

Fig. 3 Calculated IR absorption spectra for q-TIP4P/F liquid water at 300 K, obtained after damping each ATCF with a Hann window of width $\tau = 600$ fs. The QCMD results are plotted in each panel (solid black line). The TRPMD, CMD and QCMD results in the $\omega < 4250$ cm^{-1} region are taken from ref. 44.

clearly that the inability of the ring-polymer methods to reproduce these peaks cannot be attributed to ‘real-time coherence’ (which is also omitted by LSC-IVR). This failing is most likely caused by the neglect of Matsubara fluctuations around the centroid, which we know are required to describe the electrical part of the anharmonicity (*i.e.* the non-linear dependence of $\hat{\mu}$) and are probably also important for capturing the full effects of mechanical anharmonicity (although further work will be required to test this).

4.2 Condensed-phase water spectra

Figures 3 and 4 show the IR spectra calculated for liquid water at 300 K and ice I_h at 150 K. As mentioned above, the q-TIP4P/F surfaces are not accurate enough for these spectra to reproduce the experimental data⁵⁶ (in which the stretch band is much more intense and shifted to the red⁵⁷). The TRPMD, CMD and QCMD results in the $\omega < 4250$ cm^{-1} region are taken from ref. 44. The LSC-IVR results for the liquid were calculated using very similar parameters to those reported in ref.

Fig. 4 Same as Fig. 3 for q-TIP4P/F ice I_h at 150 K, with a Hann window of width $\tau = 800$ fs. The QCMD results are plotted in each panel (solid black line).

14, but there are small discrepancies between the two spectra, since our spectrum was obtained from the standard ATCF and the spectrum of ref. 14 from the Kubo ATCF. We found that the standard ATCF introduced less noise into the spectrum than the Kubo ATCF, especially in the near-IR region, but that the low-frequency (librational) part of the spectrum was in slightly less good agreement with classical MD. For the liquid, a Hann window⁵⁵ of width $\tau = 600$ fs was applied to each ATCF before computing its Fourier transform, in order to reduce ringing artefacts in the spectra. For ice, a broader window of $\tau = 800$ fs was necessary to fully resolve the spectrum (on account of the splitting of the stretch band into symmetric and antisymmetric components, which is an artefact of the q-TIP4P/F potential).

4.2.1 Fundamental bands. As discussed in ref. 44, the various ring-polymer methods behave similarly in the mid- to far-IR region of the condensed-phase spectra as they do in the gas phase; *i.e.* TRPMD gives a broadened version of the QCMD spectrum, and CMD suffers from a redshift in the stretch band (which is less than in the gas phase, presumably because the polymers spread less around librations than around free rotations). For these reasons we have assumed that QCMD is similarly

Fig. 5 Snapshots from the LSC-IVR simulation of ice I_h at 150 K, taken at 250 fs intervals along a single trajectory initialised using the LGA. The crystalline order has visibly deteriorated by 1 ps, as a result of intramolecular zero-point energy leaking into the intermolecular degrees of freedom.

close to what the exact quantum spectrum would be (which of course we cannot calculate), and have used the QCMD peaks as a reference in Figures 3 and 4. Note that the comparison of QCMD with the other ring-polymer methods and with classical MD suggests that QCMD gives a small redshift to the librational band. This was noted in ref. 44, where it was attributed to approximations made in estimating the torques on the quasi-centroids.

Figures 3 and 4 show that the LSC-IVR results are overall in reasonable agreement with the QCMD results in the mid- to far-IR region of the spectrum, but that the broadening of the LSC-IVR bend and stretch is more severe than in the gas phase, and the bend also suffers a blueshift which grows on decreasing the temperature from 300 to 150 K. These artefacts are almost certainly caused by non-conservation of the quantum Boltzmann distribution, which in the condensed phase causes zero-point energy to leak into the intermolecular degrees of freedom. Habershon and Manolopoulos investigated zero-point energy leakage in their LSC-IVR calculations in the liquid, and found that the center-of-mass temperature increases by almost 400 K during a classical trajectory of length 1 ps.¹⁴ Our 150 K ice calculations show a similar leakage (of 300 K), and snapshots from movies of LSC-IVR trajectories in ice show that this is sufficient to melt the ice within 1 ps (Fig. 5). The deterioration of the quantum Boltzmann distribution evident in Fig. 5 appears rather dramatic, but since it happens on a similar timescale to the decorrelation of the ATCF it does not lead to similarly dramatic changes in the spectrum.

4.2.2 Overtone and combination bands. As in the gas phase, LSC-IVR predicts much stronger intensity in the near-IR region of the spectrum than classical MD or any of the ring-polymer methods (see Figures 3 and 4). Based on the gas-phase results, it seems likely that these LSC-IVR bands capture the linestrengths that would have been obtained in this region of the spectrum if an exact quantum calculation had been done. We expect that LSC-IVR has artificially broadened these bands, probably more so than in a corresponding gas-phase calculation, given the large zero-point energy leakage artefacts noted above.

The relative intensities of the LSC-IVR overtone bands are different from the gas phase: the band at 7000 cm^{-1} (a stretch overtone, analogous to the 101 band in the gas-phase spectrum of Figures 1 and 2) is much stronger than the band at 5200 cm^{-1} (a stretch-bend combination band analogous to the 011 band in Figures 1 and 2). However, this has a simple explanation: when the gas-phase calcula-

Fig. 6 Calculated IR absorption spectra for q-TIP4P/F liquid water at 300 K and ice I_h at 150 K, obtained after damping each ATCF with a Hann window of width $\tau = 600$ fs and $\tau = 500$ fs, respectively. The LMon-4 results are taken from ref. 31, and the QCMD results from ref. 44. The grey dashed line in the inset is drawn at $n(\omega)\alpha(\omega) = 0$.

tions were repeated using the q-TIP4P/F dipole-moment surface, a similar change in intensity was found, implying that the gas-phase 5200 cm^{-1} peak gains most of its intensity from the non-linear terms in the Partridge-Schwenke dipole moment surface. (The q-TIP4P/F dipole moment surface is linear, so all overtones or combination bands obtained from it are caused entirely by mechanical anharmonicity.) Another difference from the gas phase is the feature at around 4000 cm^{-1} , which appears as a shoulder on the stretch fundamental band for the liquid, but for ice separates into a well-defined peak; based on its frequency, we suggest that this feature is a stretch-libration combination band.

In Fig. 6 we compare the LSC-IVR results with the QCMD and local monomer (LMon-4) results^{1,2} (taken from ref. 31), to test how well LSC-IVR reproduces the combination bands in the mid-IR region of the spectrum. (To make this comparison we had to use a narrower Hann window of width $\tau = 500$ fs to damp the ATCFs for ice at 150 K, which is why the QCMD stretch band loses its structure.) LMon-4 is a wave function-based method that focuses on the local dynamics around one

water molecule; it is thus unable to describe well the libration band, but does agree (remarkably well) with QCMD for the bend and stretch bands, and (of relevance here) is able to reproduce the bend-libration combination band at 2300 cm^{-1} (inset in Fig. 6) as well as the Fermi resonance around 3200 cm^{-1} . We see that LSC-IVR also reproduces these bands, giving comparable intensity to LMon-4 (which none of the ring-polymer methods are able to do). However, the shapes of the LSC-IVR bands are very poor. The bend-libration band is not just broadened but also contaminated by an almost equally large, adjacent peak with negative absorbance (which is clearly an artefact brought about by violation of detailed balance), and the Fermi resonance is skewed and broadened.

5 Conclusions

In gas-phase water there are two clear ‘winners’: QCMD gives the best agreement of the fundamental bands with the exact quantum results, and LSC-IVR gives fundamental bands which are almost as good as QCMD, with the advantage of also reproducing the high-frequency combination bands (albeit with strongly broadened lineshapes). In the liquid and ice, broadly the same picture seems to hold (of course we do not have exact quantum to compare with), except that now zero-point energy-leakage gives bigger errors in the LSC-IVR spectrum, especially in the bend region.

This raises the question of why QCMD, and the other ring-polymer methods (TRPMD and CMD) fail to reproduce overtones and combination bands. It is clearly not simply because they omit real-time coherence, as LSC-IVR also makes this approximation. Most likely, this shortcoming of ring-polymer methods has the same origin as their inability to describe non-linear operators at low temperatures, namely neglect of Matsubara fluctuation dynamics¹⁹ (which is mean-fielded out in QCMD and CMD, and damped off in TRPMD).^{36,37,42,44}

We speculate that it may be possible to develop a ‘super-method’ that combines the advantages of QCMD with LSC-IVR, by carrying out mean-field-averaged dynamics of a superposition of Matsubara modes which are localised in imaginary time. Such a dynamics would resemble LSC-IVR at short times, but also satisfy quantum detailed balance.

Conflicts of interest

There are no conflicts of interest to declare.

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